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A General Theory of Inequalities

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The method used by Karle & Hauptman for deriving inequalities is applied to structures possessing a centre of symmetry. It is shown that all inequalities which have been derived, or may be derived, may be found by purely algebraic means from four sets of inequalities, the fundamental inequalities. The fundamental sets, derived in a previous publication, appear among them.

1. Introduction

Though many useful inequalities have been found, it is still an open question whether other, more powerful, inequalities exist. To answer this question, a systematic derivation and enumeration of inequalities is indicated. In a previous publication (de Wolff & Bouman, 1954) this question was answered for the structure factors $U(H)$, $U(H')$, $U(2H)$, $U(2H')$, $U(H+H')$ and $U(H-H')$. A set of four inequalities was found from which all others could be derived. This result followed from the application of a new method (using the calculus of variations) and also from elementary methods used by Harker & Kasper (1948). But the last-named methods are not suited to a systematic treatment and the new method is too difficult to be applied to other sets of structure factors.

It has now been found that the method due to Karle & Hauptman (1950) leads to the complete answer, and enables us to classify all inequalities. In other words, it will be possible to give a set of inequalities from which all others may be derived. It will also be possible to write down all inequalities which may be derived from an independent set. In this paper no other symmetry elements than the centre of inversion will be treated.

2. Recapitulation of the theory of Karle & Hauptman

We consider a set of N reciprocal vectors H_p and a space (which has nothing to do with real space) of the same number of dimensions. Its coordinates are designed by X_p. Now it has been proved that the quadratic form

$$U = \sum_p \sum_q U(H_p-H_q)X_p\overline{X}_q \equiv \sum_p \sum_q U_{pq}X_p\overline{X}_q \quad (1)$$

is positive definite, if the number N is less than the number of atoms in the cell; in the other case U is only non-negative. $U(H_p-H_q)$ is the unitary structure factor

$$U(H_p-H_q) = \sum_i n_i \exp 2\pi i[(h_p-h_q)x_i + (k_p-k_q)y_i + (l_p-l_q)z_i]\,,$$

with $\sum_i n_i = 1$.

As only differences of the reciprocal vectors appear in our expressions, we may subtract H_1 from all vectors, in the new set $H_1 = 0, 0, 0$.

The quadratic form is a Hermitian form, as $U_{qp} = \overline{U}_{pq}$. This form is related to a Hermitian transformation

$$Y_p = \sum_q U_{pq}X_q \quad (2)$$

which transforms a point X_p into a point Y_p. The matrix of this transformation is

$$\begin{bmatrix} U_{11} & U_{12} & U_{13} & \ldots & U_{1N} \\ U_{21} & U_{22} & U_{23} & \ldots & U_{2N} \\ \ldots & \ldots & \ldots & \ldots & \ldots \\ U_{N1} & U_{N2} & U_{N3} & \ldots & U_{NN} \end{bmatrix}. \quad (3)$$

Now from the positive definite character of the quadratic form it follows that all principal minors of the determinant, formed from the matrix, are positive. In this way a great number of inequalities may be found. We may add that all elements on the diagonal U_{pp} are 1.

We will now consider especially centrosymmetric structures. Then the structure factors are real and the Hermitian matrix becomes a symmetric matrix. In the transformation (2) we have only to consider real values of the coordinates.

3. Exposition of the method used in this paper

We have seen that from the positive definite character of the transformation it follows that all principal minors are positive. Inversely, if all principal minors are positive, the positive definite character of U is ensured. But it can be proved (Littlewood, 1950, pp. 44–7) that it suffices to assume

$$U_{11} > 0, \quad \begin{vmatrix} U_{11} & U_{12} \\ U_{21} & U_{22} \end{vmatrix} > 0 \text{ and so on} \quad (4)$$

in order to prove U to be positive definite. Now the following considerations will prove to be useful:

(A) $U > 0$ is equivalent to the set of inequalities (4). So, if from $U > 0$ it follows that all principal minors are positive, then it follows also from the inequalities

(4). We may state this result also in this way: The inequalities (4), or $U > 0$, can only be proved from the definition of $U(H)$ with positive n_i. But if these inequalities are given, then the other inequalities, being other principal minors than those of (4), can be derived from (4) by purely algebraic means without any assumption on the form of $U(H)$. In the paper by de Wolff & Bouman (1954) examples of these algebraic deductions may be found.

(B) We have by no means exhausted the number of inequalities, which can be derived from (4). For we may choose other coordinates in the space X_p. If these new coordinates are obtained by an orthogonal transformation, the symmetric character is preserved by this change of coordinates. The new expression for U is still positive definite, and so the principal minors are positive; they constitute new derived inequalities.

The change of coordinates from X_p to X'_p is given by

$$X'_p = \sum_q a_{pq} X_q ,$$

with

$$\sum_p a^2_{pq} = 1, \ \sum_p a_{pq} a_{pr} = 0 . \tag{5}$$

This applies to a symmetric form. In the case of complex U_{pq}, and so of Hermitian forms, the properties of the change of coordinates become

$$\sum_p a_{pq} \bar{a}_{pq} = 1, \ \sum_p a_{pq} \bar{a}_{pr} = 0; \tag{5a}$$

this change is denoted by the name unitary transformation.

(C) It will be an advantage if we can choose the new coordinates in such a way that the ensuing matrix has a simpler form than the original one. In general this will not be possible, as there exist no relations between the structure factors. But for centrosymmetric structures $U(H) = U(-H)$ we have found that symmetric matrices may be simplified by a suitable change of coordinates if they are doubly symmetric, i.e. with respect to both diagonals. We have to consider separately matrices with an even and with an odd number of rows. Then the matrix

$$\begin{bmatrix} p & q & a & s & t \\ q & r & b & u & s \\ a & b & c & b & a \\ s & u & b & r & q \\ t & s & a & q & p \end{bmatrix}, \tag{6}$$

which is doubly symmetric, is transformed by the change of coordinates

$$\left.\begin{aligned} X'_1 &= \tfrac{1}{2}\sqrt{2}.X_1 + \tfrac{1}{2}\sqrt{2}.X_5 , \\ X'_2 &= \tfrac{1}{2}\sqrt{2}.X_2 + \tfrac{1}{2}\sqrt{2}.X_4 , \\ X'_3 &= X_3 , \\ X'_4 &= -\tfrac{1}{2}\sqrt{2}.X_2 + \tfrac{1}{2}\sqrt{2}.X_4 , \\ X'_5 &= -\tfrac{1}{2}\sqrt{2}.X_1 + \tfrac{1}{2}\sqrt{2}.X_5 , \end{aligned}\right\} \tag{6a}$$

into

$$\begin{bmatrix} p+t & q+s & a\sqrt{2} & 0 & 0 \\ q+s & r+u & b\sqrt{2} & 0 & 0 \\ a\sqrt{2} & b\sqrt{2} & c & 0 & 0 \\ 0 & 0 & 0 & r-u & q-s \\ 0 & 0 & 0 & q-s & p-t \end{bmatrix} . \tag{6b}$$

In the same way we find that the matrix

$$\begin{bmatrix} p & q & s & t \\ q & r & u & s \\ s & u & r & q \\ t & s & q & p \end{bmatrix} \tag{7}$$

is transformed by the same change of coordinates; omitting the middle term $X'_3 = X_3$, into

$$\begin{bmatrix} p+t & q+s & 0 & 0 \\ q+s & r+u & 0 & 0 \\ 0 & 0 & r-u & q-s \\ 0 & 0 & q-s & p-t \end{bmatrix} . \tag{7a}$$

These results are easily extended to matrices with another number of rows. Now if the quadratic forms related to these matrices are positive definite, then the equivalent statement (4) can be written with the help of simple determinants. In § 4 it will be shown that these matrices can indeed be constructed from the unitary structure factors. The transformations, mentioned in (B), can better be applied to the matrices in the form (6b) and (7a). They will give more amenable results.

4. The derivation of fundamental inequalities

Instead of studying all kinds of matrices to be derived from (3) we will consider only matrices of the form (6) or (7). As regards (6) we may construct this matrix by ascribing to the middle row the reciprocal vectors

$$-H_n \ \ldots \ -H_3 \ -H_2 \ -H_1 \ 0 \ H_1 \ H_2 \ H_3 \ \ldots \ \mathrm{H}_n . \tag{8}$$

Then the unitary structure factors at the left will be equal to those at the right. The first row is then described by adding H_n to the row, given above, so we find

$$0 \ \ldots \ H_n-H_3 \ H_n-H_2 \ H_n-H_1 \ H_n \ H_n+H_1 \ \ldots \ 2H_n . \tag{9}$$

The matrix will be doubly symmetric. This may be proved easily, or it may be seen immediately by writing down the middle part of the matrix. This is

$$\begin{bmatrix} 1 & U(H_1-H_2) & U(H_2) & U(H_1+H_2) & U(2H_2) \\ U(H_1-H_2) & 1 & U(H_1) & U(2H_1) & U(H_1+H_2) \\ U(H_2) & U(H_1) & 1 & U(H_1) & U(H_2) \\ U(H_1+H_2) & U(2H_1) & U(H_1) & 1 & U(H_1-H_2) \\ U(2H_2) & U(H_1+H_2) & U(H_2) & U(H_1-H_2) & 1 \end{bmatrix} . \tag{10}$$

Now transforming into the form (6*b*), we find

$$\begin{bmatrix} & & & 0 & 0 \\ & P & & 0 & 0 \\ & & & 0 & 0 \\ 0 & 0 & 0 & & \\ & & & Q & \\ 0 & 0 & 0 & & \end{bmatrix}$$

with

$$P \equiv \begin{bmatrix} 1+U(2H_2) & U(H_1+H_2)+U(H_1-H_2) & U(H_2)\sqrt{2} \\ U(H_1+H_2)+U(H_1-H_2) & 1+U(2H_1) & U(H_1)\sqrt{2} \\ U(H_2)\sqrt{2} & U(H_1)\sqrt{2} & 1 \end{bmatrix}, \quad (11)$$

$$Q \equiv \begin{bmatrix} 1-U(2H_2) & U(H_1+H_2)-U(H_1-H_2) \\ U(H_1+H_2)-U(H_1-H_2) & 1-U(2H_1) \end{bmatrix}. \quad (12)$$

All inequalities to be found from (10) can be found from five fundamental inequalities. We choose them by taking first the last minor and then working upward through the matrix. They are:

(I): $1-U(2H_2) > 0$,

(II): $[1-U(2H_2)][1-U(2H_1)] > [U(H_1+H_2)-U(H_1-H_2)]^2$;

(III) is identical with II.

(IV) is the product of the minor (II) and $1+U(2H_1)-2U(H_1)^2$,

so

$$1+U(2H_1) > 2U(H_1)^2 .$$

(V) states that the determinant of the entire matrix is positive, but as this determinant is the product of $|P|$ and $|Q|$ and the last is already positive (II) we find $|P| > 0$. This determinant may be written in a simpler form, by subtracting the third row, multiplied by $U(H_2)\sqrt{2}$ from the first one, and then subtracting the same row, multiplied by $U(H_1)\sqrt{2}$, from the second row. The result is

$$\begin{vmatrix} 1+U(2H_2)-2U(H_2)^2 & U(H_1+H_2)+U(H_1-H_2)-2U(H_1)U(H_2) \\ U(H_1+H_2)+U(H_1-H_2)-2U(H_1)U(H_2) & 1+U(2H_1)-2U(H_1)^2 \end{vmatrix} > 0 .$$

So, instead of five fundamental inequalities from (10), including a determinant with 5 rows (and the trivial inequality $1 > 0$), we find only four, with no more than two rows. Now the argument can be readily extended to an arbitrary number of reciprocal vectors. Writing

$$\begin{aligned} G_{ik} &= U(H_i-H_k)+U(H_i+H_k)-2U(H_i)U(H_k) , \\ G_{ii} &= 1 + U(2H_i) - 2U(H_i)^2 , \\ F_{ik} &= U(H_i-H_k)-U(H_i+H_k) , \\ F_{ii} &= 1 - U(2H_i) , \end{aligned}$$

we find that the inequalities, following from the matrix, defined by the row (9), are fully determined by the sets

$$G_{11} > 0, \quad \begin{vmatrix} G_{11} & G_{12} \\ G_{12} & G_{22} \end{vmatrix} > 0, \quad \begin{vmatrix} G_{11} & G_{12} & G_{13} \\ G_{12} & G_{22} & G_{23} \\ G_{13} & G_{23} & G_{33} \end{vmatrix} > 0, \ldots . \quad (13)$$

$$F_{11} > 0, \quad \begin{vmatrix} F_{11} & F_{12} \\ F_{12} & F_{22} \end{vmatrix} > 0, \text{ and so on} . \quad (14)$$

The first inequality of (13) and the second from (14) are found by Harker & Kasper (1948), the second from (13) by de Wolff & Bouman (1954). $F_{11} > 0$ is trivial. The inequalities contain the reciprocal vectors H_k, $2H_k$ and $H_i \pm H_k$.

5. Other fundamental inequalities

It may be remarked that we are free to choose in the matrix, defined by its first row (9), other sets of reciprocal vectors, e.g. $H_n-H_3 = H'_3$, $H_n-H_2 = H'_2$, and so on. In this case we will find seemingly different inequalities, expressed in H'_p. But evidently from § 4 the simplest way of writing the inequalities is the denomination we have used.

In order to free ourselves from this ambiguity, we can represent the reciprocal vectors in the reciprocal lattice. Then the row (8) contains the origin and next to each vector H the vector $-H$; all points form a symmetrical figure or set of points, including the origin, which is the centre of symmetry of the figure. Now the row (9) is represented by the same figure, but translated over H_n. So now the origin is one of the points, and H_n the centre of symmetry.

We turn now to matrices with an even number of rows. Clearly we can get them by cancelling the middle row and column of the matrices we have just considered. This would give no new results, as they can only yield inequalities, derivable from the sets (13) and (14). But if we now choose reciprocal axes in such a way that H_n has no longer integral values for *hkl*, while $2H_n$ does, we get new inequalities. Geometrically we can say that the new constellation, corresponding to the first row, is again a symmetrical figure, containing the origin, but the centre of symmetry does not belong to the set, not being a reciprocal vector. If now the last reciprocal vector in the row is denoted by H, then to each vector H_i there exists another H'_i with $H_i+H'_i = H$, as was the case in (9). So the first row of the matrix will be

$$O \ \ldots \ H_2 \ H_1 \ H-H_1 \ H-H_2 \ \ldots \ H . \quad (15)$$

We will refrain from writing the matrix in full, and state only that it contains unitary structure factors, belonging to H_i, $H-H_i$, $H-2H_i$, H_i-H_k and

$H-(H_i+H_k)$. This is a new set. It would be the same as the set from § 4, if $H = 0$. This, however, is impossible, as then the determinant would contain two equal rows, and so would be identically zero. Reducing the matrix in the same way as above (cf. (7) and (7*a*)) we find a set of inequalities

$$\begin{vmatrix} 1\pm U(H) & U(H_1)\pm U(H-H_1) & U(H_2)\pm U(H-H_2)\dots \\ U(H_1)\pm U(H-H_1) & 1\pm U(H-2H_1) & U(H_1-H_2)\pm U(H-H_1-H_2)\dots \\ U(H_2)\pm U(H-H_2) & U(H_1-H_2)\pm U(H-H_1-H_2) & 1\pm U(H-2H_2)\dots \\ \dots\dots & \dots\dots & \dots\dots \end{vmatrix} > 0. \quad (16)$$

Expression (16) represents two sets, one with the positive sign, the other with the negative sign. If we write

$$D_{ik} = U(H_i-H_k)+U(H-H_i-H_k)\,,$$
$$C_{ik} = U(H_i-H_k)-U(H-H_i-H_k)\,,$$

and put $H_0 = 0$, we may write (16)

$$D_{00} > 0,\ \begin{vmatrix} D_{00} & D_{01} \\ D_{01} & D_{11} \end{vmatrix} > 0,\ \begin{vmatrix} D_{00} & D_{01} & D_{02} \\ D_{01} & D_{11} & D_{12} \\ D_{02} & D_{12} & D_{22} \end{vmatrix} > 0,\ \dots, \quad (17)$$

$$C_{00} > 0,\ \begin{vmatrix} C_{00} & C_{01} \\ C_{01} & C_{11} \end{vmatrix} > 0, \text{ and so on}. \quad (18)$$

As in the case of (13) and (14), we have chosen the simplest denomination of the reciprocal vectors. We might replace H by $H_1+H_2+\dots$ without much advantage. If we consider only two reciprocal vectors, H and H_1, then this procedure gives

$$\begin{vmatrix} 1\pm U(H_1+H_2) & U(H_1)\pm U(H_2) \\ U(H_1)\pm U(H_2) & 1\pm U(H_1-H_2) \end{vmatrix} > 0\,,$$

and these are well known inequalities.

6. The complete set of fundamental inequalities

If the method, described in the preceding sections, is applied to acentric structures, we get the same results as Karle & Hauptman (1950). We can study the matrix

$$1\ U(H_1)\ U(H_2)\ \dots\ U(H_n)\,, \quad (19)$$

then all inequalities following from this matrix may be derived from the set

$$1-|U(H_1)|^2 > 0\,,$$

$$\begin{vmatrix} 1 & U(H_1) & U(H_2) \\ U(-H_1) & 1 & U(H_2-H_1) \\ U(-H_2) & U(H_1-H_2) & 1 \end{vmatrix} > 0, \text{ and so on.}$$

The last inequality has been found by Karle & Hauptman:

$$[1-|U(H_1)|^2]\,.\,[1-|U(H_2)|^2] > |U(H_1-H_2)-U(H_1)U(-H_2)|\,. \quad (20)$$

So for n vectors we get n inequalities (omitting $1 > 0$); the last one is a determinant with $n+1$ rows.

In the case of centrosymmetric structures the row can be amplified to $2n+1$ structure factors (8), or to $2n$ (15). We get then four sets of inequalities, the largest determinants having only n rows (cf. (13), (14), (17) and (18)). And these inequalities are more powerful than the aforementioned, because the original matrix, from which they are derived, contains the matrix $1\ \dots\ U(H_n)$. The four sets constitute all fundamental inequalities, with this restriction that we may relabel the reciprocal vectors H_1, H_2 etc. But in each case the two sets (13) and (14) cover other combinations of the reciprocal vectors than (17) and (18). Only in the case of two reciprocal vectors did we find that with a suitable choice of the reciprocal vectors the last two sets contain a part of the combinations of (13) and (14).

It might be asked if it is possible to construct other matrices than the doubly symmetric matrices we have used, and so get other inequalities by reducing them. We are not able to give a stringent answer to this question, but may remark that each structure factor must appear at least four times in such a matrix, if it can be reduced (in the original matrix (19) each structure factor appears twice for centric structures). As no relations are assumed between the structure factors (this may be the case for other space groups) we can reduce the matrix only if the same structure factor appears more than twice. The doubly symmetric matrix is the simplest way to fulfil this condition, and we have found no other possibilities.

We may end by asking for the condition that the inequalities become equalities, i.e. that the determinants are zero.

For the general case (3) the answer has been given by Goedkoop (1952, p. 82): the number of atoms is less than the number of rows. So the inequality (20) will be an equality for two or one atoms in the cell. The answer for the centrosymmetric structures can be found by applying the method given by Goedkoop to the matrices discussed here. As the result has no practical importance, we will mention without proof that the same rule obtains for the matrices with n or $n+1$ rows, found by reducing the doubly symmetric matrices $2n$ or $2n+1$, if we replace 'number of atoms' by 'number of pairs of atoms'. So (12) and (17*a*) will be equalities for one pair of atoms, and (11) for two pairs.

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