Furthermore, Booth's method presupposes a knowledge of the orientation which is not generally completely available. Since it does not involve plotting contour diagrams, it might, however, prove advantageous in the case of non-planar molecules.

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The Phases and Magnitudes of the Structure Factors*

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Inequalities among the coefficients of a Fourier series representing the electron density in a crystal are derived on the basis that the series represents a positive function. The procedure is formulated for obtaining all inequalities which are based on this characteristic of positiveness, and some of the simpler ones are listed. No symmetry properties are required for deriving the inequalities, but they may be readily introduced into the inequality relationships. It is indicated that application of the linear transformation theory on hermitian forms may prove fruitful in future investigation.

An extensive and fundamental system of inequalities exists among the coefficients of a Fourier series which represents a positive function. The structure factors are the coefficients in the Fourier-series representation of the positive electron density distribution function for crystals. It is the purpose of this paper to derive the fundamental system of inequalities among the structure factors and express them in a useful form.†

By making use of the symmetry characteristics which are found in crystals and the Schwarz inequality, Harker & Kasper (1948) have derived certain useful inequalities among the structure factors. An extension of this work has been made by Gillis (1948), who has applied some additional inequalities of formal mathematical analysis. In both cases it was necessary to resort to symmetry characteristics and certain standard inequalities in analysis. Implicit in their investigations though was the assumption that their distribution function was positive. In recent work on the structure of atoms‡ we have found that the electron distribution about atoms is accurately determined by a limited amount of experimental data since the distribution function is positive. This characteristic of positiveness will be seen to be alone sufficient to yield a system of inequalities which limits the phases and magnitudes of the structure factors for crystals.

Symmetry considerations are not basic to the development of the theory. However, it will be shown how symmetry relations may be introduced into the final results.

Theory

The Fourier coefficient, F_{hkl}, is defined in terms of the electron density distribution function for a crystal, $\rho(x,y,z)$, as follows:

$$F_{hkl}=V\int_0^1\int_0^1\int_0^1 \rho(x,y,z) \times \exp\left[-2\pi i(hx+ky+lz)\right]dx\,dy\,dz, \quad (1)$$

where V is the volume of the unit cell. We construct from expression (1) useful hermitian forms which will be shown to be non-negative. The forms obtained from (1) are

$$\sum_{hkl}\sum_{h'k'l'}{}_1^m X_{hkl}\overline{X}_{h'k'l'}F_{h-h',\,k-k',\,l-l'} = V\int_0^1\int_0^1\int_0^1 \rho(x,y,z)\sum_{hkl}\sum_{h'k'l'}{}_1^m X_{hkl}\overline{X}_{h'k'l'} \times \exp\{-2\pi i[(h-h')x+(k-k')y+(l-l')z]\}\,dx\,dy\,dz, \quad (m=1,2,\ldots), \quad (2)$$

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† A system of inequalities for the one-dimensional case has been found by Achyeser & Krein (1934) in their studies of the one-dimensional trigonometric moment problem.

‡ To be published (*Phys. Rev.*, February 1950). Presented at ASXRED Meeting, Columbus, Ohio, December 1948.

where each summation represents the triple sum over each index, X_{hkl} is an independent variable, and $\overline{X}_{hkl}$ is the complex conjugate of X_{hkl}.

Since $\rho(x,y,z)$ is real, $F_{hkl}=\overline{F}_{\bar{h}\bar{k}\bar{l}}$. The sextuple sum on the right side of equation (2) may be expressed as the product of a triple sum and its complex conjugate. The right side may therefore be written

$$V\int_0^1\int_0^1\int_0^1 \rho(x,y,z) \times\left|\sum_{hkl\,1}^{m} X_{hkl}\exp\left[-2\pi i(hx+ky+lz)\right]\right|^2 dxdydz. \quad (3)$$

It is seen that (3) is non-negative since $\rho(x,y,z)$ is a non-negative function. We therefore have from the left side of (2) the non-negative hermitian forms*

$$\sum_{hkl\,1}^{m}\sum_{h'k'l'} X_{hkl}\overline{X}_{h'k'l'}F_{h-h',\,k-k',\,l-l'}\geqslant 0 \quad (m=1,2,\ldots). \quad (4)$$

Not only are the inequalities (4) a necessary consequence of the positiveness of $\rho(x,y,z)$, but it may also be shown that these inequalities (4) are sufficient to insure that $\rho(x,y,z)$ be non-negative. This is of importance because it implies that any set of inequalities which is derived from $\rho(x,y,z)$ being non-negative is contained in the set which we shall derive from (4). To prove that (4) is sufficient to determine a non-negative Fourier series we assume that (4) is true and shall show that as a consequence $\rho(x,y,z)$ is non-negative.

The proof consists in showing that the function

$$\sum_{hkl\,-\infty}^{\infty}{}^{\dagger} F_{hkl}X^hY^kZ^l \quad (5)$$

is non-negative in every region $|X|\leqslant 1-\delta$, $|Y|\leqslant 1-\delta$, $|Z|\leqslant 1-\delta$, where $0<\delta<1$. The symbol $\Sigma^\dagger$ means that a negative power of any variable which appears in the sum (5) must be replaced by the conjugate complex of the variable raised to the absolute value of the power, e.g. X^{-h}, $h>0$, is to be replaced by $\overline{X}^h$. Since the density function, $\rho(x,y,z)$, is the limit of (5) as $X\to e^{2\pi ix}$, $Y\to e^{2\pi iy}$ and $Z\to e^{2\pi iz}$, it may be concluded that $\rho(x,y,z)$ is also non-negative.

Since the set of numbers $|F_{hkl}|$ is bounded, the series (5) converges uniformly and absolutely in any region $|X|\leqslant 1-\delta$, $|Y|\leqslant 1-\delta$, $|Z|\leqslant 1-\delta$, where $0<\delta<1$. It may be shown that (5) is equal to

$$\sum_{hkl\,0}^{\infty}\sum_{h'k'l'} F_{h-h',\,k-k',\,l-l'}X^h\overline{X}^{h'}Y^k\overline{Y}^{k'}Z^l\overline{Z}^{l'} \times(1-X\overline{X})(1-Y\overline{Y})(1-Z\overline{Z}). \quad (6)$$

To demonstrate this we take a typical term of (5), $F_{m,n,-p}X^mY^n\overline{Z}^p$, where $m>0$, $n>0$, $p>0$, and show that it is contained once in (6). The indices of those terms of (6) which contain $F_{m,n,-p}$ as a factor satisfy

$$h-h'=m,\quad k-k'=n,\quad l-l'=-p. \quad (7)$$

These relations may be written

$$\left.\begin{array}{l} h=h'+m,\quad k=k'+n,\quad l=l'-p, \\ \text{or}\quad h'=h-m,\quad k'=k-n,\quad l'=l+p. \end{array}\right\} \quad (8)$$

In order to obtain all those terms of (6) having $F_{m,n,-p}$ as a factor, it is important to note that only three of the relations (8) may be validly inserted into (6). Otherwise, any of the remaining relations if substituted into (6) would allow certain of the indices to take on negative values since $m,n,p>0$. The relations (8) which are therefore substituted into (6) are

$$h=h'+m,\quad k=k'+n,\quad l'=l+p. \quad (9)$$

We obtain

$$\sum_{h'k'l\,0}^{\infty} F_{m,n,-p}X^{h'+m}\overline{X}^{h'}Y^{k'+n}\overline{Y}^{k'}Z^l\overline{Z}^{l+p} \times(1-X\overline{X})(1-Y\overline{Y})(1-Z\overline{Z}), \quad (10)$$

which may be written

$$F_{m,n,-p}X^mY^n\overline{Z}^p(1-X\overline{X})(1-Y\overline{Y})(1-Z\overline{Z}) \times\sum_{h'=0}^{\infty}(X\overline{X})^{h'}\sum_{k'=0}^{\infty}(Y\overline{Y})^{k'}\sum_{l=0}^{\infty}(Z\overline{Z})^l=F_{m,n,-p}X^mY^n\overline{Z}^p, \quad (11)$$

the desired result. If we set

$$\zeta_{hkl}=X^hY^kZ^l,\quad \bar{\zeta}_{h'k'l'}=\overline{X}^{h'}\overline{Y}^{k'}\overline{Z}^{l'}, \quad (12)$$

expression (6) becomes

$$\sum_{hkl\,0}^{\infty}\sum_{h'k'l'} F_{h-h',\,k-k',\,l-l'}\zeta_{hkl}\bar{\zeta}_{h'k'l'}(1-X\overline{X})(1-Y\overline{Y})(1-Z\overline{Z}) =(1-X\overline{X})(1-Y\overline{Y})(1-Z\overline{Z}) \times\lim_{m\to\infty}\sum_{hkl\,0}^{m}\sum_{h'k'l'} F_{h-h',\,k-k',\,l-l'}\zeta_{hkl}\bar{\zeta}_{h'k'l'}\geqslant 0, \quad (13)$$

in view of (4) and $X\overline{X}<1$, $Y\overline{Y}<1$, $Z\overline{Z}<1$.

It is assumed that the first partial derivatives of $\rho(x,y,z)$ exist and are continuous at every point. This condition is sufficient to insure that the series

$$\rho(x,y,z)=\sum_{hkl\,-\infty}^{\infty} F_{hkl}\exp\left[2\pi i(hx+ky+lz)\right] \quad (14)$$

converges. In other words the series (5) converges when $X=e^{2\pi ix}$, $Y=e^{2\pi iy}$, $Z=e^{2\pi iz}$, and defines a function of X, Y, Z which is continuous in the closed region $|X|\leqslant 1$, $|Y|\leqslant 1$. $|Z|\leqslant 1$.* It therefore follows from (13) that

$$\rho(x,y,z)=\lim_{\substack{X\to e^{2\pi ix}\\ Y\to e^{2\pi iy}\\ Z\to e^{2\pi iz}}}\sum_{hkl\,-\infty}^{\infty}{}^{\dagger} F_{hkl}X^hY^kZ^l\geqslant 0. \quad (15)$$

This completes the proof that (4) implies that $\rho(x,y,z)$ is non-negative.

* Simple, but relatively weak inequalities on the coefficients may be obtained immediately from (4) by substituting arbitrary complex numbers for the independent variables X_{hkl}.

* This assumption, used to complete the proof with mathematical rigor, is no restriction in the physical sense since the infinite sums may be replaced by finite sums each having a sufficient number of terms to insure that the resulting $\rho(x,y,z)$ differs from the true one by an amount far less than that due to the errors arising from experiment. The assumption is then certainly justified.

The necessary and sufficient condition for the hermitian forms (4) to be non-negative is that a system of determinants involving the F_{hkl}'s be non-negative. Before discussing these determinants for the three-dimensional Fourier series there is an advantage in developing in detail the theory of the determinants corresponding to the one-dimensional positive Fourier series. The three-dimensional theory follows readily from the one-dimensional theory, since both are based on the theory of hermitian forms. The major effect of increasing the number of dimensions is to complicate the notation.

The one-dimensional problem

The hermitian forms associated with the one-dimensional problem may be written*

$$\sum_{h}\sum_{h'}{}^{m}_{1} X_h \overline{X}_{h'} F_{h-h'} \geqslant 0 \quad (m=1,2,\ldots), \tag{16}$$

where F_h is a coefficient in a one-dimensional positive Fourier series. The necessary and sufficient condition for (16) to hold is that the following determinants be non-negative (Dickson, 1930, pp. 81–8):†

$$\begin{vmatrix} F_0 & F_{-1} & F_{-2} & \cdots & F_{-n} \\ F_1 & F_0 & F_{-1} & \cdots & F_{-(n-1)} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ F_n & F_{n-1} & F_{n-2} & \cdots & F_0 \end{vmatrix} \geqslant 0 \quad (n=0,1,2,\ldots). \tag{17}$$

Since any rearrangement may be made on the subscripts of the independent variables of the hermitian forms (16), and since any of these variables may be set equal to zero, we may write the non-negative determinants

$$D=\begin{vmatrix} F_0 & F_{-\epsilon_1} & F_{-\epsilon_2} & \cdots & F_{-\epsilon_n} \\ F_{\epsilon_1} & F_{\epsilon_1-\epsilon_1} & F_{\epsilon_1-\epsilon_2} & \cdots & F_{\epsilon_1-\epsilon_n} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ F_{\epsilon_n} & F_{\epsilon_n-\epsilon_1} & F_{\epsilon_n-\epsilon_2} & \cdots & F_{\epsilon_n-\epsilon_n} \end{vmatrix} \geqslant 0 \quad (n=0,1,2\ldots), \tag{18}$$

where the subscripts ϵ_i, $i=1,2,\ldots,n$ are different from each other and from zero, but otherwise may take on arbitrary positive or negative values. The distinction between (17) and (18) is that in (17) the subscripts in the first column consist of all the integers from 0 to n arranged in increasing order, whereas in (18), although the subscripts in the first column also start with 0 and are distinct, they are arbitrary otherwise. Evidently (18) includes (17). It is seen that in the determinants (18) the subscripts in the first row are the same as those in the first column, but with opposite signs, and are arranged in the same order. The subscript in the ith row and jth column is obtained by adding the subscript in the ith row and first column to the subscript in the first row and jth column ($\epsilon_{ij}=\epsilon_{i1}+\epsilon_{1j}$).

The determinants (18) may be used to obtain a bound on F_{ϵ_n}. Owing to the general form of (18), this bound may be expressed in terms of some or all of the coefficients whose subscripts precede ϵ_n in numerical order or, if desired, in terms of coefficients having higher subscripts in addition to the previous ones.

In order to obtain the bound on F_{ϵ_n} we apply to (18) the expansion theorem for determinants (Muir & Metzler, 1930, pp. 132–5):

$$\begin{vmatrix} F_{\epsilon_1-\epsilon_1} & F_{\epsilon_1-\epsilon_2} & \cdots & F_{\epsilon_1-\epsilon_{n-1}} \\ F_{\epsilon_2-\epsilon_1} & F_{\epsilon_2-\epsilon_2} & \cdots & F_{\epsilon_2-\epsilon_{n-1}} \\ \cdots & \cdots & \cdots & \cdots \\ F_{\epsilon_{n-1}-\epsilon_1} & F_{\epsilon_{n-1}-\epsilon_2} & \cdots & F_{\epsilon_{n-1}-\epsilon_{n-1}} \end{vmatrix} \times D = \begin{vmatrix} F_0 & F_{-\epsilon_1} & \cdots & F_{-\epsilon_{n-1}} \\ F_{\epsilon_1} & F_{\epsilon_1-\epsilon_1} & \cdots & F_{\epsilon_1-\epsilon_{n-1}} \\ \cdots & \cdots & \cdots & \cdots \\ F_{\epsilon_{n-1}} & F_{\epsilon_{n-1}-\epsilon_1} & \cdots & F_{\epsilon_{n-1}-\epsilon_{n-1}} \end{vmatrix} \times \begin{vmatrix} F_{\epsilon_1-\epsilon_1} & F_{\epsilon_1-\epsilon_2} & \cdots & F_{\epsilon_1-\epsilon_n} \\ F_{\epsilon_2-\epsilon_1} & F_{\epsilon_2-\epsilon_2} & \cdots & F_{\epsilon_2-\epsilon_n} \\ \cdots & \cdots & \cdots & \cdots \\ F_{\epsilon_n-\epsilon_1} & F_{\epsilon_n-\epsilon_2} & \cdots & F_{\epsilon_n-\epsilon_n} \end{vmatrix}$$
$$-\begin{vmatrix} F_{\epsilon_1} & F_{\epsilon_1-\epsilon_1} & \cdots & F_{\epsilon_1-\epsilon_{n-1}} \\ F_{\epsilon_2} & F_{\epsilon_2-\epsilon_1} & \cdots & F_{\epsilon_2-\epsilon_{n-1}} \\ \cdots & \cdots & \cdots & \cdots \\ F_{\epsilon_n} & F_{\epsilon_n-\epsilon_1} & \cdots & F_{\epsilon_n-\epsilon_{n-1}} \end{vmatrix} \times \begin{vmatrix} F_{-\epsilon_1} & F_{\epsilon_1-\epsilon_1} & \cdots & F_{\epsilon_{n-1}-\epsilon_1} \\ F_{-\epsilon_2} & F_{\epsilon_1-\epsilon_2} & \cdots & F_{\epsilon_{n-1}-\epsilon_2} \\ \cdots & \cdots & \cdots & \cdots \\ F_{-\epsilon_n} & F_{\epsilon_1-\epsilon_n} & \cdots & F_{\epsilon_{n-1}-\epsilon_n} \end{vmatrix}. \tag{19}$$

The left side of (19) is the product of D and the determinant formed by omitting the first and last rows and columns of D. The first product on the right side of (19) is formed by multiplying the determinant which arises from omitting the last row and column in D by the determinant which arises from omitting the first row and column in D. The second product on the right side of (19) is formed by multiplying the determinant which arises from omitting the first row and last column in D by the determinant which arises from omitting the first column and last row in D. The rows and columns in the last determinant of (19) have been interchanged without changing its value. The determinants on the left side of (19), as well as the first two on the right side, are non-negative in view of (18). The last two determinants in (19) are complex conjugates since corresponding elements are complex conjugates.

If the determinant on the left side of (19) is called Δ and the determinants on the right side called in order $\Delta_1, \Delta_2, d, \bar{d}$, we get

$$D\Delta = \Delta_1\Delta_2 - d\bar{d}. \tag{20}$$

Since D and Δ are non-negative,

$$d\bar{d} \leqslant \Delta_1\Delta_2. \tag{21}$$

By expanding d in terms of the minor of F_{ϵ_n}, we have

$$|d| = |F_{\epsilon_n}\Delta - \Delta'|, \tag{22}$$

* The hermitian forms in (16) may be considered as a subset of the three-dimensional set since the two subscripts k, l may be included in the notation if set equal to zero. It is apparent that there are three such subsets depending upon which two of the subscripts are set equal to zero. There are also three subsets for the two-dimensional problem depending upon which one of the three subscripts is set equal to zero.

† For fixed m, n ranges from zero to $m-1$.

where

$$\Delta'=(-1)^n\begin{vmatrix} F_{\epsilon_1} & F_{\epsilon_1-\epsilon_1} & F_{\epsilon_1-\epsilon_2} & \cdots & F_{\epsilon_1-\epsilon_{n-1}} \\ F_{\epsilon_2} & F_{\epsilon_2-\epsilon_1} & F_{\epsilon_2-\epsilon_2} & \cdots & F_{\epsilon_2-\epsilon_{n-1}} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ F_{\epsilon_{n-1}} & F_{\epsilon_{n-1}-\epsilon_1} & F_{\epsilon_{n-1}-\epsilon_2} & \cdots & F_{\epsilon_{n-1}-\epsilon_{n-1}} \\ 0 & F_{\epsilon_n-\epsilon_1} & F_{\epsilon_n-\epsilon_2} & \cdots & F_{\epsilon_n-\epsilon_{n-1}} \end{vmatrix}. \tag{23}$$

Since Δ_1 and Δ_2 are non-negative, (21) and (22) imply

$$|F_{\epsilon_n}\Delta-\Delta'|\leqslant\Delta_1^{\frac{1}{2}}\Delta_2^{\frac{1}{2}}. \tag{24}$$

Finally, since Δ is non-negative, this becomes

$$|F_{\epsilon_n}-\delta|\leqslant r, \tag{25}$$

where $\delta=\Delta'/\Delta$ and $r=\Delta_1^{\frac{1}{2}}\Delta_2^{\frac{1}{2}}/\Delta$. *The coefficient* F_{ϵ_n} *is bounded in terms of others having higher and lower subscripts, in general, within a circle in the complex plane whose center is* δ *and whose radius is* r.

To complete the proof that (25), $F_0\geqslant 0$ and $|F_{\epsilon_1}|\leqslant F_0$, include all inequalities based on the positiveness of the distribution function, it must still be shown that, conversely, the system (25), $F_0\geqslant 0$ and $|F_{\epsilon_1}|\leqslant F_0$ imply the system (18). Assume then that $F_0\geqslant 0$, $|F_{\epsilon_1}|\leqslant F_0$, and that (25) holds. Our proof is by induction. Since $F_0>0$ and $|F_{\epsilon_1}|\leqslant F_0$, (18) is valid when $n=0$ or 1. We make the induction hypothesis that (18) is valid for all values of n less than some positive integer p. In (25) take $n=p$. Then Δ, Δ_1 and Δ_2 are all non-negative and the steps (21)–(25) are all reversible. Therefore (25) implies (21), and (20) becomes

$$D\Delta=\Delta_1\Delta_2-d\bar{d}\geqslant 0. \tag{26}$$

Hence

$$D\geqslant 0, \tag{27}$$

and (18) is valid for $n=p$. Since p is arbitrary this completes the induction.

The three-dimensional problem

The hermitian forms (4) constitute the basis for formulating the relationships among the Fourier coefficients in the three-dimensional case. In complete analogy with (17), the necessary and sufficient condition for (4) to hold is that an infinite set of determinants be non-negative (Dickson, 1930, pp. 81–8). Their construction will now be described.

For any choice of the value of m in (4) the corresponding determinant is of the order m^3. The indices now consist of number triples, each number being chosen from the set $0, 1, \ldots, m-1$. In the first column, the indices consist of all m^3 triples arranged in 'dictionary' order, i.e. the index α, β, γ precedes α', β', γ' if $\alpha<\alpha'$ or if $\alpha=\alpha', \beta<\beta'$ or if $\alpha=\alpha', \beta=\beta', \gamma<\gamma'$. The indices in the first row are the same and in the same order as those in the first column, but of opposite signs. The index in the ith row and the jth column, as in the one-dimensional case, is obtained by adding the index of the ith row and first column to that of the first row and jth column. As an example we write the determinant when $m=2$:

$$\begin{vmatrix} F_{000} & F_{00\bar{1}} & F_{0\bar{1}0} & F_{0\bar{1}\bar{1}} & F_{\bar{1}00} & F_{\bar{1}0\bar{1}} & F_{\bar{1}\bar{1}0} & F_{\bar{1}\bar{1}\bar{1}} \\ F_{001} & F_{000} & F_{0\bar{1}1} & F_{0\bar{1}0} & \cdots & \cdots & \cdots & \cdots \\ F_{010} & F_{01\bar{1}} & F_{000} & F_{00\bar{1}} & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ F_{111} & F_{110} & F_{101} & F_{100} & \cdots & \cdots & \cdots & F_{000} \end{vmatrix}\geqslant 0. \tag{28}$$

This is the three-dimensional analogue of (17) with $n=1$. As before, any rearrangement may be made on the subscripts of the independent variables of the hermitian forms (4), and any of these variables may be set equal to zero, so that we obtain the three-dimensional analogue of (18):

$$\begin{vmatrix} F_{000} & F_{-\epsilon_1,-\eta_1,-\zeta_1} & \cdots & F_{-\epsilon_n,-\eta_n,-\zeta_n} \\ F_{\epsilon_1,\eta_1,\zeta_1} & F_{\epsilon_1-\epsilon_1,\eta_1-\eta_1,\zeta_1-\zeta_1} & \cdots & F_{\epsilon_1-\epsilon_n,\eta_1-\eta_n,\zeta_1-\zeta_n} \\ F_{\epsilon_2,\eta_2,\zeta_2} & F_{\epsilon_2-\epsilon_1,\eta_2-\eta_1,\zeta_2-\zeta_1} & \cdots & F_{\epsilon_2-\epsilon_n,\eta_2-\eta_n,\zeta_2-\zeta_n} \\ \cdots & \cdots & \cdots & \cdots \\ F_{\epsilon_n,\eta_n,\zeta_n} & F_{\epsilon_n-\epsilon_1,\eta_n-\eta_1,\zeta_n-\zeta_1} & \cdots & F_{\epsilon_n-\epsilon_n,\eta_n-\eta_n,\zeta_n-\zeta_n} \end{vmatrix}\geqslant 0. \tag{29}$$

The indices in the first column start with 0, 0, 0 and are distinct, but are arbitrary otherwise. The indices in the first row are the same as those in the first column, but with opposite signs, and are in the same order. The index in the ith row and jth column is determined by

$$\epsilon_{ij}=\epsilon_{i1}+\epsilon_{1j},\quad \eta_{ij}=\eta_{i1}+\eta_{1j},\quad \zeta_{ij}=\zeta_{i1}+\zeta_{1j}.$$

By an analysis similar to that given by equations (18)–(25) we obtain a bound for $F_{\epsilon_n,\eta_n,\zeta_n}$,*

$$|F_{\epsilon_n,\eta_n,\zeta_n}-\delta|\leqslant r, \tag{30}$$

where

$$\delta=\frac{\Delta'}{\Delta},\quad r=\frac{\Delta_1^{\frac{1}{2}}\Delta_2^{\frac{1}{2}}}{\Delta}, \tag{31}$$

and $\Delta_1, \Delta_2, \Delta$ and Δ' are the three-dimensional generalizations of the corresponding one-dimensional determinants in equations (19) and (23). They are formed by adding the additional subscripts η and ζ as is indicated in (29).

Just as in the one-dimensional case, not only are (30), $F_{000}\geqslant 0$, and $|F_{\epsilon_1\eta_1\zeta_1}|\leqslant F_{000}$ necessary consequences of (29), but (30), $F_{000}\geqslant 0$, and $|F_{\epsilon_1\eta_1\zeta_1}|\leqslant F_{000}$ are also sufficient to insure the validity of (29).

It was pointed out in discussion with Dr A. L. Patterson that the inequalities will not in all cases bound the phases of the coefficients, even if the magnitudes of all the structure factors are known. This is easily seen to be true by considering the example in which

$$\sum_{hkl\atop -\infty}^{\infty}{}' |F_{hkl}|<2F_{000}.$$

Here the distribution function is positive regardless of the phases of the F_{hkl}. A situation as unfavourable as

* This general type of inequality applies to all non-negative Fourier series and therefore may find application to syntheses along and projections upon lines and planes.

this is not to be generally expected for electron densities in crystals, because of the high electron densities in the vicinity of the atomic nuclei.

Discussion

The foregoing theory may find application in the direct use of the derived inequalities. In addition, it will be indicated below that the non-negative hermitian forms which represent the Fourier series constitute a working basis from which many new representations of a crystal structure may be developed. The well-known Patterson representation is such an example.

Inequalities of successively increasing complexity may be obtained from (29) or (30). We write down the first four,*†

$$F_{000}\geqslant 0, \tag{32}$$

$$|F_{hkl}|\leqslant F_{000}, \tag{33}$$

$$\left|F_{h_1+h_2,k_1+k_2,l_1+l_2}-\frac{F_{h_1k_1l_1}F_{h_2k_2l_2}}{F_{000}}\right|\leqslant\frac{\begin{vmatrix}F_{000} & F_{\bar{h}_1\bar{k}_1\bar{l}_1}\\ F_{h_1k_1l_1} & F_{000}\end{vmatrix}^{\frac{1}{2}}\begin{vmatrix}F_{000} & F_{\bar{h}_2\bar{k}_2\bar{l}_2}\\ F_{h_2k_2l_2} & F_{000}\end{vmatrix}^{\frac{1}{2}}}{F_{000}}, \tag{34}$$

$$\left|F_{h_1+h_2+h_3,k_1+k_2+k_3,l_1+l_2+l_3}+\frac{\begin{vmatrix}F_{h_1k_1l_1} & F_{000} & F_{\bar{h}_2\bar{k}_2\bar{l}_2}\\ F_{h_1+h_2,k_1+k_2,l_1+l_2} & F_{h_2k_2l_2} & F_{000}\\ 0 & F_{h_2+h_3,k_2+k_3,l_2+l_3} & F_{h_3k_3l_3}\end{vmatrix}}{\begin{vmatrix}F_{000} & F_{\bar{h}_2\bar{k}_2\bar{l}_2}\\ F_{h_2k_2l_2} & F_{000}\end{vmatrix}}\right|$$

$$\leqslant\frac{\begin{vmatrix}F_{000} & F_{\bar{h}_1\bar{k}_1\bar{l}_1} & F_{\bar{h}_1+\bar{h}_2,\bar{k}_1+\bar{k}_2,\bar{l}_1+\bar{l}_2}\\ F_{h_1k_1l_1} & F_{000} & F_{\bar{h}_2\bar{k}_2\bar{l}_2}\\ F_{h_1+h_2,k_1+k_2,l_1+l_2} & F_{h_2k_2l_2} & F_{000}\end{vmatrix}^{\frac{1}{2}}\begin{vmatrix}F_{000} & F_{\bar{h}_2\bar{k}_2\bar{l}_2} & F_{\bar{h}_2+\bar{h}_3,\bar{k}_2+\bar{k}_3,\bar{l}_2+\bar{l}_3}\\ F_{h_2k_2l_2} & F_{000} & F_{\bar{h}_3\bar{k}_3\bar{l}_3}\\ F_{h_2+h_3,k_2+k_3,l_2+l_3} & F_{h_3k_3l_3} & F_{000}\end{vmatrix}^{\frac{1}{2}}}{\begin{vmatrix}F_{000} & F_{\bar{h}_2\bar{k}_2\bar{l}_2}\\ F_{h_2k_2l_2} & F_{000}\end{vmatrix}}. \tag{35}$$

Since the h, k, l's are any integers, positive, negative or zero, it is seen that any of the coefficients may be bounded in terms of sets of other coefficients, and in many different ways. In the general type of inequality of which the last two are examples, the coefficient which is being bounded lies in a circle in the complex plane whose center is given by the second term in the left member and whose radius is the right member.

In addition to limiting the phases of those coefficients whose magnitudes may be obtained from experiment the inequalities also bound the coefficients whose magnitudes are not known. If the inequalities are used to continue the series, the resulting series will be positive only if a new coefficient satisfies a set of inequalities involving all the coefficients whose magnitudes and phases have already been fixed.

The inequalities (4) have been proven to be sufficient to insure that $\rho(x,y,z)$ be non-negative. The set of inequalities (30), (32) and (33) derived from (4), of which (34) and (35) are examples, is necessary and sufficient to insure the validity of (4). Therefore all systems of inequalities based on the non-negative character of $\rho(x,y,z)$ must be included in the set (30), (32) and (33).

It is apparent that symmetry considerations have not been introduced either for the purpose of representing a non-negative Fourier series or for the purpose of deriving the inequalities. Symmetry relationships may be directly introduced into the inequalities. As an example, if the origin is assumed to be a center of symmetry, $F_{hkl}=F_{\bar{h}\bar{k}\bar{l}}$. Since, in general, $\bar{F}_{hkl}=F_{\bar{h}\bar{k}\bar{l}}$, all coefficients in (30) are real. In this case the inequalities (33), (34) and (35) limit the coefficients to intervals on the real axis.* Inequality (34), for example, then becomes

$$\left|F_{h_1+h_2,k_1+k_2,l_1+l_2}-\frac{F_{h_1k_1l_1}F_{h_2k_2l_2}}{F_{000}}\right|\leqslant\frac{(F^2_{000}-F^2_{h_1k_1l_1})^{\frac{1}{2}}(F^2_{000}-F^2_{h_2k_2l_2})^{\frac{1}{2}}}{F_{000}}. \tag{36}$$

* The h, k, l are simply related to the ϵ, η, ζ in (30) and may be arbitrary positive or negative integers or zero. For example, in (35)

$$h_i=\epsilon_i-\epsilon_{i-1},\quad k_i=\eta_i-\eta_{i-1},\quad l_i=\zeta_i-\zeta_{i-1},$$
$$i=1,2,3,\quad \epsilon_0=\eta_0=\zeta_0=0.$$

Certain choices of h, k, l should be avoided since they may lead to either (a) a zero denominator, or (b) a trivial identity which would arise if the triple ϵ_i, η_i, ζ_i were equal to the triple ϵ_j, η_j, ζ_j or 0, 0, 0 in (29), making two columns identical in (29), or (c) a bound on F_{hkl} in terms of itself. These choices may be avoided in (35), for example, by means of the following rule: If the numbers α, β, γ are chosen in any way from the sets 0, 1 or 1, 2 except that the combination $\alpha=2$, $\beta=1$, $\gamma=2$ is excluded, then the triples

$$\alpha h_1+\beta h_2+\gamma h_3,\quad \alpha k_1+\beta k_2+\gamma k_3,\quad \alpha l_1+\beta l_2+\gamma l_3$$

are to be different from 0, 0, 0.

† These inequalities may be strengthened by dividing the Fourier coefficients by a function of the atomic scattering factors which effectively concentrates the scattering material about the atomic co-ordinates (see Harker & Kasper, 1948).

* In the case of a center of symmetry, some of the determinants which arise may be factored. See Achyeser & Krein (1935).

For the special case $h_1=h_2=h$, $k_1=k_2=k$, $l_1=l_2=l$, this reduces to

$$\left|F_{2h,2k,2l}-\frac{F^2_{hkl}}{F_{000}}\right|\leqslant\frac{F^2_{000}-F^2_{hkl}}{F_{000}}, \qquad (37)$$

which implies

$$\frac{F^2_{hkl}}{F_{000}}-F_{2h,2k,2l}\leqslant F_{000}-\frac{F^2_{hkl}}{F_{000}}, \qquad (38)$$

or

$$\left(\frac{F_{hkl}}{F_{000}}\right)^2\leqslant\frac{1}{2}+\frac{1}{2}\frac{F_{2h,2k,2l}}{F_{000}}. \qquad (39)$$

This is one of the inequalities derived by Harker & Kasper (1948, p. 72).

Again, if the y axis is a twofold rotation axis then $F_{hkl}=F_{\bar{h}k\bar{l}}$, and (34) may be written

$$\left|F_{h_1\pm h_2,k_1+k_2,l_1\pm l_2}-\frac{F_{h_1k_1l_1}F_{h_2k_2l_2}}{F_{000}}\right| \leqslant\frac{(F^2_{000}-|F_{h_1k_1l_1}|^2)^{\frac{1}{2}}(F^2_{000}-|F_{h_2k_2l_2}|^2)^{\frac{1}{2}}}{F_{000}}. \qquad (40)$$

In other words, both $F_{h_1+h_2,k_1+k_2,l_1+l_2}$ and $F_{h_1-h_2,k_1+k_2,l_1-l_2}$ lie inside the circle with center at $F_{h_1k_1l_1}F_{h_2k_2l_2}/F_{000}$ and radius $(F^2_{000}-|F_{h_1k_1l_1}|^2)^{\frac{1}{2}}(F^2_{000}-|F_{h_2k_2l_2}|^2)^{\frac{1}{2}}/F_{000}$, so that the distance between them is not greater than the diameter of the circle

$$|F_{h_1+h_2,k_1+k_2,l_1+l_2}-F_{h_1-h_2,k_1+k_2,l_1-l_2}| \leqslant\frac{2(F^2_{000}-|F_{h_1k_1l_1}|^2)^{\frac{1}{2}}(F^2_{000}-|F_{h_2k_2l_2}|^2)^{\frac{1}{2}}}{F_{000}}. \qquad (41)$$

Taking the special case $h_1=h_2=h$, $k_1=-k_2=k$, $l_1=l_2=l$, and noting that $|F_{hkl}|=|F_{h\bar{k}l}|$, this reduces to

$$|F_{2h,0,2l}-F_{000}|\leqslant\frac{2(F^2_{000}-|F_{hkl}|^2)}{F_{000}}, \qquad (42)$$

whence

$$F_{000}-F_{2h,0,2l}\leqslant\frac{2(F^2_{000}-|F_{hkl}|^2)}{F_{000}}, \qquad (43)$$

or

$$\left|\frac{F_{hkl}}{F_{000}}\right|^2\leqslant\frac{1}{2}+\frac{1}{2}\frac{F_{2h,0,2l}}{F_{000}}. \qquad (44)$$

This is another inequality derived by Harker & Kasper (1948).

As a final example we take the case in which the y axis is a twofold inversion axis. Then $F_{hkl}=F_{h\bar{k}l}$ and (34) becomes

$$\left|F_{h_1+h_2,k_1\pm k_2,l_1+l_2}-\frac{F_{h_1k_1l_1}F_{h_2k_2l_2}}{F_{000}}\right| \leqslant\frac{(F^2_{000}-|F_{h_1k_1l_1}|^2)^{\frac{1}{2}}(F^2_{000}-|F_{h_2k_2l_2}|^2)^{\frac{1}{2}}}{F_{000}}. \qquad (45)$$

As before,

$$|F_{h_1+h_2,k_1+k_2,l_1+l_2}-F_{h_1+h_2,k_1-k_2,l_1+l_2}| \leqslant\frac{2(F^2_{000}-|F_{h_1k_1l_1}|^2)^{\frac{1}{2}}(F^2_{000}-|F_{h_2k_2l_2}|^2)^{\frac{1}{2}}}{F_{000}}, \qquad (46)$$

and the case

$$h_1=-h_2=h,\quad k_1=k_2=k,\quad l_1=-l_2=l,$$

reduces to

$$|F_{0,2k,0}-F_{000}|\leqslant\frac{2(F^2_{000}-|F_{hkl}|^2)}{F_{000}}, \qquad (47)$$

and finally to the Harker–Kasper inequality

$$\left|\frac{F_{hkl}}{F_{000}}\right|^2\leqslant\frac{1}{2}+\frac{1}{2}\frac{F_{0,2k,0}}{F_{000}}. \qquad (48)$$

Since the Harker–Kasper and Gillis inequalities were derived on the assumption that ρ is non-negative, and since the inequalities (30) include all inequalities which can be obtained on this basis, it was to have been anticipated that the Harker–Kasper and Gillis inequalities would be included in the set (30).

Other types of inequalities using symmetry properties may be obtained by inserting the additional relationships into the determinants (29). For example, if the y axis is a twofold rotation axis, whence

$$F_{hkl}=F_{\bar{h}k\bar{l}},$$

and we choose a fourth-order determinant (29) in which F_{hkl} and $F_{\bar{h}\bar{k}\bar{l}}$ occur twice along the secondary diagonal, the determinant may be factored to yield*

$$|F_{h_1k_1l_1}\pm F_{h_2k_1l_2}| \lesseqgtr(F_{000}\pm F_{h_1+h_2,0,l_1+l_2})^{\frac{1}{2}}(F_{000}\pm F_{h_1-h_2,0,l_1-l_2})^{\frac{1}{2}}, \qquad (49)$$

where either < holds for both signs, or > holds for both signs, or = holds for at least one sign. This means that $F_{h_1k_1l_1}$ lies either in the interior of two intersecting circles, or the exterior of both circles or on the boundary of at least one. This type of inequality contains only information which is already included in the set (30). However, it may have more usefulness in application. We have not exploited further the possibility of obtaining new types of inequalities by means of introducing symmetry relations into the determinants (29) in which the coefficient of interest and its complex conjugate occur more than once.

The application of any linear transformations to the variables of the hermitian forms (4) yields other hermitian forms which are evidently non-negative. The determinants associated with these lead to different inequalities which are nevertheless equivalent to the original ones. The inequalities related to these new hermitian forms may be more useful. This may be illustrated by deriving the hermitian forms which represent a Patterson series from those which represent the original series by means of a linear transformation. For example, the hermitian form containing two variables may be transformed to the hermitian form

* As before the h, k, l are simply related to the ϵ, η, ζ in (29) and may be arbitrary positive or negative integers or zero.

corresponding to the Patterson series in accordance with the following scheme:

$$\begin{pmatrix} F_0 & F_{\bar{n}} \\ F_n & F_0 \end{pmatrix} \rightarrow \begin{pmatrix} F_0+|F_n| & 0 \\ 0 & F_0-|F_n| \end{pmatrix} \rightarrow \begin{pmatrix} F_0^2+|F_n|^2 & 0 \\ 0 & F_0^2-|F_n|^2 \end{pmatrix} \rightarrow \begin{pmatrix} F_0^2 & |F_n|^2 \\ |F_n|^2 & F_0^2 \end{pmatrix}. \quad (50)$$

The first matrix represents the hermitian form

$$F_0X_1\overline{X}_1+F_nX_1\overline{X}_2+F_{\bar{n}}X_2\overline{X}_1+F_0X_2\overline{X}_2$$

related to the original series, and the last matrix represents the hermitian form corresponding to the Patterson series. The second matrix is the diagonal form of the first and may be derived from it by a linear transformation. The third and fourth matrices are similarly related. Evidently a linear transformation relates the second and third matrices.

The practical significance of this type of transformation is that the inequalities associated with the Patterson series involve only the magnitudes of the Fourier coefficients. These inequalities have the obvious advantage that the quantities contained in them are directly derivable from experiment. Perhaps other intermediate cases occur in which inequalities arise that contain some complex coefficients and the magnitudes of others. Certainly, it is worth while investigating the further implications of linear transformation theory.

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Intensity of X-ray Reflexion from Perfect and Mosaic Absorbing Crystals

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The variation of the integrated Bragg reflexion of perfect absorbing crystals with the degree of asymmetry of the reflexion, structure factor and wave-length is studied theoretically and compared with that of ideally mosaic absorbing crystals. It is shown that the integrated reflexion of a perfect crystal is always less than that of a corresponding mosaic crystal. If absorption is very large, or if the reflexion is very asymmetric, the integrated reflexion of the perfect crystal approaches asymptotically that of the mosaic crystal. Approximate formulae are given for the integrated reflexion as a function of asymmetry of the reflexion, structure factor, and absorption coefficient. It is suggested that accurate determinations of structure factors may be made by the use of asymmetric reflexions for which the integrated reflexion becomes more nearly independent of the texture of the crystals.

1. Introduction

Recent experiments on the variation of the integrated reflexion of crystals with wave-length of the X-rays (Wooster & Macdonald, 1948) and asymmetry of the reflexion (Evans, Hirsch & Kellar, 1948) led the authors to a theoretical investigation of the integrated reflexion of perfect absorbing crystals as a function of the degree of asymmetry of the reflexion,* structure factor and absorption coefficient. For a mosaic crystal, expressions have been derived previously for the variation of integrated reflexion with these factors (see James, 1948). For a perfect crystal the dynamical theory of X-ray reflexions, as developed by Ewald (1918, 1924), Kohler (1933) and von Laue (1941), takes all these variables into account and leads to an expression for the intensity of the X-ray beam reflected by the crystal at a particular setting (e.g. Zachariasen, 1945). To obtain the integrated reflexion, it is necessary to integrate this expression over a range of settings of the crystal. Such an integration can be carried out analytically only in some special cases. Thus, when absorption is negligible, the well-known Darwin (1914) formula is obtained. When absorption is very large, it will be shown in a later section that the integrated reflexion tends to equal that for a mosaic crystal. In the general case the reflexion curves can be calculated and integrated graphically. Examples of such curves have been given by Prins (1930), Parratt (1932), Renninger (1934, 1937*a*) Zachariasen (1945), etc., and Renninger has also performed the graphical integration in a few special cases.

The present authors have attacked the problem in a general way. From Zachariasen's treatment of the dynamical theory, it follows that the effects of degree

* A reflexion is asymmetric if the reflecting planes make an angle with the surface of the crystal.