5. Il serait interessant de suivre le mécanisme des déformations des monocristaux lors de la courbure;* indépendamment de son intérêt théorique, cette étude serait utile pour préciser les conditions optima de préparation des monochromateurs.

On sait que des cristaux d'aluminium légèrement déformés peuvent montrer des taches de Laue focalisées sur lesquelles l'existence de stries indique l'état de subdivision du monocristal global en petits blocs monocristallins légèrement désorientés, appelé 'Polygonisation' (Orowan, 1947; Guinier & Tennevin, 1949; Cahn, 1949.)

Une première étude de monocristaux courbés d'aluminium qui donnent des raies spectrales fines sur le cylindre de focalisation de 40 cm. de diamètre, ne nous a pas permis d'observer des stries sur des taches de Laue focalisées à 25 cm. Il faut remarquer que des cristaux courbés ne doivent pas être *fortement* polygonisés pour qu'ils donnent une bonne focalisation en rayonnement monochromatique. Le cristal plastique courbé le plus convenable pour la spectroscopie peut être schématisé comme suit: les dislocations provoquées par la courbure sont distribuées uniformément de telle sorte que le nombre des plans réticulaires normaux aux faces de la lame croit régulièrement, depuis la face concave jusqu'à la face convexe. Il est probable que la courbure introduit des dislocations irrégulières d'où résultent des déformations locales très fortes. Le recuit produirait une réorganisation telle que les dislocations se répartissent d'une manière à peu près uniforme. S'il en est ainsi, les lames plastiques utilisables seraient des édifices à constantes réticulaires invariables à travers l'épaisseur, à nombre croissant de plans réticulaires normaux, vers la face convexe. Tandis que les lames élastiques courbées fonctionnent comme des édifices à constantes réticulaires variables en fonction de l'épaisseur, où une fibre neutre moyenne conserve seule les caractères du cristal non déformé.

Les lames d'aluminium planes ou déformées sont donc susceptibles d'emplois avantageux dans la technique des rayons X. Leur application peut être étendue à d'autres rayonnements.

* Yen & Hibbard (1949) viennent de publier quelques résultats obtenus sur des cristaux d'aluminium courbés par application d'une tension en deux points; l'étude aux rayons X a été faite seulement par des diagrammes de Laue.

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Remarks on the Theory of Phase Limiting Inequalities and Equalities

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The inequalities derived by Karle & Hauptman are discussed in more detail. The simplifications resulting from symmetry are studied, and it is shown that the relations derived by Harker & Kasper are only those that correspond to the totally symmetric representation of the point group. In the discrete-atom approximation, part of the inequalities reduces to equalities, special cases of which have been reported earlier by Banerjee and by Buerger.

Introduction

By substituting the analytical expression of the structure factor for the various symmetries in Schwarz's inequality, Harker & Kasper (1948) obtained a number of relations that limit the real part of some structure factors in terms of the magnitudes of others. In a generalization of this work Karle & Hauptman (1949) have shown that, independent of the symmetry, a set of inequalities involving structure factors can be derived from the fact that the electron density must be non-

negative. This assumption is found to be implicit in the treatment by Harker & Kasper.

In the present paper the application of symmetry conditions to the Karle–Hauptman treatment is discussed. To facilitate the introduction of symmetry operations the basic inequality is first derived in a slightly modified way.

In the last section it will be shown that the usual assumption of discrete atoms not only considerably increases the power of the inequalities, but reduces some of them to equalities.

1. Mathematical preliminaries

If $f(\mathbf{r})$ and $g(\mathbf{r})$ are functions of the position vector in ordinary space $\mathbf{r}$, both piecewise continuous, the scalar product of the function-vectors $\mathbf{f}$ and $\mathfrak{g}$ is defined as

$$(\mathbf{f}.\mathfrak{g})=\int \mathbf{f}^*(\mathbf{r})\,g(\mathbf{r})\,d\tau, \tag{1·1}$$

where the integration is over the unit cell.‡ It follows that

$$(\mathfrak{g}.\mathbf{f})=(\mathbf{f}.\mathfrak{g})^*. \tag{1·2}$$

In particular we have

$$(\mathbf{f}.\mathbf{f})=\int f^*(\mathbf{r})f(\mathbf{r})\,d\tau\geqslant 0. \tag{1·3}$$

We now introduce a set of $(n+1)$ different functions $v^p(\mathbf{r})\,(p=0,1,\ldots,n)$, and suppose $f(\mathbf{r})$ to be a linear combination of these

$$f(\mathbf{r})=\sum_{p=0}^{n} x^{p*}v^p(\mathbf{r})=x\dagger.v(\mathbf{r}), \tag{1·4}$$§

Here x and $v(\mathbf{r})$ are $(n+1)\times 1$-dimensional matrices with elements x^p and $v^p(\mathbf{r})$ respectively. We expand the left side of the inequality in (1·3) in terms of the $\mathbf{v}^p$ and find

$$0\leqslant \sum_{p=0}^{n}\sum_{q=0}^{n} x^{p*}(\mathbf{v}^q.\mathbf{v}^p)x^q, \tag{1·5}$$

or, more concisely,

$$0\leqslant x\dagger.F.x, \tag{1·6}$$

where the elements of the $(n+1)\times(n+1)$ matrix F are

$$F^p_q=(\mathbf{v}^q.\mathbf{v}^p). \tag{1·7}$$

From (1·2) we see that this matrix is hermitian:

$$F^q_p=F^{p*}_q. \tag{1·8}$$

The inequality (1·6) has to hold for any x and is therefore equivalent to the $(n+1)$ inequalities

$$0\leqslant \det{}^{(m)}F \quad (m=0,1,\ldots,n), \tag{1·9}$$

where the determinants in the right are formed from F by omitting all but the first $(m+1)$ rows and columns. Various other ways of stating this result will be found useful in this paper. If F is partly diagonal, i.e.

$$F=\mathrm{diag}\,(F_1,F_2,\ldots,F_i,\ldots,F_k), \tag{1·10}$$

then (1·9) is replaced by similar sets of inequalities for each of the smaller matrices F_i. In particular, if F is completely diagonal (or brought into that form by a transformation), we have for the characteristic numbers

$$0\leqslant\lambda_m \quad (m=0,1,\ldots,n). \tag{1·11}$$

The last set of inequalities can of course also be obtained directly from (1·6) by substituting successively all the characteristic vectors x_m, defined by

$$F.x_m=\lambda_m x_m \quad (m=0,1,\ldots,n). \tag{1·12}$$

Finally, the trace T_i of the determinants F_i, being equal to the sum of their characteristic numbers, must also be non-negative.

2. The Karle–Hauptman treatment

Let

$$\mathbf{H}_p \quad (p=0,1,\ldots,n) \tag{2·1}$$

be a set of different reciprocal-lattice vectors and $\rho(\mathbf{r})$ the electron density. Then we may take for the functions $v^p(\mathbf{r})$

$$v^p(\mathbf{r})=\rho(\mathbf{r})^{\frac{1}{2}}\exp\,[2\pi i\mathbf{H}_p.\mathbf{r}]. \tag{2·2}$$

By substituting this in (1·7), making use of the fact that

$$\rho(\mathbf{r})\geqslant 0, \tag{2·3}$$

we find for the elements of the matrix F

$$F^p_q=\int\rho(\mathbf{r})\exp\,[2\pi i(\mathbf{H}_p-\mathbf{H}_q).\mathbf{r}]\,d\tau=F_{\mathbf{H}_p-\mathbf{H}_q}, \tag{2·4}$$

which are the Fourier coefficients of $\rho(\mathbf{r})$ associated with the reciprocal-lattice points $\mathbf{H}_p-\mathbf{H}_q\ (p,q=0,1,\ldots,n)$. Thus (1·9) gives us $(n+1)$ inequalities involving these structure factors. For each new reciprocal-lattice vector that is added to the set $\mathbf{H}_p$ one more inequality is obtained. Apparently no generality is lost if we take $\mathbf{H}_0=0$, since differences only of the vectors $\mathbf{H}_p$ occur in the determinants.

In Karle & Hauptman's paper, expansions are given for the determinants leading to expressions that limit $F_{\mathbf{H}_m}$ to a circle in the complex plane, the center and radius of which are functions of the remaining structure factors. Furthermore, it is shown that if the Fourier coefficients obey (1·9), the electron density is non-negative.

It should be noted that any system of inequalities (1·9) contains the trivial relation

$$0\leqslant \det{}^{(0)}F=F^0_0=F_{\mathbf{0}}. \tag{2·5}$$

It may be factored out by carrying out the first step of the diagonalization process

$$P\dagger.F.P=\mathrm{diag}\,(F_{\mathbf{0}},G), \tag{2·6}$$

where

$$P=\begin{pmatrix} 1 & 0 & 0 & \ldots 0\\ -F_{\mathbf{H}_1}/F_{\mathbf{0}} & 1 & 0 & \ldots 0\\ -F_{\mathbf{H}_2}/F_{\mathbf{0}} & 0 & 1 & \ldots 0\\ \vdots & & & \vdots\\ -F_{\mathbf{H}_n}/F_{\mathbf{0}} & 0 & 0 & \ldots 1 \end{pmatrix} \tag{2·7}$$

and

$$G^p_q=F_{\mathbf{H}_p-\mathbf{H}_q}-\frac{F_{\mathbf{H}_p}F^*_{\mathbf{H}_q}}{F_{\mathbf{0}}} \quad (p,q=1,2,\ldots,n). \tag{2·8}$$

‡ See, for example, Murnaghan (1948). The function-vector concept is at first intended as nothing but a convenient notation. In the last section it will help to make clear the analogy between the continuous-density and discrete-atom treatments.

§ Matrix elements are labeled according to the following convention: A^p_q is the element of matrix A in row p, column q. The adjoint matrix $A\dagger$ has elements $(A\dagger)^p_q=A^{q*}_p$. An $m\times n$ matrix is understood to have m rows and n columns. The elements of column vectors carry a single superscript.

The remaining n inequalities are obtained by forming determinants from the elements of G,

$$0 \leqslant \det^{(m)} F \quad (m=1,2,\ldots,n) \tag{2·9}$$

or

$$0 \leqslant y\dagger . G . y \tag{2·10}$$

for any y. Nearly all the inequalities derived by Harker & Kasper can be obtained from (2·10) by substituting numerical values for the coefficients y^p.

3. Special choices for the vector set H_p

In the relations (1·9) the $(m+1)$ diagonal elements obviously are all F_0. For each structure factor on one side of the diagonal, its complex conjugate appears on the opposite side. The number of different structure factors, excluding F_0, therefore is $\frac{1}{2}m(m+1)$. However, this number is a maximum and may be considerably reduced by a special choice of the vectors $\mathbf{H}_p$, in either of two ways:

(A) Reduction of the number of different vectors $\mathbf{H}_p - \mathbf{H}_q$. For example, if in the case $m=3$, which in general involves the 6 different reciprocal-lattice points

$$\left.\begin{array}{llll} \mathbf{H}_1, & & & \\ \mathbf{H}_2 & \mathbf{H}_2-\mathbf{H}_1, & & \\ \mathbf{H}_3 & \mathbf{H}_3-\mathbf{H}_1 & \mathbf{H}_3-\mathbf{H}_2, & \end{array}\right\} \tag{3·1}$$

we take $\mathbf{H}_3=\mathbf{H}_2+\mathbf{H}_1$, this number is reduced to 4:

$$\left.\begin{array}{lll} \mathbf{H}_1, & & \\ \mathbf{H}_2 & \mathbf{H}_2-\mathbf{H}_1, & \\ \mathbf{H}_2+\mathbf{H}_1 & \mathbf{H}_2 & \mathbf{H}_1. \end{array}\right\} \tag{3·2}$$

(For this system, the two inequalities

$$(H_{\mathbf{H}_1} \pm F_{\mathbf{H}_2})^2 \leqslant (F_0 \pm F_{\mathbf{H}_2+\mathbf{H}_1})(F_0 \pm F_{\mathbf{H}_2-\mathbf{H}_1}) \tag{3·3}$$

hold if the structure factors are real. They were used by Gillis (1948) in the case of oxalic acid dihydrate.)

As no two of the vectors $\mathbf{H}_p$ can be equal, the minimum number of different vectors $\mathbf{H}_p - \mathbf{H}_q$ is m. This limit is reached by making the special choice

$$\mathbf{H}_0=0, \quad \mathbf{H}_p=p.\mathbf{H}, \quad (p=1,2,\ldots,n; \quad \mathbf{H}\neq 0), \tag{3·4}$$

for then each of the vectors

$$\mathbf{H}_p - \mathbf{H}_q = (p-q).\mathbf{H} \tag{3·5}$$

belongs to the set (3·4). The resulting inequalities could of course be equally well derived from the fact that the projection of $\rho(\mathbf{r})$ on a line in the direction $\mathbf{H}$ must be a non-negative function.

(B) A choice of the $\mathbf{H}_p$ such that some of the reciprocal-lattice vectors $\mathbf{H}_p - \mathbf{H}_q$ are related by symmetry. Then, of course, the corresponding structure factors are no longer independent.

4. Use of symmetry conditions

Though the principle, referred to at the end of the last section, may be applied in many different ways, we shall discuss here only the very special choice

$$\mathbf{H}_0=0, \quad \mathbf{H}_p=\phi_p.\mathbf{H} \quad (p=1,2,\ldots,s; \quad \mathbf{H}\neq 0), \tag{4·1}$$‡

where the ϕ_p are the symmetry operations of the point group (or one of its subgroups) and s is its order. The functions $v_p(\mathbf{r})$ as defined by (2·2) are now of the form

$$\left.\begin{array}{l} v^0(\mathbf{r})=\rho(\mathbf{r})^{\frac{1}{2}} \\ v^p(\mathbf{r})=\rho(\mathbf{r})^{\frac{1}{2}} \exp\left[2\pi i \phi_p.\mathbf{H}.\mathbf{r}\right] \end{array}\right\} \quad (p=1,2,\ldots,s). \tag{4·2}$$

However, it will be found useful to introduce a different set of functions

$$\left.\begin{array}{l} w^0(\mathbf{r})=\rho(\mathbf{r})^{\frac{1}{2}} \\ w^p(\mathbf{r})=\rho(\mathbf{r})^{\frac{1}{2}} \exp\left[2\pi i \mathbf{H}.\mathbf{r}.S_p\right] \end{array}\right\} \quad (p=1,2,\ldots,s), \tag{4·3}$$

where the S_p are the operations of the space group, related to those of the point group by

$$S_p \equiv [\phi_p, \mathbf{t}_p], \tag{4·4}$$

i.e.

$$\mathbf{r}.S_p = \mathbf{r}.\phi_p + \mathbf{t}_p. \tag{4·5}$$

The relation between the $v^p(\mathbf{r})$ and $w^p(\mathbf{r})$ is therefore

$$\left.\begin{array}{l} w^0(\mathbf{r})=v^0(\mathbf{r}), \\ w^p(\mathbf{r})=v^p(\mathbf{r}) \exp\left[2\pi i \mathbf{H}.\mathbf{t}_p\right]. \end{array}\right\} \tag{4·6}$$

Keeping in mind that $\rho(\mathbf{r})$ is invariant under any S_p,

$$\rho(\mathbf{r}.S_p)=\rho(\mathbf{r}), \tag{4·7}$$

we find the following expressions for the matrix elements F_q^p:

$$(\mathbf{w}^0.\mathbf{w}^0)=F_0, \tag{4·8}$$

$$(\mathbf{w}^0.\mathbf{w}^p)=\int \rho(\mathbf{r}) \exp\left[2\pi i \mathbf{H}.\mathbf{r}.S_p\right] d\tau = F_{\mathbf{H}}, \tag{4·9}$$

$$\begin{aligned} (\mathbf{w}^q.\mathbf{w}^p) &= \int \rho(\mathbf{r}) \exp\left[2\pi i \mathbf{H}.\mathbf{r}.(S_p - S_q)\right] d\tau \\ &= \int \rho(\mathbf{r}) \exp\left[2\pi i \mathbf{H}.\mathbf{r}.(S_r - E)\right] d\tau \\ &= F_{(\phi_r - I).\mathbf{H}} \exp\left[2\pi i \mathbf{H}.\mathbf{t}_r\right]. \end{aligned} \tag{4·10}$$

In the last equation

$$E \equiv [1,0] \tag{4·11}$$

is the identity operation and S_r is related to S_p and S_q by

$$S_p = S_q.S_r. \tag{4·12}$$

There are of course $(s-1)$ structure factors of the type $F_{(\phi_r - I).\mathbf{H}}$, some of which may be equal, and thus the total number of structure factors in the equations (4·8–4·10), not counting F_0, is s. In this section a set of inequalities will be derived, each of which contains all these structure factors and includes earlier Harker–Kasper relations. A simpler set, more suitable for practical application, will be discussed in the next section.

To transform F, we introduce a set of s new functions by making linear combinations of the

$$w^p(\mathbf{r}) \qquad (p=1,2,\ldots,s),$$

$$\left.\begin{array}{l} z_{i\beta}^{\alpha}(\mathbf{r}) = \sum_{p=1}^{s} [\Gamma_i(\phi_p)]_{\beta}^{\alpha} . w^p(\mathbf{r}) \\ \sum_{i=1}^{k} l_i^2 = s \end{array}\right\} \quad \begin{array}{l} (\alpha,\beta=1,2,\ldots,l_i; \\ i=1,2,\ldots,k). \end{array} \tag{4·13}$$

Here $[\Gamma_i(\phi_p)]_{\beta}^{\alpha}$ is an element of the $l_i \times l_i$ dimensional matrix corresponding to ϕ_p in the ith irreducible repre-

‡ Zachariasen's (1945) notation for symmetry operations is used.

sentation Γ_i of the point group; k is the number of classes. The matrix elements obtained from these new functions are

$$(\mathbf{z}^{\gamma}_{j\epsilon}.\mathbf{z}^{\alpha}_{i\beta})=\sum_{p=1}^{s}\sum_{q=1}^{s}[\Gamma_i(\phi_p)]^{\alpha}_{\beta}.[\Gamma_j(\phi_q)]^{\gamma *}_{\epsilon}.(\mathbf{w}^q.\mathbf{w}^p). \quad (4\cdot14)$$

We write ϕ_p as the product of ϕ_q and ϕ_r according to (4·12)

$$[\Gamma_i(\phi_p)]^{\alpha}_{\beta}=\sum_{\nu=1}^{l_i}[\Gamma_i(\phi_q)]^{\alpha}_{\nu}.[\Gamma_i(\phi_r)]^{\nu}_{\beta}, \quad (4\cdot15)$$

and use (4·11), finding

$$(\mathbf{z}^{\gamma}_{j\epsilon}.\mathbf{z}^{\alpha}_{i\beta})=\sum_{\nu=1}^{l_i}\sum_{q=1}^{s}[\Gamma_j(\phi_q)]^{\gamma *}_{\epsilon}.[\Gamma_i(\phi_q)]^{\alpha}_{\nu}\sum_{r=1}^{s}[\Gamma_i(\phi_r)]^{\nu}_{\beta} \times F_{(\phi_r-I).\mathbf{H}}\exp[2\pi i\mathbf{H}.\mathbf{t}_r]. \quad (4\cdot16)$$

The sum over q is at once found from the orthogonality relation

$$\sum_{q=1}^{s}[\Gamma_j(\phi_q)]^{\gamma *}_{\epsilon}.[\Gamma_i(\phi_q)]^{\alpha}_{\nu}=\delta_{ij}\delta_{\alpha\gamma}\delta_{\epsilon\nu}\frac{s}{l_i}, \quad (4\cdot17)$$

where the δ's are Kronecker symbols, and so finally

$$(\mathbf{z}^{\gamma}_{j\epsilon}.\mathbf{z}^{\alpha}_{i\beta})=\delta_{ij}\delta_{\alpha\gamma}\frac{s}{l_i}\sum_{r=1}^{s}[\Gamma_i(\phi_r)]^{\epsilon}_{\beta}.F_{(\phi_r-I).\mathbf{H}} \times\exp[2\pi i\mathbf{H}.\mathbf{t}_r] \quad (4\cdot18)$$

$$(\alpha,\beta,\gamma,\epsilon=1,2,\ldots,l_i;\quad i,j=1,2,\ldots,k).$$

Thus the matrix formed from the functions $z^{\alpha}_{i\beta}$ has the form

$$\mathrm{diag}\,(F_1,F_2,\ldots,F_i,\ldots,F_k),$$

where the matrices F_i are of dimension $l_i^2\times l_i^2$. Their trace is easily found

$$\begin{aligned}T_i&=\sum_{\alpha=1}^{l_i}\sum_{\beta=1}^{l_i}(\mathbf{z}^{\alpha}_{i\beta}.\mathbf{z}^{\alpha}_{i\beta})\\&=\sum_{\alpha=1}^{l_i}\sum_{\beta=1}^{l_i}\frac{s}{l_i}\sum_{r=1}^{s}[\Gamma_i(\phi_r)]^{\beta}_{\beta}.F_{(\phi_r-I).\mathbf{H}}\exp[2\pi i\mathbf{H}\cdot\mathbf{t}_r]\\&=s\sum_{r=1}^{s}\chi_i(\phi_r).F_{(\phi_r-I).\mathbf{H}}\exp[2\pi i\mathbf{H}.\mathbf{t}_r], \quad (4\cdot19)\end{aligned}$$

where $\chi_i(\phi_r)$ is the trace (character) of $\Gamma_i(\phi_r)$. These quantities must be non-negative,

$$0\leqslant\sum_{r=1}^{s}\chi_i(\phi_r)F_{(\phi_r-I).\mathbf{H}}\exp[2\pi i\mathbf{H}.\mathbf{t}_r]. \quad (4\cdot20)$$

This set of inequalities may be strengthened somewhat by adding our original function $w^0(\mathbf{r})$ to the set (4·13). The additional matrix elements are rapidly found from (4·8) and (4·9):

$$(\mathbf{w}^0.\mathbf{w}^0)=F_0, \quad (4\cdot21)$$

$$(\mathbf{w}^0.\mathbf{z}^{\alpha}_{i\beta})=\sum_{r=1}^{s}[\Gamma_i(\phi_r)]^{\alpha}_{\beta}F_{\mathbf{H}}=\delta_{i1}sF_{\mathbf{H}}. \quad (4\cdot22)$$

(Γ_1 is understood to be the totally symmetric representation.) F_1 is thus enlarged to a matrix of dimensions 2×2. From the non-negativity of its determinant we have

$$(\mathbf{w}^0.\mathbf{z}^1_{11}).(\mathbf{z}^1_{11}.\mathbf{w}^0)\leqslant(\mathbf{w}^0.\mathbf{w}^0).(\mathbf{z}^1_{11}.\mathbf{z}^1_{11}), \quad (4\cdot23)$$

or

$$s^2.|F_{\mathbf{H}}|^2\leqslant s.F_0.\sum_{r=1}^{s}F_{(\phi_r-I).\mathbf{H}}\exp[2\pi i\mathbf{H}.\mathbf{t}_r]. \quad (4\cdot24)$$

This inequality is stronger than the first one of the set (4·20), which differs from it in that the left side is zero. It may be included in the complete set by writing

$$\delta_{i1}.|F_{\mathbf{H}}|^2\leqslant\frac{1}{s}\sum_{r=1}^{s}\chi_i(\phi_r)F_{(\phi_r-I).\mathbf{H}}\exp[2\pi i\mathbf{H}.\mathbf{t}_r] \quad (i=1,2,\ldots,k). \quad (4\cdot25)$$

The first of these relations is easily recognized as the general form of a large class of Harker–Kasper inequalities.‡ The remaining inequalities have been ignored by these authors. All may be found directly from (2·8) and (2·10) by substituting (4·1) and $y^p=\chi_i(\phi_r)$.

5. Inequalities involving a single phase angle

It was shown in § 3 that, in the absence of symmetry, the number of different structure factors in the inequalities (1·9) is at least m. However, the relation for $m=1$ does not give any information on the phase of the single structure factor it contains,

$$0\leqslant\begin{vmatrix}F_0 & F^*_{\mathbf{H}_1}\\F_{\mathbf{H}_1} & F_0\end{vmatrix}, \quad (5\cdot1)$$

and we may therefore state that no restrictions on single phase angles can be found. The inequalities lead only to relations between two or more phase angles.

Independent phase-angle determinations are no longer impossible if the crystal possesses symmetry. The necessary inequalities follow from the fact that each of the 3×3 determinants with elements $F^p_q=(\mathbf{w}^q.\mathbf{w}^p)$ ($p,q=0,1,r$, where $r\neq0$ or 1 and S_1 is understood to be the identity operation E) of the matrix F discussed in the last section is non-negative,

$$0\leqslant\begin{vmatrix}F_0 & F^*_{\mathbf{H}} & F^*_{\mathbf{H}}\\F_{\mathbf{H}} & F_0 & F^*_{(\phi_r-I).\mathbf{H}}\exp[-2\pi i\mathbf{H}.\mathbf{t}_r]\\F_{\mathbf{H}} & F_{(\phi_r-I).\mathbf{H}}\exp[2\pi i\mathbf{H}.\mathbf{t}_r] & F_0\end{vmatrix} \quad (r=2,3,\ldots,s). \quad (5\cdot2)$$

This may be written

$$\left|\frac{F_{(\phi_r-I).\mathbf{H}}}{F_0}\exp[2\pi i\mathbf{H}.\mathbf{t}_r]-\left|\frac{F_{\mathbf{H}}}{F_0}\right|^2\right|\leqslant1-\left|\frac{F_{\mathbf{H}}}{F_0}\right|^2, \quad (5\cdot3)$$

or, in all cases where $F_{(\phi_r-I).\mathbf{H}}\exp[2\pi i\mathbf{H}.\mathbf{t}_r]$ is real,

$$\left|\frac{F_{\mathbf{H}}}{F_0}\right|^2\leqslant\frac{1}{2}+\frac{1}{2}\frac{F_{(\phi_r-I).\mathbf{H}}}{F_0}\exp[2\pi i\mathbf{H}.\mathbf{t}_r]. \quad (5\cdot4)$$

Inequalities of this type may be used to determine the phase angles of structure factors $F_{(\phi_r-I).\mathbf{H}}$ independent of any other phase angle. They are more suited for practical application than the rather complicated set (4·25), where each inequality contains all these structure factors. (As a matter of fact, the k relations (4·25) contain more than k different structure factors $F_{(\phi_r-I).\mathbf{H}}$ if one or more classes contain symmetry operations with different rotation axes; in these cases the relations (4·25) may be made equivalent to (5·4) by the addition of the inequalities of type (4·25) for the various subgroups.) Clearly, for $s=2$ the two sets are identical.

‡ A direct generalization of Harker & Kasper's treatment has been given by MacGillavry (1950).

6. Equalities

From the first paper of Harker & Kasper on, use has been made of the fact that the inequalities can be considerably strengthened by assuming the electron-density function to be the superposition of spherically symmetrical atomic-density functions,

$$\rho(\mathbf{r})=\sum_{j=1}^{N} Z_j.\varphi(|\mathbf{r}-\mathbf{r}_j|), \tag{6·1}$$

where N is the number of atoms, Z_j the atomic number and $\mathbf{r}_j$ the position of atom j. Instead of the $F_{\mathbf{H}}$, unitary factors are then introduced,

$$U_{\mathbf{H}}=\sum_{j=1}^{N} n_j \exp[2\pi i\mathbf{H}.\mathbf{r}_j], \tag{6·2}$$

where

$$n_j=\frac{Z_j}{\sum_{j=1}^{N} Z_j} \tag{6·3}$$

is the fraction of the electrons that belongs to the jth atom. If $f(\mathbf{H})$ is the Fourier transform of $\varphi(\mathbf{r})$, the relation between the $F_{\mathbf{H}}$ and $U_{\mathbf{H}}$ is

$$U_{\mathbf{H}}=\frac{F_{\mathbf{H}}}{f(\mathbf{H})\sum_{j=1}^{N} Z_j}. \tag{6·4}$$

We now introduce the $(n+1)\times N$-dimensional matrix v with elements

$$v_j^p=n_j^{\frac{1}{2}}\exp[2\pi i\mathbf{H}_p.\mathbf{r}_j] \quad (p=0,1,\ldots,n;\quad j=1,2,\ldots,N), \tag{6·5}$$

and another matrix, of dimension $(n+1)\times(n+1)$,

$$U=v.v\dagger. \tag{6·6}$$

Let the rows of v be denoted by v^p, then

$$U_q^p=v^p.v^q\dagger=\sum_{j=1}^{N} v_j^p.v_j^{q*}, \tag{6·7}$$

and by substitution of (6·5) and (6·2)

$$U_q^p=U_{\mathbf{H}_p-\mathbf{H}_q}. \tag{6·8}$$

Thus U is analogous with the matrix F, defined in (2·4), but its elements are the unitary structure factors (Fourier coefficients of the atomic peak function) in the reciprocal-lattice points $\mathbf{H}_p-\mathbf{H}_q$. The same inequalities hold therefore. However, U has the additional property (6·6) [compare also (6·7) with (1·7)] and as a consequence of this

$$\begin{aligned}\det{}^{(m)}U=\det{}^{(m)}(v.v\dagger)&\geqslant 0 \quad \text{if } m<N\\ &=0 \quad \text{if } m\geqslant N.\end{aligned} \tag{6·9}$$

(To show this, one writes

$$x\dagger.U.x=x\dagger.v.v\dagger.x=(v\dagger.x)\dagger.(v\dagger.x)=y\dagger.y\geqslant 0; \tag{6·10}$$

then, if $v\dagger$ has more columns than rows, an $x\neq 0$ can always be found such that $y=v\dagger.x=0$; this requires $U.x=0$ for $x\neq 0$ and thus $\det U=0$.)

This result may be stated: if in our original set of inequalities (1·9) the $F_{\mathbf{H}_p-\mathbf{H}_q}$ are replaced by unitary structure factors, those with $m\geqslant N$ reduce to equalities.

Special cases of these equalities have already been described earlier:

(*a*) For the particular choice (3·4) for the base vectors $\mathbf{H}_p$ we have

$$U_q^p=U_{(p-q).\mathbf{H}} \tag{6·11}$$

and the equality with $m=N$ of the set (6·9) is the general form of the equations derived by Banerjee (1933).

(*b*) If there is one atom per asymmetric unit, i.e. $N=s$, and we choose the set (4·1) (i.e. $n=s$), the determinant of the matrix F in §4 must be zero. Consequently, the equality sign must hold in at least one of the relations (4·25). It has already been shown by Buerger (1948) that this is the case for the first of these relations.

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