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An Assessment of the Power of the Non-Negativity Criterion as Used in X-ray Crystal Structure Determinations

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It is shown why the requirement of reality coupled with that of non-negativity and certain symmetry of the electron-density function constitutes a weak criterion in space groups lacking translational symmetry elements, at least in so far as the requirements mentioned are exploited by any Harker–Kasper inequalities. In space groups with translational symmetry operations the situation is fundamentally different.

Notation

$_gF(\mathbf{h}) = \gamma(\mathbf{h}).F(\mathbf{h})$, where $\gamma(\mathbf{h})$ is a real or complex contingently vanishing coefficient which may imply e.g. 'sharpening' of ϱ_{correct}, 'unitarization' or normalization of $F(\mathbf{h})$, partial summation and/or generalization of phase angle (within certain limits).

$\alpha(\mathbf{h})$ is an arbitrary (correct or incorrect) phase angle of the complex structure factor $_gF(\mathbf{h}) = |_gF(\mathbf{h})| \exp[i\alpha(\mathbf{h})]$.

$_g\varrho(\mathbf{r})$ $\quad _g\varrho(\mathbf{r}) = \dfrac{1}{V}\sum\limits_{\mathbf{h}} {_gF(\mathbf{h})}.\exp[-2\pi i\mathbf{h}.\mathbf{r}]$.

$\tilde{Z}$ is the complex conjugate of Z.

$\oint$ indicates integration over complete period (cell).

$j, k, l, m, p, q, \mu, \nu$ are positive integers.

n is the symmetry number.

C_i is the ith symmetry operator (see MacGillavry (1950)). The letter i is also used for $\sqrt{-1}$ as no mistake can be caused thereby.

$\varphi_i, \mathbf{t}_i$ $\quad \varphi_i.\mathbf{r}+\mathbf{t}_i = C_i.\mathbf{r}$ where φ_i is the matrix part and $\mathbf{t}_i$ the translational part of the ith symmetry operation.

$Z_\perp$ is the projection of Z on to the real axis i.e. the real part of Z.

$\equiv$ is a congruence sign, the modulus always being 2π.

f is any complex function of $\mathbf{r}$.

N is determinantal order.

Introduction

Starting with the generalized function (generalized phase angles)

$$_g\varrho(\mathbf{r}, \alpha) = \frac{1}{V}\sum_{\mathbf{h}} {_gF(\mathbf{h})}.\exp[-2\pi i\mathbf{h}.\mathbf{r}]\,, \quad (1)$$

the fundamental problem of structure determination is to find and make use of additional information rendering $_g\varrho$ physically sensible. We shall first of all suppose that ϱ and indeed any $_g\varrho$ is real i.e. that, for every generalization,

$$_gF(\mathbf{h}) = {_g\tilde{F}}(-\mathbf{h})\,. \quad (2)$$

We attempt to appraise the criterion of non-negativity and symmetry, especially in so far as these properties are exploited in the derivation of the Harker–Kasper inequalities (Harker & Kasper (1948), MacGillavry (1950)).

Cochran (1952) discusses the integral (here given in a modified form)

$$\oint {_g\varrho^3(\mathbf{r})}\,dv(\mathbf{r}) = \frac{1}{V^2}\sum_{\mathbf{h}+\mathbf{h}'+\mathbf{h}''=0} {_gF(\mathbf{h})}.{_gF(\mathbf{h}')}.{_gF(\mathbf{h}'')} \quad (3)$$

and states that in case of centrosymmetry the α's found by means of the Harker–Kasper inequalities or by the Sayre (1952) equalities are those making (3) maximum positive. (For exposition see Cochran & Woolfson (1955) and Cochran (1955).)

We shall use a more extensive treatment and prove that

(i) the Harker–Kasper inequalities, irrespective of symmetry, fix lower, and only lower, limits to the real parts of the terms

$$\left.\begin{aligned} &{_gF(\mathbf{h})}.{_gF(\mathbf{h}')}.{_gF(\mathbf{h}'')} = |{_gF(\mathbf{h})}.{_gF(\mathbf{h}')}.{_gF(\mathbf{h}'')}| \\ &\quad \times \exp\{i[\alpha(\mathbf{h})+\alpha(\mathbf{h}')+\alpha(\mathbf{h}'')]\}\,, \\ &\text{where} \qquad \mathbf{h}+\mathbf{h}'+\mathbf{h}''=0\,, \end{aligned}\right\} \quad (4)$$

and thereby a lower limit—if, for an infinite $_gF$ series, it puts any finite limit at all—to the sum (3),

(ii) for translation-free (possibly centered) space groups the absolute maximum in α space of sum (3) is generally *not* associated with the correct phases.

There is a reservation to (i) which we shall return to in the discussion. The absolute maximum mentioned in (ii) is easily visualized and gives a picture of the amount of freedom of movement in α space left by the inequalities.

Development

Let us start with a general linear combination of ${}_gF(\mathbf{h}^{(\nu)})$'s (compare MacGillavry (1950)):

$$\sum_{\nu=1}^{m} \gamma'(\mathbf{h}^{(\nu)})_g F(\mathbf{h}^{(\nu)}) = \sum_{\nu=1}^{m} \gamma'(\mathbf{h}^{(\nu)}) \times \frac{1}{n} \oint {}_g\varrho(\mathbf{r}) \cdot \sum_{i=0}^{n-1} \exp\,[2\pi i \mathbf{h}^{(\nu)} . C_i . \mathbf{r}] . dv(\mathbf{r})$$

$$= \frac{1}{n} \oint {}_g\varrho(\mathbf{r}) \sum_{\nu=1}^{m} \sum_{i=0}^{n-1} \gamma'(\mathbf{h}^{(\nu)}) . \exp\,[2\pi i \mathbf{h}^{(\nu)} . C_i . \mathbf{r}] . dv(\mathbf{r})\,, \quad (5)$$

where (primed) $\gamma'(\mathbf{h}^{(\nu)})$ is a quite arbitrary (non-vanishing), complex coefficient of

$${}_gF(\mathbf{h}^{(\nu)}) = \gamma(\mathbf{h}^{(\nu)}) . F(\mathbf{h}^{(\nu)})\,.$$

${}_gF(\mathbf{h}^{(\nu)})$ corresponds to a ${}_g\varrho(\mathbf{r})$ that is non-negative (this restriction for—unprimed—$\gamma(\mathbf{h}^{(\nu)})$ remains until otherwise specified). We shall go as far as to study (5) by means of Schwarz's inequality.

Applying a straightforward generalization of MacGillavry's treatment one obtains the following condition:

$$\left| \sum_{\nu=1}^{m} \gamma'(\mathbf{h}^{(\nu)}) . {}_gF(\mathbf{h}^{(\nu)}) \right|^2 \le \frac{{}_gF(0)}{n} \sum_{k=0}^{n-1} \left\{ \sum_{\nu=1}^{m} |\gamma'(\mathbf{h}^{(\nu)})|^2 . {}_gF(\mathbf{h}^{(\nu)} . \varphi_k - \mathbf{h}^{(\nu)}) \times \exp\,[2\pi i \mathbf{h}^{(\nu)} . \mathbf{t}_k] + 2 \cdot \sum_{\substack{\nu=2 \\ \nu>\mu}}^{m} \sum_{\mu=1}^{m-1} \{\gamma'(\mathbf{h}^{(\nu)}) . \tilde{\gamma}'(\mathbf{h}^{(\mu)}) . {}_gF(\mathbf{h}^{(\nu)} . \varphi_k - \mathbf{h}^{(\mu)}) \times \exp\,[2\pi i \mathbf{h}^{(\nu)} . \mathbf{t}_k]\}_\perp \right\} . \quad (6)$$

(6) may lead to the condition that the real part of a term

$${}_gF(\mathbf{h}^{(\nu)} . \varphi_k - \mathbf{h}^{(\nu)}) . \exp\,[2\pi i \mathbf{h}^{(\nu)} . \mathbf{t}_k] \quad (7)$$

should not be less than a certain value (which may depend upon the α values assigned to other terms in (6)). This can be expressed in the way that the argument of expression (7) i.e.

$$\begin{aligned} &\arg\{{}_gF(\mathbf{h}^{(\nu)} . \varphi_k - \mathbf{h}^{(\nu)})\} + \arg\{\exp\,[2\pi i \mathbf{h}^{(\nu)} . \mathbf{t}_k]\} \\ &\equiv \alpha(\mathbf{h}^{(\nu)} . \varphi_k - \mathbf{h}^{(\nu)}) + \alpha(\mathbf{h}^{(\nu)}) - \alpha(\mathbf{h}^{(\nu)} . \varphi_k) \\ &\equiv \alpha(\mathbf{h}^{(\nu)} . \varphi_k - \mathbf{h}^{(\nu)}) + \alpha(\mathbf{h}^{(\nu)}) + \alpha(-\mathbf{h}^{(\nu)} . \varphi_k)\,, \end{aligned} \quad (8)$$

should have (or be congruent to) a value in a certain interval $(-\beta', \beta')$ where $0 \le \beta' \le \pi$. (Notice that

$$(\mathbf{h}^{(\nu)} . \varphi_k - \mathbf{h}^{(\nu)}) + (\mathbf{h}^{(\nu)}) + (-\mathbf{h}^{(\nu)} . \varphi_k) = 0.)$$

This is in accord with the general statement (i) about (4).

(6) may further lead to the requirement that a term

$$\{\gamma'(\mathbf{h}^{(\nu)}) . \tilde{\gamma}'(\mathbf{h}^{(\mu)}) . {}_gF(\mathbf{h}^{(\nu)} . \varphi_k - \mathbf{h}^{(\mu)}) . \exp\,[2\pi i \mathbf{h}^{(\nu)} . \mathbf{t}_k]\}_\perp \quad (9)$$

should exceed a certain value (which may again depend on the values assigned to other terms in (6)). (6) is valid for any choice of γ''s. In so far as the left member of (6) is considered, the most rigorous expression obtains for all $\gamma'(\mathbf{h}^{(\nu)}) . {}_gF(\mathbf{h}^{(\nu)})$'s having the same argument, say, zero. With such γ''s the result is, that the argument of (9) (not projected) i.e.

$$\begin{aligned} &-\alpha(\mathbf{h}^{(\nu)}) + \alpha(\mathbf{h}^{(\mu)}) + \alpha(\mathbf{h}^{(\nu)} . \varphi_k - \mathbf{h}^{(\mu)}) \\ &+ \alpha(\mathbf{h}^{(\nu)}) - \alpha(\mathbf{h}^{(\nu)} . \varphi_k) \\ &\equiv \alpha(\mathbf{h}^{(\mu)}) + \alpha(\mathbf{h}^{(\nu)} . \varphi_k - \mathbf{h}^{(\mu)}) + \alpha(-\mathbf{h}^{(\nu)} . \varphi_k)\,, \end{aligned} \quad (10)$$

should have (or be congruent to) a value in a certain interval $(-\beta'', \beta'')$ about the real axis. (Notice that the reciprocal vectors in (10) may be any three vectors adding up to zero.) This is again in agreement with the general statement (i).

Consequently (6) always leads to results in accordance with statement (i). (6), however, does not cover all Harker–Kasper inequalities derivable from (5). Alternative forms may be found if it is possible to factorize

$$\sum_{\nu=1}^{m} \sum_{i=0}^{n-1} \gamma'(\mathbf{h}^{(\nu)}) . \exp\,[2\pi i \mathbf{h}^{(\nu)} . C_i . \mathbf{r}]\,. \quad (11)$$

The case $m=1$ was treated by MacGillavry (1950) with the contingently applicable result

$$|{}_gF(\mathbf{h})|^2 \le \frac{1}{n} \sum_{j=0}^{p-1} {}_gF(\mathbf{h} . \varphi'_j - \mathbf{h}) . \exp\,[2\pi i \mathbf{h} . \mathbf{t}'_j] \times \sum_{k=0}^{q-1} {}_gF(\mathbf{h} . \varphi''_k - \mathbf{h}) . \exp\,[2\pi i \mathbf{h} . \mathbf{t}''_k]\,, \quad (12)$$

where both sums are positive. (For the meaning of the suffixed and primed operators, see the original paper.)

The conclusion is again that the argument of some term, say the jth, i.e.

$$\alpha(\mathbf{h} . \varphi'_j - \mathbf{h}) + \alpha(\mathbf{h}) + \alpha(-\mathbf{h} . \varphi'_j)\,, \quad (13)$$

should have (or be congruent to) a value in a certain interval $(-\beta''', \beta''')$. (Notice that $(\mathbf{h} . \varphi'_j - \mathbf{h}) + (\mathbf{h}) + (-\mathbf{h} . \varphi'_j) = 0$.) This is still in concordance with our contention (i).

In *the general case* ($m \ge 2$) there is always the factorization type

$$\sum_{\nu=1}^{m} \sum_{i=0}^{n-1} \gamma'(\mathbf{h}^{(\nu)}) . \exp\,[2\pi i \mathbf{h}^{(\nu)} . C_i . \mathbf{r}] = \exp\,[2\pi i \mathbf{h}^{(\nu_1)} . C_{i_1} . \mathbf{r}] \times \sum_{\nu=1}^{m} \sum_{i=0}^{n-1} \gamma'(\mathbf{h}^{(\nu)}) . \exp\,[2\pi i (\mathbf{h}^{(\nu)} . C_i - \mathbf{h}^{(\nu_1)} \cdot C_{i_1}) . \mathbf{r}] \quad (14)$$

exemplified by Harker & Kasper (1948). Use of the resolution (14) brings one back to (6). There are, however, sometimes other resolutions, e.g. one leading to the important relation

$$|_gF(\mathbf{h}) \pm {_gF}(\mathbf{h}')|^2 \le \{_gF(0) \pm {_gF}(\mathbf{h}+\mathbf{h}')\}\{_gF(0) \pm {_gF}(\mathbf{h}-\mathbf{h}')\}\,, \quad (15)$$

valid by centrosymmetry. We attempt a general resolution of

$$\sum_{\nu=1}^{m}\sum_{i=0}^{n-1}\gamma'(\mathbf{h}^{(\nu)}).\exp[2\pi i\mathbf{h}^{(\nu)}.C_i.\mathbf{r}] = \sum_{\nu=1}^{m}\sum_{i=0}^{n-1}\gamma'(\mathbf{h}^{(\nu)}).\exp[2\pi i\mathbf{h}^{(\nu)}.\mathbf{t}_i].\exp[2\pi i\mathbf{h}^{(\nu)}.\varphi_i.\mathbf{r}] \quad (16)$$

under the form of

$$\sum_{k=0}^{p-1}\gamma_k'.\exp[2\pi i\mathbf{h}_k'.\mathbf{t}_k'].\exp[2\pi i\mathbf{h}_k'.\varphi_k'.\mathbf{r}] \times \sum_{l=0}^{q-1}\gamma_l''.\exp[2\pi i\mathbf{h}_l''.\mathbf{t}_l''].\exp[2\pi i\mathbf{h}_l''.\varphi_l''.\mathbf{r}]$$
$$= \sum_{k=0}^{p-1}\sum_{l=0}^{q-1}\gamma_k'.\gamma_l''.\exp[2\pi i(\mathbf{h}_k'.\mathbf{t}_k'+\mathbf{h}_l''.\mathbf{t}_l'')] \times\exp[2\pi i(\mathbf{h}_k'.\varphi_k'+\mathbf{h}_l''.\varphi_l'').\mathbf{r}]\,, \quad (17)$$

where γ, $\mathbf{h}$, φ, and $\mathbf{t}$ (in (17)) are submitted to no advance condition (indexing of $\mathbf{h}$ and priming of φ has not the same implication as in MacGillavry (1950): the φ's may be any matrix operators). We identify (16) with (17), supposing

$$p.q=m.n\,. \quad (18)$$

For each k and l there must be a ν and i—say $\nu_{k,l}$ and $i_{k,l}$—such that

$$\mathbf{h}^{(\nu_{k,l})}.\varphi_{i_{k,l}} = \mathbf{h}_k'.\varphi_k'+\mathbf{h}_l''.\varphi_l''\,. \quad (19)$$

We further identify

$$\gamma'(\mathbf{h}^{(\nu_{k,l})}) = \gamma_k'.\gamma_l''\,, \quad (20)$$

and claim

$$2\pi.\mathbf{h}^{(\nu_{k,l})}.\mathbf{t}_{i_{k,l}} \equiv 2\pi(\mathbf{h}_k'.\mathbf{t}_k'+\mathbf{h}_l''.\mathbf{t}_l'')\,. \quad (21)$$

When (16) is identical with (17), (5) gives

$$\left|\sum_{\nu=1}^{m}\gamma'(\mathbf{h}^{(\nu)})_gF(\mathbf{h}^{(\nu)})\right|^2 \le \frac{1}{n^2}\oint {_g\varrho}(\mathbf{r}) \times\left|\sum_{k=0}^{p-1}\gamma_k'.\exp[2\pi i\mathbf{h}_k'.\mathbf{t}_k'].\exp[2\pi i\mathbf{h}_k'.\varphi_k'.\mathbf{r}]\right|^2 dv(\mathbf{r}) \times\oint {_g\varrho}(\mathbf{r}) \times\left|\sum_{l=0}^{q-1}\gamma_l''.\exp[2\pi i\mathbf{h}_l''.\mathbf{t}_l''].\exp[2\pi i\mathbf{h}_l''.\varphi_l''.\mathbf{r}]\right|^2 dv(\mathbf{r})\,. \quad (22)$$

Partly developing as above ((5) to (6)) gives

$$\left|\sum_{\nu=1}^{m}\gamma'(\mathbf{h}^{(\nu)}).{_gF}(\mathbf{h}^{(\nu)})\right|^2 \le \frac{1}{n^2} \times\left\{\sum_{k=0}^{p-1}|\gamma_k'|^2.{_gF}(0)+2\sum_{\substack{k=1\\k>k'}}^{p-1}\sum_{k'=0}^{p-2}\{\gamma_k'.\tilde{\gamma}_{k'}' \times{_gF}(\mathbf{h}_k'.\varphi_k'-\mathbf{h}_{k'}'.\varphi_{k'}').\exp[2\pi i(\mathbf{h}_k'.\mathbf{t}_k'-\mathbf{h}_{k'}'.\mathbf{t}_{k'}')]\}_\perp\right\}$$
$$\times\left\{\sum_{l=0}^{q-1}|\gamma_l''|^2.{_gF}(0)+2\sum_{\substack{l=1\\l>l'}}^{q-1}\sum_{l'=0}^{q-2}\{\gamma_l''\tilde{\gamma}_{l'}'' \times{_gF}(\mathbf{h}_l''.\varphi_l''-\mathbf{h}_{l'}''.\varphi_{l'}'').\exp[2\pi i(\mathbf{h}_l''.\mathbf{t}_l''-\mathbf{h}_{l'}''.\mathbf{t}_{l'}'')]\}_\perp\right\}. \quad (23)$$

(We have no reason here to investigate under what premises the development can be carried further.)

We again make the left member as large as possible, setting

$$\arg\{\gamma'(\mathbf{h}^{(\nu)})\} \equiv -\alpha(\mathbf{h}^{(\nu)})\ (+\text{constant})\,. \quad (24)$$

Then one can show, using (19), (20), and (21), that the argument of the k, k'th term (not projected) of the first parenthesis of (23) is congruent to

$$\alpha(\mathbf{h}^{(\nu_{k,l})}.\varphi_{i_{k,l}}-\mathbf{h}^{(\nu_{k',l})}.\varphi_{i_{k',l}}) + \alpha(-\mathbf{h}^{(\nu_{k,l})}.\varphi_{i_{k,l}})+\alpha(\mathbf{h}^{(\nu_{k',l})}.\varphi_{i_{k',l}})\,, \quad (25)$$

and correspondingly for the second parenthesis (l, l'th term):

$$\alpha(\mathbf{h}^{(\nu_{k,l})}.\varphi_{i_{k,l}}-\mathbf{h}^{(\nu_{k,l'})}.\varphi_{i_{k,l'}}) + \alpha(-\mathbf{h}^{(\nu_{k,l})}.\varphi_{i_{k,l}})+\alpha(\mathbf{h}^{(\nu_{k,l'})}.\varphi_{i_{k,l'}})\,. \quad (26)$$

Since both parentheses of (23) are positive, statement (i) follows. As (23) (with the special case (6)) covers all Harker–Kasper inequalities, this result confirms statement (i).

We now turn to (ii).

Let us set out from *any* α's satisfying all Harker–Kasper relations (e.g. correct α's) and consider

$$|\Sigma\alpha| \equiv |\alpha(\mathbf{h})+\alpha(\mathbf{h}')+\alpha(\mathbf{h}'')|\,, \quad \text{where} \quad \mathbf{h}+\mathbf{h}'+\mathbf{h}''=0\,. \quad (27)$$

One can always assume that $|\Sigma\alpha| \le \pi$. Any α''s giving

$$|\Sigma\alpha'| \le |\Sigma\alpha| \quad (28)$$

for every $\mathbf{h}$ triplet give a ${_g\varrho}$ function 'virtually non-negative' in the meaning that the Harker–Kasper inequalities are satisfied and such that (3) assumes a value equal to or larger than the correct one.

For all space groups which do not imply translational operations (except possibly centering translations) (28) has the trivial solution $\alpha' \equiv 0$ (or an equivalent one depending on choice of origin). This corresponds to a centrosymmetric ${_g\varrho}$ function—which we will designate ${_g\varrho_{\text{extreme}}}$—characterized by an extreme 'electron' accumulation in a point with the lowest number of positions. In all cases complicated enough, and for

$_gF$ series complete enough, to call for special attention, $_g\varrho_{\text{extreme}}$ is highly dissimilar to $_g\varrho_{\text{correct}}$. As Harker–Kasper inequalities cannot discriminate between these two, the result gained by the inequalities must necessarily be very meager.

It is conceivable that the Harker–Kasper inequalities and, for sufficiently limited series, the maximization of (3), might lead to several alternative sets of α's of which one is (equivalent to) the trivial set and one is correct (centrosymmetry). In this case some extra condition must be used for discrimination.

If there is a translational part of some symmetry operator an accumulation of 'electrons' as just discussed is impossible: there are, for any $\mathbf{r}$ origin, α-relations repugnant to the trivial solution. It can be proved moreover, that at least for complete $_gF$ series no other solutions exist for which all $|\Sigma\alpha'| \equiv 0$: they would become identical with the trivial case after appropriate origin translation. This means that at least an extreme 'electron' accumulation is impossible. Centrosymmetric examples prove that neither is there necessarily any general point (plus equivalent positions) such that, in the case of virtual non-negativity, the real parts of all Fourier terms are non-negative in the point. Whether, for a complicated structure, the Harker–Kasper inequalities, or the maximization of (3), might give a decisive clue to the structure sought is thus still an open question for space groups with translations. At any rate the positions in α space of the maximum of the sum (3) (compare (4)) are no longer independent of the magnitude of the coefficients $|_gF(\mathbf{h})\,.\,_gF(\mathbf{h}')\,.\,_gF(\mathbf{h}'')|$.

General considerations and discussion

One may ask whether other non-negativity criteria than those we have used can eliminate $_g\varrho_{\text{extreme}}$ in case of translation-free space groups, i.e. whether 'virtual non-negativity' is true non-negativity. It can be shown by examples that $_g\varrho_{\text{extreme}}$ is not necessarily non-negative. The following arguments make it probable, however, that there can exist no reliable inequality capable of excluding the trivial solution.

Starting with the generalized Schwarz's inequality

$$\begin{vmatrix} \oint \tilde{f}_0 f_0 dv & \oint \tilde{f}_1 f_0 dv & \ldots\ldots \oint \tilde{f}_{N-1} f_0 dv \\ \oint \tilde{f}_0 f_1 dv & \oint \tilde{f}_1 f_1 dv & \ldots\ldots \oint \tilde{f}_{N-1} f_1 dv \\ \cdots & \cdots & \cdots \\ \oint \tilde{f}_0 f_{N-1} dv & \oint \tilde{f}_1 f_{N-1} dv & \ldots\ldots \oint \tilde{f}_{N-1} f_{N-1} dv \end{vmatrix} \geq 0 \tag{29}$$

(see e.g. Goedkoop (1950)) one gets particularly for

$$\left.\begin{aligned} f_\nu &= {_g\varrho^{\frac{1}{2}}}\,.\exp\,[2\pi i\mathbf{h}^{(\nu)}.\,\mathbf{r}] \\ \mathbf{h}^{(0)} &= 0 \end{aligned}\right\} \tag{30}$$

and non-negative $_g\varrho$, the Karle–Hauptman (1950) inequalities (compare Goedkoop (1950), § 2), which are necessary and sufficient conditions for non-negativity.

We have specialized (29) by setting $N=2$ (Schwarz's inequality) but generalized f_1 to

$$\left.\begin{aligned} f_1 &= {_g\varrho^{\frac{1}{2}}} \sum_{\nu=1}^{m} \sum_{i=0}^{n-1} \gamma'(\mathbf{h}^{(\nu)})\,.\exp\,[2\pi i\mathbf{h}^{(\nu)}.\,C_i\,.\,\mathbf{r}] \\ (f_0 &= {_g\varrho^{\frac{1}{2}}}) \end{aligned}\right\} \tag{31}$$

thus arriving at (6). The resulting inequalities were utilized by assigning those arguments to $\gamma'(\mathbf{h}^{(\nu)})$ that make the left member ('the smaller member') as large as possible. An alternative strategy, using Schwarz's inequality, is to assign values to the coefficients in such a way that the larger member becomes as small as possible, or to examine both members. Our function f_1, (31), is, however, not suited to such a procedure (for $n>1$): the γ''s are independent of i (compare e.g. (6)). In case one still uses inequality (6) or (23) according to the more elaborate strategy, the result might possibly be at variance with our statement (i) in the Introduction. This is the reason for the reservation made there.

If one sets

$$\left.\begin{aligned} f_1 &= {_g\varrho^{\frac{1}{2}}} \sum_{\nu=1}^{m} \sum_{i=0}^{n-1} \gamma_i'(\mathbf{h}^{(\nu)})\,.\exp\,[2\pi i\mathbf{h}^{(\nu)}.\,C_i\,.\,\mathbf{r}] \\ f_0 &= {_g\varrho^{\frac{1}{2}}} \end{aligned}\right\} \tag{32}$$

the result of applying Schwarz's inequality is

$$\begin{aligned} &_gF(0)\,.\oint {_g\varrho} \left| \sum_{\nu=1}^{m} \sum_{i=0}^{n-1} \gamma_i'(\mathbf{h}^{(\nu)})\,.\exp\,[2\pi i\mathbf{h}^{(\nu)}.\,C_i\,.\,\mathbf{r}] \right|^2 dv(\mathbf{r}) \\ &\geq \left| \oint {_g\varrho} \sum_{\nu=1}^{m} \sum_{i=0}^{n-1} \gamma_i'(\mathbf{h}^{(\nu)}) \exp\,[2\pi i\mathbf{h}^{(\nu)}.\,C_i\,.\,\mathbf{r}]\,dv(\mathbf{r}) \right|^2 \end{aligned} \tag{33}$$

or, developing according to MacGillavry

$$\begin{aligned} &_gF(0)\,.\sum_{k=0}^{n-1} \sum_{\nu=1}^{m} \sum_{\mu=1}^{m} (\Sigma\,\gamma_i'(\mathbf{h}^{(\nu)})\tilde{\gamma}_j'(\mathbf{h}^{(\mu)}))_k \\ &\quad \times {_gF}(\mathbf{h}^{(\nu)}.\,\varphi_k - \mathbf{h}^{(\mu)})\,.\exp\,[2\pi i\mathbf{h}^{(\nu)}.\,\mathbf{t}_k] \\ &\quad \geq \left| \sum_{\nu=1}^{m} \left(\sum_{i=0}^{n-1} \gamma_i'(\mathbf{h}^{(\nu)}) \right) {_gF}(\mathbf{h}^{(\nu)}) \right|^2, \end{aligned} \tag{34}$$

where the sum

$$(\Sigma\gamma_i'(\mathbf{h}^{(\nu)})\,.\,\tilde{\gamma}_j'(\mathbf{h}^{(\mu)}))_k$$

is to be taken over all i (or j, n pairs) defining a certain $C_k = C_i\,.\,C_j^{-1}$.

The complete collection of inequalities of type (33) (or (34)) together constitutes a necessary *and sufficient* condition for non-negativity: (33) is a stronger form of Karle & Hauptman's fundamental inequality (their expression (3), put ≥ 0).

A general discussion of the use of (34) is very intricate. (34) does not necessarily lead to (i) because $_g\varrho_{\text{extreme}}$ might be negative. However, it is not very difficult to prove that if strong inequalities are to be developed from (34), γ' should be made independent of i (j).* The resulting inequality is then identical with our starting point (6).

There is reason to believe that *any* non-negativity criterion able to exclude $_g\varrho_{\text{extreme}}$ in case of translation-free space groups must be weak: $_g\varrho_{\text{extreme}}$ probably cannot contain deep negative minima.

$_g\varrho_{\text{extreme}}$ has a very high positive maximum in the origin. A deep negative minimum in $\pm\mathbf{r}_1$ would make the corresponding, generalized Patterson function (which in this case belongs to the same space group as $_g\varrho_{\text{extreme}}$) negative round about $\pm\mathbf{r}_1$ provided small contributions do not happen to cooperate so that the negativity is cancelled. The generalized Patterson function derived from (1) and (2) is, however, known to be independent of α, i.e. to be non-negative if $_g\varrho_{\text{correct}}$ is.

It therefore seems that there can exist at least no simple and reliable non-negativity criterion capable of excluding $_g\varrho_{\text{extreme}}$. (There might anyhow exist some $_g\varrho(\alpha)$ rather similar to $_g\varrho_{\text{extreme}}$ and non-negative.)

The fact that

$$\left.\begin{array}{r}\alpha(\mathbf{h})+\alpha(\mathbf{h}')+\alpha(\mathbf{h}'')\doteq 0\\ \text{for}\quad \Sigma\mathbf{h}=0\end{array}\right\}\qquad(35)$$

is statistically true (Cochran (1955)) in a case that is rather the opposite of the extreme case is compatible with our result only if the average frequency curve flattens out with increasing number of atoms in the cell. This is so, which means that the statistical relation becomes less and less valuable the more complicated the structure is (compare Cochran (1955), equation (7) and his Discussion).

As far as is known to the author no complicated structure with a translation-free space group has been solved by using Harker–Kasper inequalities or by maximization of expression (3). Our result shows that this must be so. On the other hand, practical examples prove that for structures with translational symmetry elements, Harker–Kasper inequalities (see e.g. Kasper, Lucht & Harker (1950)), or maximization of expression (3), (see e.g. Cochran & Douglas (1955)) can be of decisive value even in rather complicated cases.

* A series of inequalities not covered by Harker & Kasper (1948) but covered by (34) ($m=1$, the smaller member vanishing) is given in Goedkoop (1950) (inequality (4·20) for $i \neq 1$). The coefficients χ are functions of r ($i+1$, in our notation).

Conclusion

The non-negativity condition or the maximization of expression (3) (unaided by other criteria) is insufficient for complicated structures (several atoms per cell of the heaviest kind) in space groups lacking glide planes and screw axes. This conclusion has led the author to formulate and develop a more general condition for ϱ. The result will be published.

This paper was written in context with an investigation of the structures of ferric chloride hydrates, and I herewith express my gratitude for a grant from the Nobel Committee of Chemistry. The work has been done in the inspiring atmosphere of the Institute of Prof. G. Hägg and I feel much indebted to him for having read the rough copy.

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