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Structure-Factor Relations and Phase Determination

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The method of inequalities, begun by Harker & Kasper, is extended and new types of inequalities are established for the structure-factors of a centro-symmetric crystal. The techniques for obtaining relations are described and examples are given of inequalities derived by each of the various methods.

1. Formulation of the problem

1·1. The main purpose of this paper is to extend the results of Harker & Kasper (1948). We shall keep to their notation for simplicity, but shall recapitulate an explanation of its significance in § 1·3. In § 3 we shall derive several large classes of inequalities satisfied by the structure-factors and, in practical cases, these will often be sufficient to determine their phases. In this paper we shall consider only the case of a centro-symmetric structure, but the method can be readily adapted to deal with any other symmetry elements. The general idea is to make use of the symmetry to obtain appropriate analytic forms for the structure-factors in terms of the (unknown) atomic co-ordinates, and then to apply to these forms some of the standard inequalities of mathematical analysis. Harker & Kasper have shown how to use the Schwarz Inequality in this way. For our purpose we shall be using a much wider range of inequalities.

We shall discuss in § 4 some of the general implications of the method as well as possible extensions.

1·2. We shall assume that the structure in question has a centre of symmetry at the origin and that we can approximate to the atoms by points of appropriate scattering power. Then the electron-density function is given by

$$\rho(x, y, z) = \sum_{hkl=-\infty}^{\infty} F_{hkl} \cos 2\pi (hx+ky+lz), \quad (1\text{–}1)$$

where $$F_{hkl} = \sum_{j=1}^{N} f^{(j)}_{hkl} \cos 2\pi (hx_j+ky_j+lz_j), \quad (1\text{–}2)$$

(and in particular is real). The summation is taken over all the atoms of the basic cell, N in number; (x_j, y_j, z_j) are the unknown co-ordinates of the jth atom; and $f^{(j)}_{hkl}$ is its scattering power in the (hkl) direction.

We now introduce the assumption that there exists a function f_{hkl} of hkl, and positive numbers Z_j, depending on j alone, such that

$$f^{(j)}_{hkl} = Z_j f_{hkl}. \quad (1\text{–}3)$$

Put $$\sum_{j=1}^{N} Z_j = Z, \quad (1\text{–}4)$$

and $$Z_j/Z = n_j; \quad (1\text{–}5)$$

then, by (1–2), (1–3) and (1–5),

$$F_{hkl} = f_{hkl} \sum_{j=1}^{N} Z_j \cos 2\pi (hx_j+ky_j+lz_j)$$
$$= Zf_{hkl} \sum_{j=1}^{N} n_j \cos 2\pi (hx_j+ky_j+lz_j). \quad (1\text{–}6)$$

We define

$$\hat{F}_{hkl} = F_{hkl}/Zf_{hkl}, \quad (1\text{–}7)$$

and so $$\hat{F}_{hkl} = \sum_{j=1}^{N} n_j \cos 2\pi (hx_j+ky_j+lz_j), \quad (1\text{–}8)$$

where, by (1–4) and (1–5), the n_j's are positive and

$$\sum_{j=1}^{N} n_j = 1.$$

$\hat{F}_{hkl}$ as defined by (1–7) is a simplified designation for ${}^{A}\hat{F}_{hkl}$ as used in the paper of Harker & Kasper (defined in their equation (12)).

In practice we observe the values of $|F_{hkl}|$ (or at least some of them), but we cannot determine directly from observation whether F_{hkl} is positive or negative. By (1–7) F_{hkl} has the same sign as $\hat{F}_{hkl}$ and we shall be interested in methods for determining the sign of the latter.

1·3. It is desirable at this point to consider the significance of (1–3). It amounts to the assumption that the atomic scattering curves of the individual atoms of the crystal are proportional to one another. This will certainly be accurate if the atoms do not differ from each other 'too much'. In particular it will be a good approximation for organic structures containing only carbon, nitrogen, oxygen and hydrogen, since the scattering power of hydrogen may be neglected. The approximation is most likely to break down for structures in which a few atoms are much heavier than the others, but it is precisely in these cases that we can get a good idea of many of the signs by other methods. Moreover, a close examination of the proofs in § 3 reveals that we never in fact use the assumption (1–3) to the full. We do not assume that the various atomic scattering curves are proportional, but only that the sets of values they take at a small number of different points are so proportional. However, it seems worth while to make the full assumption since it greatly simplifies the notation. And in all the applications we have made so far it has been fully justified by the results.

2. Mathematical preliminaries

2·1. We shall be basing our arguments on some results from the field of pure analysis and we quote them here.

2·2. *Theorem A (Hölder's Inequality).* If $a_1, a_2, \ldots, a_n$, $b_1, b_2, \ldots, b_n$ are real or complex numbers and p, q any two real numbers such that $1/p+1/q=1$, then

$$\left|\sum_{r=1}^{n} a_r b_r\right| \leqslant \left\{\sum_{r=1}^{n} |a_r|^p\right\}^{1/p} \left\{\sum_{r=1}^{n} |b_r|^q\right\}^{1/q}, \quad (2\text{–}1)$$

with equality if and only if there exist numbers λ, μ (not both zero) such that $\lambda a_r + \mu b_r = 0$ $(r=1, 2, \ldots, n)$.

2·3. *Theorem B.* Suppose that $x_1, x_2, \ldots, x_n$ are any n positive real numbers and $\zeta_1, \zeta_2, \ldots, \zeta_n$ are n non-negative real numbers such that $\sum_{r=1}^{n} \zeta_n = 1$. Denote $\left(\sum_{r=1}^{n} \zeta_r x_r^\alpha\right)^{1/\alpha}$ by M_α. Then, if $0<\alpha<\beta$,

$$M_\alpha \leqslant M_\beta; \quad (2\text{–}2)$$

with equality if, and only if, either the x_r's are all equal or some $\zeta_r = 1$.

2·4. *Theorem C.* Under the conditions of Theorem B, $\log\left(\sum_{r=1}^{n} \zeta_r x_r^\alpha\right)$ (i.e. $\alpha \log M_\alpha$) is a convex function of α.

A function $f(\alpha)$ is said to be *convex* if it is continuous and the curve $y=f(\alpha)$ has the property that the chord joining any two of its points lies entirely above the corresponding arc. This may be expressed analytically as follows: If α_1, α_2 are any two values of the independent variable, and t_1, t_2 any two positive numbers whatever,

$$f\left(\frac{t_1\alpha_1 + t_2\alpha_2}{t_1+t_2}\right) \leqslant \frac{1}{t_1+t_2}\,[t_1 f(\alpha_1) + t_2 f(\alpha_2)]. \quad (2\text{–}3)$$

2·5. *Theorem D.* If $0 \leqslant x_r \leqslant 1$, $\zeta_r \geqslant 0$ $(r=1, 2, \ldots, n)$ and $\alpha<\beta$, then

$$\sum_{r=1}^{n} \zeta_r x_r^\alpha \geqslant \sum_{r=1}^{n} \zeta_r x_r^\beta. \quad (2\text{–}4)$$

Finally, we shall have occasion to use a special case of Theorem A when $p=q=2$, and so we state it as a separate result.

2·6. *Theorem A′ (Cauchy's Inequality).* Under the conditions of Theorem A,

$$\left|\sum_{r=1}^{n} a_r b_r\right|^2 \leqslant \sum_{r=1}^{n} |a_r|^2 \sum_{r=1}^{n} |b_r|^2, \quad (2\text{–}5)$$

with the same condition for equality as in Theorem A.

The reader is referred to the book of Hardy, Littlewood & Pòlya (1934) for proofs of the first three theorems. We merely remark here that Theorem B is deducible from Theorem A and Theorem C from Theorem B. To see Theorem D we need only observe that

$$x_r^\alpha \geqslant x_r^\beta \geqslant 0 \quad (r=1, 2, \ldots, n),$$

and so

$$\zeta_r x_r^\alpha \geqslant \zeta_r x_r^\beta,$$

and the theorem follows by summing this last inequality.

3. Inequalities for the $\hat{F}$ values

3·1. *Implications of Theorem B.* For a given H we have

$$\hat{F}_H = \sum_{j=1}^{N} n_j \cos\theta_j, \quad \text{where } \theta_j = 2\pi\,(hx_j + ky_j + lz_j).$$

Here H stands for the triple suffix (hkl); nH then indicates $(nh.nk.nl)$ while $H+H'$, $H-H'$, etc. have their obvious meanings.

By Theorem B above we know that, if $0<\alpha<\beta$,

$$\left\{\sum_{j=1}^{N} n_j\,|\cos\theta_j|^\alpha\right\}^{1/\alpha} \leqslant \left\{\sum_{j=1}^{N} n_j\,|\cos\theta_j|^\beta\right\}^{1/\beta},$$

and so, *a fortiori*,

$$\left|\sum_{j=1}^{N} n_j \cos^\alpha\theta_j\right|^{1/\alpha} \leqslant \left\{\sum_{j=1}^{N} n_j\,|\cos\theta_j|^\beta\right\}^{1/\beta}. \quad (3\text{–}1)$$

Now suppose that β is an even positive integer and α any integer less than β. In these circumstances we can drop the $||$ sign in the right-hand side of (3–1) and so

$$\left|\sum_{j=1}^{N} n_j \cos^\alpha\theta_j\right|^{1/\alpha} \leqslant \left|\sum_{j=1}^{N} n_j \cos^\beta\theta_j\right|^{1/\beta}, \quad (3\text{–}2)$$

where, of course, the roots in this inequality are both taken positive. Now $\cos^\alpha\theta_j$ can be expressed as a linear combination of cosines of multiples of θ_j and we make use of the fact that

$$\sum_{j=1}^{N} n_j \cos n\theta_j = \sum_{j=1}^{N} n_j \cos 2\pi n\,(hx_j + ky_j + lz_j) = \hat{F}_{nH}.$$

(i) We take as the simplest case $\alpha=1$, $\beta=2$. This gives

$$\left|\sum_{j=1}^{N} n_j \cos\theta_j\right| \leqslant \left|\sum_{j=1}^{N} n_j \cos^2\theta_j\right|^{\frac{1}{2}},$$

i.e.

$$\begin{aligned}\hat{F}_H^2 &\leqslant \sum_{j=1}^{N} n_j \cos^2\theta_j \\ &\leqslant \tfrac{1}{2}\sum_{j=1}^{N} n_j\,(1+\cos 2\theta_j) \\ &\leqslant \tfrac{1}{2}\,(1+\hat{F}_{2H}). \end{aligned} \quad (3\text{–}3)$$

This inequality was obtained by Harker & Kasper (1948). It may sometimes be used to determine the sign of F_{2H}. For example, if $|\hat{F}_H| = 0{\cdot}8$ and $|\hat{F}_{2H}| = 0{\cdot}5$, we have from (3–3)

$$0{\cdot}64 \leqslant \tfrac{1}{2}\,(1 \pm 0{\cdot}5).$$

But this is satisfied only if we take the + sign, i.e. $\hat{F}_{2H} = +0{\cdot}5$. On the other hand, no useful determination is obtained if $|\hat{F}_H| \leqslant \frac{1}{2}$, $|\hat{F}_{2H}| = \frac{1}{2}$.

(ii) If we take $\alpha=3$, $\beta=4$, we get

$$\left|\sum_{j=1}^{N} n_j \cos^3\theta_j\right|^{\frac{1}{3}} \leqslant \left\{\sum_{j=1}^{N} n_j \cos^4\theta_j\right\}^{\frac{1}{4}},$$

i.e.
$$\left|\sum_{j=1}^{N} n_j \frac{\cos 3\theta_j+3\cos\theta_j}{4}\right|^{\frac{1}{3}} \leqslant \left\{\sum_{j=1}^{N} n_j \frac{\cos 4\theta_j+4\cos 2\theta_j+3}{8}\right\}^{\frac{1}{4}},$$

i.e.
$$|\hat{F}_{3H}+3\hat{F}_H|^{\frac{1}{3}} \leqslant \frac{1}{2^{\frac{1}{12}}}[\hat{F}_{4H}+4\hat{F}_{2H}+3]^{\frac{1}{4}}. \tag{3–4}$$

If we already know some of the signs, we may use (3–4) to determine others.

(iii) Taking $\alpha=1$, $\beta=4$, we get

$$|\hat{F}_H| \leqslant \left[\frac{\hat{F}_{4H}+4\hat{F}_{2H}+3}{8}\right]^{\frac{1}{4}}, \tag{3–5}$$

i.e.
$$\hat{F}_H^4 \leqslant \tfrac{1}{8}(\hat{F}_{4H}+4\hat{F}_{2H}+3). \tag{3–6}$$

If $\hat{F}_{2H}$ is known to be negative and $\hat{F}_H$ is not negligibly small, (3–6) may give a strong inequality for $\hat{F}_{4H}$ which might well determine its sign.

Clearly by varying α and β this method can be made to yield a large number of inequalities. These will all have some features in common. The $\hat{F}$'s on the greater side will always have suffixes which are even multiples of H, and the highest multiple of H occurring as a suffix on the greater side will be greater than that on the smaller side.

3·2. *Implications of Theorem C.* In this paragraph we are interested in the implications of Theorem C. We write M_α for

$$\left\{\sum_{j=1}^{N} n_j |\cos\theta_j|^\alpha\right\}^{1/\alpha},$$

and Theorem C tells us that $\alpha \log M_\alpha$ is a convex function of α. Let μ_1, μ_2 be any two positive numbers such that $\mu_1+\mu_2=1$ and α, β any two positive numbers at all. Then the convexity property can be stated as

$$(\mu_1\alpha+\mu_2\beta)\log M_{\mu_1\alpha+\mu_2\beta} \leqslant \mu_1\alpha\log M_\alpha+\mu_2\beta\log M_\beta, \tag{3–7}$$

i.e.
$$M_{\mu_1\alpha+\mu_2\beta}^{\mu_1\alpha+\mu_2\beta} \leqslant M_\alpha^{\mu_1\alpha} M_\beta^{\mu_2\beta}. \tag{3–8}$$

We now face the same sort of difficulty as that which limited us in § 3·1. We wish to get rid of the || sign in the definition of the M_α, etc. so as to be able to express everything in terms of the $\hat{F}$'s. On the left-hand side of (3–8) we may in fact just ignore the absolute value sign, a step which can only strengthen the inequality. However, we can deal with the right-hand side only if α and β are both even integers. For example, take $\alpha=2$, $\beta=4$, $\mu_1=\mu_2=\frac{1}{2}$. Then

$$M_3^3 \leqslant M_2 M_4^2,$$

and so, *a fortiori*,

$$\left|\sum_{j=1}^{N} n_j \cos^3\theta_j\right|^3 \leqslant \left(\sum_{j=1}^{N} n_j\cos^2\theta_j\right)\left(\sum_{j=1}^{N} n_j\cos^4\theta_j\right)^2.$$

By the same sort of argument as that used above, we get

$$\left|\frac{\hat{F}_{3H}+3\hat{F}_H}{4}\right|^3 \leqslant \left(\frac{1+\hat{F}_{2H}}{2}\right)\left(\frac{3+4\hat{F}_{2H}+\hat{F}_{4H}}{8}\right)^2,$$

i.e.

$$|\hat{F}_{3H}+3\hat{F}_H|^3 \leqslant \tfrac{1}{2}(1+\hat{F}_{2H})(3+4\hat{F}_{2H}+\hat{F}_{4H})^2. \tag{3–9}$$

By taking different values of μ_1, μ_2, α, β we can get a whole range of similar inequalities; these will all be subject to the limitations described at the end of § 3·1.

3·3. *Implications of Theorem D.* We now consider Theorem D. It again follows from this theorem that, if $\alpha<\beta$,

$$\sum_{j=1}^{N} n_j |\cos\theta_j|^\alpha \geqslant \sum_{j=1}^{N} n_j |\cos\theta_j|^\beta. \tag{3–10}$$

As before, to make use of (3–10) we must assume that α is an even integer. Taking $\alpha=2$, $\beta=3$, we get

$$|\hat{F}_{3H}+3\hat{F}_H| \leqslant 2(1+\hat{F}_{2H}). \tag{3–11}$$

Here again we can get a whole class of inequalities by varying α and β. In these inequalities an H value and its odd multiples still appear as subscripts on the smaller side—necessarily so for reasons which have already been explained. However, there is one difference from the results of §§ 3·1 and 3·2 in that now the *highest* multiple of H appears on the smaller side.

3·4. *Use of* $1\pm\cos\theta_j$. We introduce here a method which enables us to free ourselves from the restrictions imposed by the absolute-value signs in our sums. The idea can be applied in several ways and we begin with the simplest. Clearly, for every j,

$$1\pm\cos\theta \geqslant 0,$$

and so, by Theorem B,

$$\left[\sum_{j=1}^{N} n_j(1\pm\cos\theta_j)^\alpha\right]^{1/\alpha} \leqslant \left[\sum_{j=1}^{N} n_j(1\pm\cos\theta_j)^\beta\right]^{1/\beta}, \tag{3–12}$$

if $0<\alpha<\beta$. Let us consider some applications.

(i) If $\alpha=1$, $\beta=2$, we have

$$\left(\sum_{j=1}^{N} n_j+\sum_{j=1}^{N} n_j\cos\theta_j\right)^2 \leqslant \sum_{j=1}^{N} n_j(1+2\cos\theta_j+\cos^2\theta_j),$$

i.e.
$$(1+\hat{F}_H)^2 \leqslant 1+2\hat{F}_H+\tfrac{1}{2}(1+\hat{F}_{2H}),$$

i.e.
$$\hat{F}_H^2 \leqslant \tfrac{1}{2}(1+\hat{F}_{2H}).$$

Thus we are led back to the simple inequality (3–3) as a special case.

(ii) Now consider $\alpha=1$, $\beta=3$. We get

$$\left\{\sum_{j=1}^{N} n_j(1+\cos\theta_j)\right\}^3 \leqslant \sum_{j=1}^{N} n_j(1+\cos\theta_j)^3,$$

i.e. $(1+\hat{F}_H)^3 \leqslant 1+3\hat{F}_H+\frac{3}{2}(1+\hat{F}_{2H})+\frac{1}{4}(\hat{F}_{3H}+3\hat{F}_H)$,

i.e.
$$\hat{F}_H^3+3\hat{F}_H^2-\tfrac{3}{4}\hat{F}_H \leqslant \tfrac{1}{4}\hat{F}_{3H}+\tfrac{3}{2}(1+\hat{F}_{2H}). \tag{3–13}$$

(iii) Again take $\alpha=2$, $\beta=3$. Then

$$\left\{\sum_{j=1}^{N} n_j\,(1+\cos\theta_j)^2\right\}^3 \leqslant \left\{\sum_{j=1}^{N} n_j\,(1+\cos\theta_j)^3\right\}^2,$$

i.e.
$$\{1+2\hat{F}_H+\tfrac{1}{2}\,(1+\hat{F}_{2H})\}^3 \leqslant \{1+3\hat{F}_H+\tfrac{3}{2}\,(1+\hat{F}_{2H}) + \tfrac{1}{4}\,(\hat{F}_{3H}+3\hat{F}_H)\}^2. \quad (3\text{–}14)$$

In this way we can get inequalities with odd multiples of H on the greater side. But there is a further extension possible. In the relation (3–12) we need not suppose that α and β are integers. In the general case we can expand the binomials $(1+\cos\theta_j)^\alpha$ and $(1+\cos\theta_j)^\beta$ in powers of $\cos\theta_j$, express each power of $\cos\theta_j$ in the expansions as a linear combination of cosines of multiples of θ_j, and in this way build up an inequality connecting the $\hat{F}_{nH}$'s for various values of n. It is understood that, to the accuracy of this whole theory, it will rarely be necessary or even useful to retain more than the first few terms of the binomial expansions. Let us consider some actual cases.

(iv) Take $\alpha=\tfrac{1}{2}$, $\beta=1$. Then

$$\left[\sum_{j=1}^{N} n_j\,(1+\cos\theta_j)^{\frac{1}{2}}\right]^2 \leqslant \sum_{j=1}^{N} n_j\,(1+\cos\theta_j),$$

i.e.
$$\sum_{j=1}^{N} n_j\,(1+\tfrac{1}{2}\cos\theta_j-\tfrac{1}{8}\cos^2\theta_j+\tfrac{1}{16}\cos^3\theta_j) \leqslant \left[\sum_{j=1}^{N} n_j\,(1+\cos\theta_j)\right]^{\frac{1}{2}},$$

i.e.
$$1+\tfrac{1}{2}\hat{F}_H-\tfrac{1}{16}\,(1+\hat{F}_{2H})+\tfrac{1}{64}\,(\hat{F}_{3H}+3\hat{F}_H) \leqslant (1+\hat{F}_H)^{\frac{1}{2}} = 1+\tfrac{1}{2}\hat{F}_H-\tfrac{1}{8}\hat{F}_H^2+\tfrac{1}{16}\hat{F}_H^3.$$

Hence
$$4\hat{F}_H^3-8\hat{F}_H^2-3\hat{F}_H+4 \geqslant \hat{F}_{3H}-4\hat{F}_{2H}. \quad (3\text{–}15)$$

This rather complicated relation may be directly useful only in favourable circumstances, but we have quoted it here as an example of the type of relation which may be proved to suit special cases as they arise.

3·5. *Use of general* $f(\theta_j)$. In the last paragraph we used $\sum_{j=1}^{N} n_j\,(1\pm\cos\theta_j)^\alpha$. However, the idea can be extended almost indefinitely. Take any *even* function $f(\theta)$ which is *positive* in $0\leqslant\theta\leqslant\pi$ and has period 2π. We can then assert that

$$\left\{\sum_{j=1}^{N} n_j\,[f(\theta_j)]^\alpha\right\}^{1/\alpha}$$

is an increasing function of α. Our next step is to expand $\{f(\theta)\}^\alpha$ as a Fourier cosine series, thus expressing

$$\sum_{j=1}^{N} n_j\,[f(\theta_j)]^\alpha$$

as a linear combination of $\hat{F}_{nH}$'s for different values of n. Then by comparing the values of the expressions for two values of α we get an inequality for the $\hat{F}_{nH}$'s. In practice it will not be necessary to retain many terms of the Fourier series, especially if $f(\theta)$ is a sufficiently smooth function, and the final inequality will be correspondingly simplified.

For example, we may assert that

$$\left\{\sum_{j=1}^{N} n_j\,|\cos\tfrac{1}{2}\theta_j|^2\right\}^{\frac{1}{2}} \leqslant \left\{\sum_{j=1}^{N} n_j\,|\cos\tfrac{1}{2}\theta_j|^3\right\}^{\frac{1}{3}}. \quad (3\text{–}16)$$

But (Whittaker & Watson, 1927, p. 191), for all real x,

$$|\cos^3 x| = \frac{8}{3\pi}\{\tfrac{1}{2}+\tfrac{3}{5}\cos 2x+\tfrac{3}{35}\cos 4x-\tfrac{1}{105}\cos 6x\ldots\}, \quad (3\text{–}17)$$

and so (taking $x=\tfrac{1}{2}\theta_j$)

$$\{\tfrac{1}{2}\,(1+\hat{F}_H)\}^{\frac{1}{2}} \leqslant \left\{\frac{8}{3\pi}\,(\tfrac{1}{2}+\tfrac{3}{5}\hat{F}_H+\tfrac{3}{35}\hat{F}_{2H})\right\}^{\frac{1}{3}},$$

ignoring the higher terms,
and hence

$$(1+\hat{F}_H)^{\frac{3}{2}} \leqslant 2{\cdot}38\,(\tfrac{1}{2}+\tfrac{3}{5}\hat{F}_H+\tfrac{3}{35}\hat{F}_{2H}). \quad (3\text{–}18)$$

If we had started with $|\sin\tfrac{1}{2}\theta_j|$ instead of $|\cos\tfrac{1}{2}\theta_j|$, we should have got

$$(1-\hat{F}_H)^{\frac{3}{2}} \leqslant 2{\cdot}38\,(\tfrac{1}{2}-\tfrac{3}{5}\hat{F}_H+\tfrac{3}{25}\hat{F}_{2H}). \quad (3\text{–}19)$$

Clearly (3–18) and (3–19) may be rewritten as

$$(1+|\hat{F}_H|)^{\frac{3}{2}} \leqslant 2{\cdot}38\,(\tfrac{1}{2}+\tfrac{3}{5}\,|\hat{F}_H|+\tfrac{3}{35}\hat{F}_{2H}), \quad (3\text{–}20)$$

and
$$(1-|\hat{F}_H|)^{\frac{3}{2}} \leqslant 2{\cdot}38\,(\tfrac{1}{2}-\tfrac{3}{5}\,|\hat{F}_H|+\tfrac{3}{35}\hat{F}_{2H}). \quad (3\text{–}20')$$

In fact, if $\hat{F}_H>0$, (3–20) and (3–20′) are simply (3–18), (3–19) respectively. On the other hand, if $F_H<0$, they are the same inequalities in the opposite order.

These may give a sign for F_{2H} in cases where (3–3) fails. Suppose, for example, that $|F_H|=0{\cdot}58$, $|\hat{F}_{2H}|=0{\cdot}28$. Then (3–3) gives

$$0{\cdot}34 \leqslant \tfrac{1}{2}\,(1\pm 0{\cdot}28),$$

and both signs satisfy the inequality. However, it may easily be verified that, to satisfy (3–20), we must have $F_{2H}>0$ though, incidentally, (3–20′) could be satisfied by either sign of F_{2H}.

3·5. We conclude this section with some further results. Of these (3–21), (3–22) and (3–25) are due to Harker & Kasper (1948). We shall prove only (3–23) and (3–24).

For a centro-symmetric crystal:

$$(\hat{F}_H+\hat{F}_{H'})^2 \leqslant (1+\hat{F}_{H+H'})\,(1+\hat{F}_{H-H'}), \quad (3\text{–}21)$$

$$(\hat{F}_H-\hat{F}_{H'})^2 \leqslant (1-\hat{F}_{H+H'})\,(1-\hat{F}_{H-H'}), \quad (3\text{–}22)$$

$$(\hat{F}_H+\hat{F}_{H'})^4 \leqslant \tfrac{1}{4}\,(3+4\hat{F}_{H+H'}+\hat{F}_{2H+2H'}) \times (3+4\hat{F}_{H-H'}+\hat{F}_{2H-2H'}), \quad (3\text{–}23)$$

$$(\hat{F}_H-\hat{F}_{H'})^4 \leqslant \tfrac{1}{4}\,(3-4\hat{F}_{H+H'}-\hat{F}_{2H+2H'}) \times (3-4\hat{F}_{H-H'}-\hat{F}_{2H-2H'}). \quad (3\text{–}24)$$

For a crystal with space group $P2_1/n$:

$$\hat{F}_{0kl}^2 \leqslant \tfrac{1}{4}\,(1\pm\hat{F}_{0,2k,0}\pm\hat{F}_{0,0,2l}+\hat{F}_{0,2k,2l}), \quad (3\text{–}25)$$

the $\pm$ sign being taken according as $k+l$ is even or odd.

Proof of (3–23). For this we require an extension of Hölder's Inequality which says (Hardy, Littlewood & Pòlya, 1934, p. 24):

If $a_1, a_2, \ldots, a_n$; $b_1, b_2, \ldots, b_n$; $c_1, c_2, \ldots, c_n$ are any $3n$ real or complex numbers, and p, q, r are three positive real numbers such that $1/p+1/q+1/r=1$, then

$$\left|\sum_{j=1}^{n} a_j b_j c_j\right| \leqslant \left[\sum_{j=1}^{n} |a_j|^p\right]^{1/p} \times \left[\sum_{j=1}^{n} |b_j|^q\right]^{1/q} \left[\sum_{j=1}^{n} |c_j|^r\right]^{1/r}. \quad (3\text{–}26)$$

Now

$$\begin{aligned}\hat{F}_H+\hat{F}_{H'} &= \sum_{j=1}^{N} n_j \{\cos 2\pi\,(hx_j+ky_j+lz_j) \\ &\qquad + \cos 2\pi\,(h'x_j+k'y_j+l'z_j)\} \\ &= 2\sum_{j=1}^{N} n_j \cos\pi\,[(h+h')\,x_j+(k+k')\,y_j+(l+l')\,z_j] \\ &\qquad \times \cos\pi\,[(h-h')\,x_j+(k-k')\,y_j+(l-l')\,z_j].\end{aligned}$$

Take

$$a_j=n_j^{\frac{1}{2}},\quad b_j=n_j^{\frac{1}{4}}\cos\pi\,[(h+h')\,x_j+(k+k')\,y_j+(l+l')\,z_j],$$

$$c_j=n_j^{\frac{1}{4}}\cos\pi\,[(h-h')\,x_j+(k-k')\,y_j+(l-l')\,z_j]$$

and $p=2$, $q=r=4$. Then

$$\begin{aligned}\tfrac{1}{2}\,|\hat{F}_H+\hat{F}_{H'}| &\leqslant \left\{\sum_{j=1}^{N} n_j\right\}^{\frac{1}{2}} \\ &\quad\times\left\{\sum_{j=1}^{N} n_j \cos^4\pi\,[(h+h')\,x_j+(k+k')\,y_j+(l+l')\,z_j]\right\}^{\frac{1}{4}} \\ &\quad\times\left\{\sum_{j=1}^{N} n_j \cos^4\pi\,[(h-h')\,x_j+(k-k')\,y_j+(l-l')\,z_j]\right\}^{\frac{1}{4}} \\ &=\left\{\frac{1}{8}\sum_{j=1}^{N} n_j\,[3+4\cos 2\pi\,((h+h')\,x_j+(k+k')\,y_j+(l+l')\,z_j) \right.\\ &\qquad \left. +\cos 4\pi\,((h+h')\,x_j+(k+k')\,y_j+(l+l')\,z_j)]\right\}^{\frac{1}{4}} \\ &\quad\times\left\{\frac{1}{8}\sum_{j=1}^{N} n_j\,[3+4\cos 2\pi\,((h-h')\,x_j+(k-k')\,y_j+(l-l')\,z_j) \right.\\ &\qquad \left. +\cos 4\pi\,((h-h')\,x_j+(k-k')\,y_j+(l-l')\,z_j)]\right\}^{\frac{1}{4}}\end{aligned}$$

Here we have used the relation

$$\cos^4\theta=\tfrac{1}{8}\,(3+4\cos 2\theta+\cos 4\theta).$$

Hence

$$\tfrac{1}{16}\,|\hat{F}_H+\hat{F}_{H'}|^4 \leqslant \tfrac{1}{64}\,[3+4\hat{F}_{H+H'}+\hat{F}_{2H+2H'}] \times [3+4\hat{F}_{H-H'}+\hat{F}_{2H-2H'}]$$

and (3–23) follows.

The proof of (3–24) is very similar, except that we now use the relation

$$\sin^4\theta=\tfrac{1}{8}\,(3-4\cos 2\theta-\cos 4\theta),$$

and the rest goes much as before.

4. Conclusion

4·1. It follows from the nature of the inequalities that the bigger the value of $|\hat{F}_H|$ the greater our chance of deducing its sign. That principle is subject to some qualification in detail, but is true in general. Put quite crudely, what it amounts to is this. The bigger the value of $|\hat{F}_H|$ the bigger the difference between $+\hat{F}_H$ and $-\hat{F}_H$, and so the better our prospects of being able to discriminate between the two analytically.

4·2. The application of the Harker-Kasper relations and also some of those derived above has led to the correct determination of many signs for a number of known structures. In particular the data on oxalic acid obtained by Robertson & Woodward (1936) have been examined in detail. In this case it was possible to find directly the signs of some forty-two of the $h0l$ terms. A fuller account of this work will be published later.

The practical consideration of these problems has suggested an interesting observation. There were a number of cases in which both signs satisfied the inequality, one of them by a comfortable margin and the other by only a relatively small margin. In almost all such cases it was the former sign which was the correct one. That suggests that the method may have some power in reserve, in the sense that there are still fundamentally stronger inequalities to be discovered.

4·3. We have not considered any symmetry elements other than the centre of symmetry. However, to each such element corresponds a complete theory like that developed in § 3. For the general idea behind such a development the reader should consult the paper of Harker & Kasper.

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