

Limitations on the Determination of Phases by Means of Inequalities*

BY E. W. HUGHES

Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California, U.S.A.

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The inequality method of determining signs of Fourier coefficients is discussed from the point of view of the average sizes of the coefficients. It is shown theoretically and confirmed empirically that for crystals containing atoms of approximately the same atomic factor, the root-mean-square average of $|\hat{F}|$ is $1/\sqrt{N}$, where N is the number of atoms per cell. It is shown empirically that for N larger than about ten, \hat{F} values are distributed about zero approximately according to the normal error curve. With these results it is first shown that the power of the inequalities varies little with symmetry if the number of atoms in the asymmetric unit is kept constant. It is then shown that the simple inequalities cannot solve crystals of greater than moderate complexity, as judged by the number of atoms in the asymmetric unit, and that to attempt more complicated crystals will require more complicated inequalities. It is suggested that experimental errors may limit the usefulness of these more complicated expressions to the same range of crystals that can be solved by complete three-dimensional, absolute-scale Patterson methods. Attention is called to an older method by Banerjee.

Harker & Kasper (1948) have proposed an analytical method for determining phases of structure factors from their magnitudes, involving inequalities, and Gillis (1948) has described more complicated and presumably more powerful inequalities in extension of their work. These authors have ably presented the mechanics and the advantages of the method. I would like to point out some practical limitations based on the sizes of the observed intensities.

The importance of the magnitudes of the 'unitary crystal structure factors', $\hat{F}_{hkl} = F_{hkl}/\sum f_j$, for the success of this method is obvious and Gillis (1948, §4.1) has stated the case succinctly: '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.' It is important therefore to consider how large, on the average, we may expect these quantities to be for crystals of varying complexity.

For the purpose of such a discussion it is convenient and proper to assume that the N atoms of the unit cell are all the same; this is the important limiting case and from the solution for it one may estimate the result for any specific case. For this special case the fraction of the electrons in the unit cell which is on any one atom is $1/N$. Then, following the notation of the previous authors, we have for a crystal with no symmetry

$$\hat{F}_{hkl} = \sum_1^N \frac{1}{N} e^{2\pi i \theta_j},$$

and $(\hat{F}\hat{F}^*)_{hkl} = |\hat{F}_{hkl}|^2 = \sum_1^N \sum_1^N \frac{1}{N^2} e^{2\pi i(\theta_j - \theta_{j'})}$.

Separating terms for which $j=j'$ gives

$$|\hat{F}_{hkl}|^2 = \frac{1}{N} + \sum_{j \neq j'}^N \sum_{j'}^N \frac{1}{N^2} e^{2\pi i(\theta_j - \theta_{j'})}.$$

Upon averaging this expression by summing over all possible hkl 's and dividing by the number of such hkl 's we may expect the double sum to average to zero, since in general negative and positive values of all magnitudes are equally probable. This will be true if the data are sufficiently extensive to resolve the peak at the origin of the corresponding 'sharpened-up' Patterson series from neighboring peaks; for the summing of $|\hat{F}_{hkl}|^2$ over all hkl 's gives the value of the Patterson function at the origin, while summing the double sum over hkl gives the contribution *at the origin* from all peaks having maxima elsewhere (Patterson, 1935). The abrupt termination of the series will produce diffraction effects, but for N sufficiently large these will tend to cancel at the origin for the present case where all atoms are the same. Thus we have

$$\overline{|\hat{F}_{hkl}|^2} = 1/N,$$

and for the root-mean-square value

$$\hat{\sigma}_{hkl} = (\overline{|\hat{F}_{hkl}|^2})^{\frac{1}{2}} = 1/\sqrt{N}.$$

If the crystal has symmetry such that the general or special position occupied is p -fold for a simple cell, and the asymmetric unit present consists of n identical atoms, so that $N = pn$, application of the above procedure to the general hkl reflections which are not suppressed by symmetry shows that, as before,

$$\overline{|\hat{F}_{hkl}|^2} = 1/N = 1/pn,$$

and

$$\hat{\sigma}_{hkl} = 1/\sqrt{N} = 1/\sqrt{pn}.$$

But for special types of planes, with one or two of the indices zero or otherwise systematically restricted, one

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may obtain different values. Thus for space group $P2_1/a$ with general positions occupied, $p=4$, $N=4n$, and for general hkl 's one finds $|\overline{\hat{F}}|^2 = \frac{1}{4}(1/n)$, but for $h0l$'s or $0k0$'s $|\overline{\hat{F}}|^2 = \frac{1}{2}(1/n)$. For centered cells, if one ignores reflections forbidden by the centering, the values of $|\overline{\hat{F}}_{hkl}|^2$ correspond to those of a related primitive cell. If one deals with F rather than with \hat{F} , one finds that $\overline{F^2}$ is proportional to N , except as above when some indices are zero; then $\overline{F^2}$ may be larger by some integral factor.

The reliability of these expressions may be judged from Table 1 where calculated and observed values of $\hat{\sigma}$ are compared for several substances.

In computing observed values the unobservably small values were included at one-half of their estimated maximum possible value. These do not influence the result much, but this procedure is more accurate than either ignoring them or calling them zero. Although the calculated values are for cells containing only one kind of atom and the trial structures contain carbon and nitrogen, we see that the agreement is within the experimental errors, which include those for determining both the absolute scale and the temperature factor.

on parameters not imposed by crystal symmetry, should be easily recognized and might be useful. Deviations will also occur unless the data correspond to Patterson projections for which the peak at the origin can be resolved from all others by 'sharpening-up', as discussed above. The examples of Table 1 have been chosen to meet this criterion. For sufficiently extensive three-dimensional data this difficulty cannot arise.

We may now consider the use of inequalities for sign determination in the light of these results. The simple inequalities of Harker and Kasper may be written in the general form

$$|\hat{F}_{hkl}|^2 \leq \frac{1}{p} [1 + \phi(\hat{F})],$$

where p is as above and $\phi(\hat{F})$ is some function of \hat{F} 's related to \hat{F}_{hkl} , usually a sum. This may be rewritten

$$p |\hat{F}_{hkl}|^2 - 1 \leq \phi(\hat{F}).$$

Now we have seen that $|\overline{\hat{F}}_{hkl}|^2 = 1/pn$, so, if n , the size of the asymmetric unit, is kept constant, the left side of the inequality will, on the average, be the same for all symmetries. The right side is more difficult to discuss. The terms in $\phi(\hat{F})$ are not all of the same average size, since \hat{F} 's with various indices zero occur and,

Table 1. Comparison of calculated and observed values of $\hat{\sigma}$

Example	Zone	Space group	Position	n	$\hat{\sigma}$ calc.	$\hat{\sigma}$ obs.	$ \overline{\hat{F}} $ obs.	$ \overline{\hat{F}} /\hat{\sigma}$
Dicyandiamide (Hughes, 1940)	$h0l$	$A2/a$	gen.	6	0.289	0.309	0.241	0.78
Melamine (Hughes, 1941)	$h0l$	$P2_1/a$	gen.	9	0.235	0.246	0.186	0.76
Melamine (Hughes, 1941)	$0kl$	$P2_1/a$	gen.	9	0.167	0.167	0.137	0.82
Cyanuric triazide (Knaggs, 1935)	$hk0$	$C6_3/m$	(h)	5	0.182	0.183	0.147	0.80
							Mean	0.79

In the penultimate column the observed values of $|\overline{\hat{F}}|$ are given. These are nearly a constant fraction of $\hat{\sigma}_{\text{obs}}$ and the average of the ratio, 0.79, is almost exactly $\sqrt{(2/\pi)} = 0.798$, the ratio expected if the distribution of \hat{F} values about zero follows the normal error curve. Since $|\hat{F}| \leq 1$, they cannot follow such a curve exactly, but plots of the data used in computing Table 1 indicate that the values do follow such a curve approximately and this will probably be true if N is large enough to prevent the occurrence of large numbers of large $|\hat{F}|$'s. This empirical result is of considerable importance as it shows that if N is sufficiently large we may expect only about 10% of the $|\hat{F}|$'s to exceed $1.7\hat{\sigma}$ and about one in a thousand to exceed $3.3\hat{\sigma}$. It thus provides a method for estimating how many $|\hat{F}|$'s of a given size may be expected for a crystal of given complexity. These predictions are followed closely by the data on which Table 1 is based; there are no $|\hat{F}|$'s exceeding $3.3\hat{\sigma}$ out of 420 observations, and 44 exceeding $1.7\hat{\sigma}$.

These rules may not be followed exactly for exceptional cases, such as for certain $|\hat{F}|$'s in a layer structure; if the layering is in some family of planes, the \hat{F} 's of orders of these planes will all be 1 regardless of the predicted value of $\hat{\sigma}$. Such deviations, due to restrictions

as noted above, some of these have larger average values than do those with all indices different from zero. Moreover, some of the terms are multiplied by constant factors. The number of terms increases with increasing p , but the average size of the terms generally decreases with increasing p , n always being constant. Inspection of the expressions for a number of space groups suggests that the average sum of the absolute magnitudes of the terms in $\phi(\hat{F})$ increases with increasing p even though the average size of each term generally decreases. Now in order to establish a sign for a given \hat{F} it is necessary that it be large enough to contravert the inequality even if all the other \hat{F} 's involved should happen to be of opposite sign, but merely to establish that the \hat{F} 's of $\phi(\hat{F})$ are not all negative it is only required that the sum of their absolute magnitudes exceed the inequality. It therefore seems reasonable to expect that as p increases it will become easier to establish sign relationships between two or more \hat{F} 's, but more difficult to establish an actual sign. Thus, it seems doubtful if one can say that the inequalities 'become more powerful as the number of symmetry elements increases'. This statement would be true uncontestedly if N , rather than n , were kept constant, for then the average sizes of the \hat{F} 's would not decrease as

p increases. But this hardly seems a fair way to make the comparison, since it is almost universally customary to judge the difficulty of a crystal structure determination by, among other items, the size of the asymmetric unit.

By far the most important conclusion to be drawn from these values of $\hat{\sigma}$ is one regarding the overall applicability of the inequalities. We see that as n increases and $\hat{\sigma}$ decreases there will be a smaller and smaller fraction of the \hat{F} 's which can be given signs by the simple inequalities, and finally for large enough n the number of signs fixed will be so few that a start cannot be made upon the structure determination by Fourier syntheses.

For oxalic acid dihydrate, a known crystal reworked by Gillis (1948) as a test, $n=4$. Dekaborane, a crystal presenting great difficulties because of twinning, volatility and faulty chemistry, has been solved by Kasper, Lucht & Harker (1948) by means of inequalities. At first sight this appears to have $n=10$, but actually each of the atoms is related to another one by rigorous general non-crystallographic relationships between their parameters; and upon working out the details the problem corresponds to $n=5$ both with regard to the size of the \hat{F} 's and the nature of the inequalities used, which were those of space group $Pnmm$ and a pseudo-cell with one-half the volume of the smallest true cell.

It thus appears that these two successful applications are not fair tests of the ability of this method to solve the more complicated problems of interest to-day, some of which have been solved by older methods with n as high as 20 or more. In this connection it may be noted that the simple inequalities are unable to solve the melamine problem, $n=9$, with the data available ($h0l$ and $0kl$); with some 150 \hat{F} 's large enough to be observed only two signs are fixed for the second-order \hat{F} 's, and the latter are quite small. Two sign relationships are also established for pairs of \hat{F} 's.

For β -carotene, a hydrocarbon (Taylor, 1937) with space group $P2_1/c$ and $n=20$, we expect $\hat{\sigma}_{hkl}=0.112$ and $\hat{\sigma}_{h0l}=0.158$, and for this latter zone it appears unlikely that any \hat{F} will exceed 0.520 in absolute value. Taylor gives the absolute measurements for the seventy-five reflections of largest spacing and no $|\hat{F}|$ exceeds 0.24. The simple inequalities can fix no signs for those data given by Taylor, and it appears fairly certain that they could fix no signs for the entire crystal if data were available.

Thus, in attempting to solve more and more complicated problems it is certain that one must resort to more and more complicated inequalities. In discussing these complicated inequalities the previous authors make statements to the effect that 'if some of the signs are already known, these inequalities provide powerful tools for determining the remaining signs'. This is true, but for the situation envisaged here the simpler inequalities will have produced few, or even no signs as a

basis for further operations and the more complicated expressions will have to work without assistance.

Then, however, two further complications arise. These inequalities involve a progressively larger and larger number of terms, and often terms of higher and higher degree. Firstly, these facts will make the method more tedious and time-consuming, and Harker & Kasper have already described it as laborious. And secondly, the influence of experimental errors in the \hat{F} 's will become more and more critical. These errors involve not only the actual error in each F , but also the scale factor, the temperature factor or factors and the errors involved in assuming, in deriving the inequalities, that $f_j=fZ_j$, with the last error sometimes more serious than usually supposed. When numbers containing errors are raised to powers, the resulting percentage errors are roughly proportional to the powers, and upon adding such terms the overall probable percentage error in the sum, for errors of the size encountered in measurements of \hat{F} , may easily become so large as to vitiate the application of these more complicated inequalities. Experience with a related sign-determining method, referred to below, which involves many terms and some of higher degree, has emphasized these doubts regarding the usefulness of complicated relationships.

It does not seem practical at the moment to estimate theoretically what limit, if any, the experimental errors will set. It does, however, seem fair to say that, until it is proved otherwise by actual accomplishment, it would be unwarranted to assert that the method of inequalities is able to solve problems that generally cannot be solved by complete three-dimensional, sharpened-up, absolute-scale Patterson methods. It would seem wiser, *pro tem.*, to consider the method as a useful and welcome adjunct to the whole body of existing methods rather than as a technique destined to outmode all others. It is apt to be particularly useful in problems such as dekaborane where the chemistry is obscure or even wrong.

The power of the complete three-dimensional sharpened-up Patterson synthesis is perhaps not as widely realized as it should be, perhaps because of the tediousness of computing such a complete series before the recent development of rapid mechanical and electrical summing devices. It utilizes all the information put into the inequality method and has the additional advantage that all reliable chemical and physical evidence available can be utilized in interpreting the diagram. Although in his original paper Patterson (1935) pointed out the advantages of sharpening-up the series by dividing the data by f^2 , very few investigators have ever used this refinement. Harker & Kasper (1948) have stated that such sharpening is 'almost essential' to the inequality method. Experience in this Laboratory (Schomaker & Shoemaker, to be published) indicates that although in the past solutions have often resulted from ordinary

Patterson functions, the use of complete sharpened-up absolute data will greatly extend the power of the method.

In conclusion I would like to recall to attention a much earlier attempt at deriving the signs of Fourier coefficients from their magnitudes. The paper by Banerjee (1933) appears to have been generally overlooked in the current interest in this subject. Gillis (1948, §4.3) has suggested the probable existence of fundamentally stronger relationships. Obviously the most powerful relationships possible, ignoring the difficulties arising from experimental errors, are rigorous equations (not inequalities) relating \hat{F} 's. Banerjee showed how, with the theory of symmetric functions, some such relationships could be derived for crystals containing one kind of atom and a center of symmetry. He applied his method to the 00*l* data of anthracene and obtained all the signs correctly. No further work along these lines appears to have been

reported. It is possible in principle to extend Banerjee's results to more general crystals, for example by means of bipartite and tripartite symmetric functions, but for the multiparameter problems of interest to-day the expressions promise to be too complicated for practical use.

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An Extension of Banerjee's Method for Determining Signs of Fourier Coefficients*

BY E. W. HUGHES

Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California, U.S.A.

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Banerjee has given a linear relationship between certain structure factors, F_{hkl} , of a crystal which may be useful in determining their signs. His equation is applicable only to crystals containing but one kind of atom. In this note a similar equation is derived for 'unitary structure factors', \hat{F}_{hkl} , which is applicable to any crystal.

In a previous article (Hughes, 1949) attention has been called to the work of Banerjee (1933) on the determination of signs of Fourier coefficients from their magnitudes. His results are applicable only to crystals containing one kind of atom.

One of his results may, however, be easily extended to the more general case and this will be given here as it might prove useful in checking or determining signs for crystals of not too great complexity.

Let us rewrite the expression for \hat{F} in Banerjee's notation

$$\hat{F}_{hkl} = \sum_1^N q_j \alpha_j^h \beta_j^k \gamma_j^l,$$

where q_j is the fraction of the electrons on the j th atom, $\alpha_j = e^{2\pi i \alpha_j}$, and similarly for β_j and γ_j .

We then set up a polynomial in the dummy variables u , v and w corresponding to α , β and γ , such that the

α_j 's, for instance, are roots of the polynomial

$$u^h v^k w^l \prod_j^N (u - \alpha_j) = u^{N+h} v^k w^l + a_1 u^{N+h-1} v^k w^l + \dots + a_{N-1} u^{h+1} v^k w^l + a_N u^h v^k w^l,$$

where h , k and l may be chosen arbitrarily.

If there is a center of symmetry at the origin, and no atoms are located at centers of symmetry, the roots occur in reciprocal pairs ($\alpha_1 = \alpha_2^{-1}$ etc.) and in these circumstances $a_N = 1$, $a_{N-1} = a_1$, etc., thus reducing the number of constants a_i to $\frac{1}{2}N$. Substitution of any α_j , β_j , γ_j triple into this polynomial causes it to vanish since the α_j 's are all roots. Making this substitution and multiplying by q_j yields, for our special case,

$$q_j (\alpha_j^{N+h} \beta_j^k \gamma_j^l + \alpha_j^h \beta_j^k \gamma_j^l) + a_1 q_j (\alpha_j^{N+h-1} \beta_j^k \gamma_j^l + \alpha_j^{h+1} \beta_j^k \gamma_j^l) + \dots + a_{\frac{1}{2}N} q_j \alpha_j^{2N+h} \beta_j^k \gamma_j^l = 0.$$

Summing the N equations with all possible j 's and comparing with the expression for \hat{F}_{hkl} yields

$$\hat{F}_{N+h,k,l} + \hat{F}_{hkl} + a_1 (\hat{F}_{N-1+h,k,l} + \hat{F}_{h+1,k,l}) + \dots + a_{\frac{1}{2}N} \hat{F}_{\frac{1}{2}N+h,k,l} = 0.$$

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