

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\*

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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,  $\alpha_j = e^{2\pi i x_j}$ , and similarly for  $\beta_j$  and  $\gamma_j$ .

We then set up a polynomial in the dummy variables  $u$ ,  $v$  and  $w$  corresponding to  $\alpha$ ,  $\beta$  and  $\gamma$ , such that the

$\alpha_j$ '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  $\alpha_j$ ,  $\beta_j$ ,  $\gamma_j$  triple into this polynomial causes it to vanish since the  $\alpha_j$ '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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The  $a_i$ 's are independent of the chosen values of  $h$ ,  $k$ ,  $l$  and there are similar equations with constants  $b_i$  and  $c_i$  for variable  $k$  or  $l$  respectively. When  $k=l=0$  one can simplify the result by using the facts that  $\hat{F}_{h00} = \hat{F}_{\bar{h}00}$  and  $\hat{F}_{000} = 1$ .

By a simple transformation an analogous equation can be written which corresponds to any set of parallel row lines in reciprocal space in the way that the given equation corresponds to rows parallel to the axis  $a_0^*$ . But there can be no more than three independent sets of constants for a crystal.

This equation can be applied only if the unit cell is large enough in one direction to show at least  $(N+1)$   $\hat{F}$ 's with two indices constant. This in itself is a severe limitation. The constants  $a_i$  are related to the  $x$  coordinates of the atoms through Newton's relations and for Banerjee's special case are directly related to the  $\hat{F}_{h00}$ 's. Since the equation is linear in the  $\hat{F}$ 's a scale factor may be included, so that it is applicable to relative as well as to absolute data. If enough signs are known, so that the  $a$ 's can be calculated, the equation can be used to obtain other signs or sign relationships quite rapidly for other rows with  $k$  and  $l$  constant. Thus, for example, if the  $h0l$  reflections have been signed they

may be used to calculate the  $a_i$ 's and  $c_i$ 's and the equation used on the  $hkl$  data.

With  $a_i$ 's calculated from the  $x$  parameters this method gave correct results on the larger  $\hat{F}_{h0l}$ 's for dicyandiamide (Hughes, 1940). For this projection  $N=2n=12$ . This, however, is not a very severe test.

With more symmetry than a symmetry center there are additional relationships between the roots and consequently further reduction in the number of the various constants. One may also use the fact that with higher symmetry the number of equivalent planes in a form is generally greater. For example, with a mirror plane perpendicular to the  $a_0$  axis of the crystal,  $\hat{F}_{hkl} = \hat{F}_{\bar{h}kl}$ , with consequent simplification of an equation like that above.

If atoms occur in special positions of a space group, there will be one or more roots with special fixed values, such as  $\pm 1$ . Such roots must be included in the polynomial when deriving an appropriate equation for the  $\hat{F}$ 's.

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## The Measurement and Correction of Intensities from Single-Crystal X-ray Photographs

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An account is given of the effect of spot size in single-crystal X-ray photographs on the errors in intensity measurements made by eye estimation and by direct photometry of the negative. It is shown how direct photometry of the negative has been used to obtain intensities from equi-inclination Weissenberg photographs to within an accuracy of  $\pm 10\%$ . Charts are given for the simultaneous correction of X-ray intensities for Lorentz and polarization factors for equi-inclination Weissenberg photographs and for rotation and oscillation photographs.

### The measurement of X-ray intensities

Direct measurements of integrated X-ray intensities may be made on the instruments described by Robinson (1933), Dawton (1937) and Robertson & Dawton (1941), or that suggested by Wiebenga (1947). Indirect measurements may be carried out by the methods suggested by Dawton (1938). However, most single-crystal workers, in recent years, have measured X-ray intensities by eye comparison of a standard intensity

scale against the series of unknown spots. The intensity scale is made by successively exposing different portions of a piece of X-ray film to a suitable reflexion for various time intervals during which the X-ray output is maintained constant.

Eye estimation of intensities is physically tiring and liable to serious error owing to the fact that the unknown spots have not the same size or variations in density as the spots of the intensity scale. Furthermore,