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The Critical Examination of a Weak Sign Relationship Between Structure Factors

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The probability of the sign of the product $U_{\mathbf{h}-\mathbf{h}'}U_{\mathbf{h}+\mathbf{h}'}$ is derived as a function of $U_{\mathbf{h}}U_{\mathbf{h}'}$. It is found that $U_{\mathbf{h}-\mathbf{h}'}U_{\mathbf{h}+\mathbf{h}'}$ cannot be shown to be negative with a probability much exceeding $\frac{1}{2}$, a result at variance with a prediction made by Gillis in a previous paper.

1. Introduction

In a recent short communication Gillis (1956) has suggested the following conditional sign relationship as an aid to structure determination: if

$$|U_{\mathbf{h}}|^2+|U_{\mathbf{h}'}|^2 \ll |U_{\mathbf{h}+\mathbf{h}'}U_{\mathbf{h}-\mathbf{h}'}| \,, \tag{1}$$

then

$$s(\mathbf{h}+\mathbf{h}') \approx -s(\mathbf{h}-\mathbf{h}') \,, \tag{2}$$

where $s(\mathbf{h})$ represents the sign of $U_{\mathbf{h}}$ and the symbol $\approx$ means 'probably equals'. The test of this relationship made by Gillis on the structure of *p*-nitroaniline led him to believe that, subject to condition (1) being satisfied, (2) holds with high probability.

A previous investigation of similar relationship by the present author had given much less favourable indications. The form of this relationship was that

$$\text{if} \quad U_{\mathbf{h}}U_{\mathbf{h}'} \quad \text{is small} \,, \tag{3}$$

then

$$s(\mathbf{h}+\mathbf{h}') \approx -s(\mathbf{h}-\mathbf{h}') \,. \tag{4}$$

Condition (3) includes (1) but is more general in that it requires only one of $U_{\mathbf{h}}$ or $U_{\mathbf{h}'}$ to be small.

To each of the sign relationships hitherto reported there corresponds an inequality relationship which can be used to relate signs with certainty when the unitary structure factors involved are sufficiently large. It is interesting to note in this instance that if

$$(|U_{\mathbf{h}}|-|U_{\mathbf{h}'}|)^2 > (1-|U_{\mathbf{h}+\mathbf{h}'}|)(1-|U_{\mathbf{h}-\mathbf{h}'}|) \,, \tag{5}$$

then a Harker–Kasper inequality can show that $s(\mathbf{h}+\mathbf{h}')s(\mathbf{h}-\mathbf{h}')$ is certainly negative (Gillis, 1948). This suggests that the most favourable condition for sign relationship (2) is that one of $U_{\mathbf{h}}$ and $U_{\mathbf{h}'}$ should be large and the other small, or, in other words, that condition (3) should hold and condition (1) should be contravened.

The analysis of the following section finds theoretically the probability that $s(\mathbf{h}+\mathbf{h}')s(\mathbf{h}-\mathbf{h}')$ is positive (or negative) as a function of $U_{\mathbf{h}}U_{\mathbf{h}'}$. The statistical mathematics is of the same type as has been used previously by Wilson (1949), Woolfson (1954) and Cochran & Woolfson (1955) and suffers from the same limitations. It will therefore be assumed, as in these previous papers, that the unitary structure factors considered are not unduly large.

2. Theory of the sign relationship

We shall consider a centrosymmetrical structure containing N equal atoms per unit cell. Then

$$U_{\mathbf{h}} = 2\sum_{j=1}^{N/2} n_j \cos 2\pi\mathbf{h}.\mathbf{r}_j \,, \tag{6}$$

where $n_j = N^{-1}$.

We also have

$$U_{\mathbf{h}-\mathbf{h}'}+U_{\mathbf{h}+\mathbf{h}'} = 4\sum_{j=1}^{N/2} n_j \cos 2\pi\mathbf{h}.\mathbf{r}_j \cos 2\pi\mathbf{h}'.\mathbf{r}_j \,. \tag{7}$$

By application of the central-limit theorem, (as used by Wilson (1949) and Woolfson (1954)), it may be shown that the probability of $U_{\mathbf{h}-\mathbf{h}'}+U_{\mathbf{h}+\mathbf{h}'}$ being between X and $X+dX$ is

$$P(X)dX = (2\pi\sigma^2)^{-\frac{1}{2}} \exp\left\{-\frac{(X-\overline{X})^2}{2\sigma^2}\right\}dX \,, \tag{8}$$

where

$$\overline{X} = 2U_{\mathbf{h}}U_{\mathbf{h}'} \,,$$

and

$$\sigma^2 = \frac{2}{N}(1+U_{2\mathbf{h}})(1+U_{2\mathbf{h}'})-\frac{8}{N}U_{\mathbf{h}}^2U_{\mathbf{h}'}^2$$

$$\simeq \frac{2}{N}(1+U_{2\mathbf{h}})(1+U_{2\mathbf{h}'})$$

if $U_{\mathbf{h}}$ and $U_{\mathbf{h}'}$ are not too large.

In addition we have

$$U_{\mathbf{h}-\mathbf{h}'}-U_{\mathbf{h}+\mathbf{h}'} = 4\sum_{j=1}^{N/2} n_j \sin 2\pi\mathbf{h}.\mathbf{r}_j \sin 2\pi\mathbf{h}'.\mathbf{r}_j \,. \tag{9}$$

If

$$2\sum_{j=1}^{N/2} n_j \sin 2\pi\mathbf{h}.\mathbf{r}_j = \chi_{\mathbf{h}}$$

and

$$2\sum_{j=1}^{N/2} n_j \sin 2\pi\mathbf{h}'.\mathbf{r}_j = \chi_{\mathbf{h}'} \,,$$

then it can be shown that the probability of $U_{\mathbf{h}-\mathbf{h}'}-U_{\mathbf{h}+\mathbf{h}'}$ being between Y and $Y+dY$ is

$$P'(Y)dY = (2\pi\eta^2)^{-\frac{1}{2}} \exp\left\{-\frac{(Y-\overline{Y})^2}{2\eta^2}\right\} dY\,, \quad (10)$$

where

$$\overline{Y} = 2\chi_{\mathbf{h}}\chi_{\mathbf{h}'}\,,$$

and

$$\eta^2 = \frac{2}{N}(1-U_{2\mathbf{h}})(1-U_{2\mathbf{h}'}) - \frac{8}{N}\chi_{\mathbf{h}}^2\chi_{\mathbf{h}'}^2$$
$$\simeq \frac{2}{N}(1-U_{2\mathbf{h}})(1-U_{2\mathbf{h}'})\,.$$

In any particular case the value of $\chi_{\mathbf{h}}\chi_{\mathbf{h}'}$ is not known and hence the actual distribution of $U_{\mathbf{h}-\mathbf{h}'}-U_{\mathbf{h}+\mathbf{h}'}$ as given by equation (10) cannot be determined.

The distribution of $\chi_{\mathbf{h}}$ can be found by the application of the central-limit theorem. The probability that $\chi_{\mathbf{h}}$ lies between y and $y+dy$ is

$$\psi(y)dy = \{2\pi N^{-1}(1-U_{2\mathbf{h}})\}^{-\frac{1}{2}} \exp\left\{-\frac{Ny^2}{2(1-U_{2\mathbf{h}})}\right\} dy\,. \quad (11)$$

If the product $\chi_{\mathbf{h}}\chi_{\mathbf{h}'}$ lies between μ and $\mu+d\mu$ and $\chi_{\mathbf{h}}$ lies between y and $y+dy$, then $\chi_{\mathbf{h}'}$ must lie between μ/y and $(\mu+d\mu)/y$. The probability that $\chi_{\mathbf{h}}$ and $\chi_{\mathbf{h}'}$ will be between these limits simultaneously is

$$\frac{1}{y}\psi(y)\psi\left(\frac{\mu}{y}\right)d\mu\, dy\,.$$

The probability that $\chi_{\mathbf{h}}\chi_{\mathbf{h}'}$ will lie between μ and $\mu+d\mu$ for all possible values of y is thus

$$\xi(\mu)d\mu = \int_{y=-1}^{1}\frac{1}{y}\psi(y)\psi\left(\frac{\mu}{y}\right)d\mu\, dy$$
$$= \frac{N}{2\pi}\{(1-U_{2\mathbf{h}})(1-U_{2\mathbf{h}'})\}^{-\frac{1}{2}}\int_{y=-1}^{1}\frac{1}{y}$$
$$\times \exp\left\{-\frac{Ny^2}{2(1-U_{2\mathbf{h}})}-\frac{N\mu^2}{2y^2(1-U_{2\mathbf{h}'})}\right\}dy\,d\mu\,.$$

Making the substitution $t = Ny^2/2(1-U_{2\mathbf{h}})$, we find

$$\xi(\mu)d\mu = \frac{N}{4\pi}\{(1-U_{2\mathbf{h}})(1-U_{2\mathbf{h}'})\}^{-\frac{1}{2}}\int_{t=-N/2(1-U_{2\mathbf{h}})}^{N/2(1-U_{2\mathbf{h}})}\frac{1}{t}$$
$$\times \exp\left\{-t-\frac{N^2\mu^2}{4t(1-U_{2\mathbf{h}})(1-U_{2\mathbf{h}'})}\right\}dt\,d\mu\,.$$

When N is reasonably large the limits of the integration may be replaced by $+\infty$ and $-\infty$. Then we have

$$\xi(\mu)d\mu = \frac{N}{2\pi}\{(1-U_{2\mathbf{h}})(1-U_{2\mathbf{h}'})\}^{-\frac{1}{2}}$$
$$\times K_0\left(\frac{N\mu}{\{(1-U_{2\mathbf{h}})(1-U_{2\mathbf{h}'})\}^{\frac{1}{2}}}\right)d\mu\,, \quad (12)$$

where $K_0(x)$ is the zero-order Bessel function of the second kind (Watson, 1922, pp. 78 and 183). Although the actual value of μ is not known, we may now find the expected distribution of $U_{\mathbf{h}-\mathbf{h}'}-U_{\mathbf{h}+\mathbf{h}'}$ by combining equations (10) and (12). The average probability that $U_{\mathbf{h}-\mathbf{h}'}-U_{\mathbf{h}+\mathbf{h}'}$ lies between Y and $Y+dY$ will be

$$\overline{P'(Y)}dY = \int_{\mu=-1}^{1}P'(Y)\xi(\mu)dY\,d\mu$$
$$= \left(\frac{N}{4\pi}\right)^{3/2}\{(1-U_{2\mathbf{h}})(1-U_{2\mathbf{h}'})\}^{-1}$$
$$\times\int_{\mu=-1}^{1}K_0\left(\frac{N\mu}{\{(1-U_{2\mathbf{h}})(1-U_{2\mathbf{h}'})\}^{\frac{1}{2}}}\right)$$
$$\times\exp\left\{-\frac{N(Y-2\mu)^2}{4(1-U_{2\mathbf{h}})(1-U_{2\mathbf{h}'})}\right\}dY\,d\mu\,.$$

For moderate values of N the function within the integration decreases rapidly with increasing μ and the limits of the integration may be replaced by $+\infty$ and $-\infty$.

Substituting

$$\frac{N\mu}{\{(1-U_{2\mathbf{h}})(1-U_{2\mathbf{h}'})\}^{\frac{1}{2}}} = x$$

and

$$\frac{Y}{4\{(1-U_{2\mathbf{h}})(1-U_{2\mathbf{h}'})\}^{\frac{1}{2}}} = Z\,,$$

we have

$$\overline{P'(Y)}dY = \left\{\frac{4\pi^3}{N}(1-U_{2\mathbf{h}})(1-U_{2\mathbf{h}'})\right\}^{-\frac{1}{2}}$$
$$\times\exp(-4NZ^2)\int_{x=-\infty}^{\infty}K_0(x)$$
$$\times\exp\left(-\frac{x^2}{N}\right)\exp(-4Zx)dx\,dY \quad (13)$$

$$= \left\{\frac{4\pi^3}{N}(1-U_{2\mathbf{h}})(1-U_{2\mathbf{h}'})\right\}^{-\frac{1}{2}}\exp(-4NZ^2)F(N,Z)\,, \quad (14)$$

where $F(N, Z)$ is the function of N and Z given by the integration in equation (13). This has been computed by numerical means for a range of values of N and Z, the results being shown in Table 1.

Table 1. $F(N, Z)$

Z	$N=30$	$N=50$	$N=100$
0·000	1·525	1·541	1·564
0·025	1·531	1·548	1·572
0·050	1·550	1·569	1·594
0·075	1·583	1·605	1·633
0·100	1·632	1·660	1·693
0·125	1·701	1·738	1·779
0·150	1·796	1·846	1·901
0·175	1·925	1·997	2·079
0·200	2·104	2·210	2·397
0·225	2·353	2·535	2·883
0·250	2·697	3·077	3·616

We shall now consider a case where

$$|U_{\mathbf{h}-\mathbf{h}'}|+|U_{\mathbf{h}+\mathbf{h}'}| = \alpha$$

and

$$|U_{\mathbf{h}-\mathbf{h}'}|-|U_{\mathbf{h}+\mathbf{h}'}| = \beta\,.$$

If $s(\mathbf{h}-\mathbf{h}')s(\mathbf{h}+\mathbf{h}')$ is positive then either

$$U_{\mathbf{h}-\mathbf{h}'}+U_{\mathbf{h}+\mathbf{h}'}=\alpha,\quad U_{\mathbf{h}-\mathbf{h}'}-U_{\mathbf{h}+\mathbf{h}'}=\beta$$

or

$$U_{\mathbf{h}-\mathbf{h}'}+U_{\mathbf{h}+\mathbf{h}'}=-\alpha,\quad U_{\mathbf{h}-\mathbf{h}'}-U_{\mathbf{h}+\mathbf{h}'}=-\beta\,.$$

If $s(\mathbf{h}-\mathbf{h}')s(\mathbf{h}+\mathbf{h}')$ is negative then either

$$U_{\mathbf{h}-\mathbf{h}}+U_{\mathbf{h}+\mathbf{h}'}=\beta,\quad U_{\mathbf{h}-\mathbf{h}'}-U_{\mathbf{h}+\mathbf{h}'}=\alpha$$

or

$$U_{\mathbf{h}-\mathbf{h}'}+U_{\mathbf{h}+\mathbf{h}'}=-\beta,\quad U_{\mathbf{h}-\mathbf{h}'}-U_{\mathbf{h}+\mathbf{h}'}=-\alpha\,.$$

The probability that $s(\mathbf{h}-\mathbf{h}')s(\mathbf{h}+\mathbf{h}')$ is positive, $\varphi(+)$, divided by the probability that $s(\mathbf{h}-\mathbf{h}')s(\mathbf{h}+\mathbf{h}')$ is negative, $\varphi(-)$, is thus given by

$$\frac{\varphi(+)}{\varphi(-)}=\frac{P(\alpha)\overline{P}'(\beta)+P(-\alpha)\overline{P}'(-\beta)}{P(\beta)\overline{P}'(\alpha)+P(-\beta)\overline{P}'(-\alpha)}$$

$$=\frac{\exp\left\{-\dfrac{N\beta^2}{4(1-U_{2\mathbf{h}})(1-U_{2\mathbf{h}'})}\right\}}{\exp\left\{-\dfrac{N\alpha^2}{4(1-U_{2\mathbf{h}})(1-U_{2\mathbf{h}'})}\right\}}\times\frac{F\left[N,\dfrac{\beta}{4\{(1-U_{2\mathbf{h}})(1-U_{2\mathbf{h}'})\}^{\frac{1}{2}}}\right]}{F\left[N,\dfrac{\alpha}{4\{(1-U_{2\mathbf{h}})(1-U_{2\mathbf{h}'})\}^{\frac{1}{2}}}\right]}$$

$$\times\frac{\exp\left\{-\dfrac{N(\alpha-2U_{\mathbf{h}}U_{\mathbf{h}'})^2}{4(1+U_{2\mathbf{h}})(1+U_{2\mathbf{h}'})}\right\}+\exp\left\{-\dfrac{N(\alpha+2U_{\mathbf{h}}U_{\mathbf{h}'})^2}{4(1+U_{2\mathbf{h}})(1+U_{2\mathbf{h}'})}\right\}}{\exp\left\{-\dfrac{N(\beta-2U_{\mathbf{h}}U_{\mathbf{h}'})^2}{4(1+U_{2\mathbf{h}})(1+U_{2\mathbf{h}'})}\right\}+\exp\left\{-\dfrac{N(\beta+2U_{\mathbf{h}}U_{\mathbf{h}'})^2}{4(1+U_{2\mathbf{h}})(1+U_{2\mathbf{h}'})}\right\}}\qquad(15)$$

It can be seen from the form of equation (15) that $\varphi(+)/\varphi(-)$ is an even function of $U_{\mathbf{h}}U_{\mathbf{h}'}$ so that this quantity may be replaced by its modulus. However, the value of $\varphi(+)/\varphi(-)$ does depend on a knowledge of the signs of $U_{2\mathbf{h}}$ and $U_{2\mathbf{h}'}$, information which is not generally available.

Let us see how we can make use of equation (15) by its application to an example. The data are taken from the (010) projection of adenylic acid. Although this projection does not contain equal resolved atoms we shall take $N=50$, the total number of atoms in the unit cell. The data are

$$|U_{\mathbf{h}+\mathbf{h}'}|=|U_{40\bar{4}}|=0\cdot29,\qquad |U_{\mathbf{h}'}|=|U_{20\bar{1}}|=0\cdot10,$$
$$|U_{\mathbf{h}-\mathbf{h}'}|=|U_{00\bar{2}}|=0\cdot31,\qquad |U_{2\mathbf{h}}|=|U_{40\bar{6}}|=0\cdot16,$$
$$|U_{\mathbf{h}}|=|U_{20\bar{3}}|=0\cdot08,\qquad |U_{2\mathbf{h}'}|=|U_{40\bar{2}}|=0\cdot20.$$

We now consider the four possible ways of allocating signs to $U_{2\mathbf{h}}$ and $U_{2\mathbf{h}'}$:

(i) $U_{2\mathbf{h}}=0\cdot16,\quad U_{2\mathbf{h}'}=0\cdot20$,
(ii) $U_{2\mathbf{h}}=0\cdot16,\quad U_{2\mathbf{h}'}=-0\cdot20$,
(iii) $U_{2\mathbf{h}}=-0\cdot16,\quad U_{2\mathbf{h}'}=0\cdot20$,
(iv) $U_{2\mathbf{h}}=-0\cdot16,\quad U_{2\mathbf{h}'}=-0\cdot20$,

and calculate the value of $\varphi(+)/\varphi(-)$ for each of these. These are

(i) 3·980, (iii) 0·904,
(ii) 0·864, (iv) 0·171.

The corresponding values of $\varphi(+)$ and $\varphi(-)$ are

$$\left.\begin{array}{ll}\text{(i)} & \varphi(+)=0\cdot799,\ \varphi(-)=0\cdot201\,,\\ \text{(ii)} & \varphi(+)=0\cdot464,\ \varphi(-)=0\cdot536\,,\\ \text{(iii)} & \varphi(+)=0\cdot475,\ \varphi(-)=0\cdot525\,,\\ \text{(iv)} & \varphi(+)=0\cdot146,\ \varphi(-)=0\cdot854\,.\end{array}\right\}\qquad(16)$$

It can be seen that the values of $\varphi(+)$ and $\varphi(-)$ depend very much on the signs of $U_{2\mathbf{h}}$ and $U_{2\mathbf{h}'}$. Generally these are not known, and the true values of $\varphi(+)$ and $\varphi(-)$ cannot be determined. It is possible, however, to assess the probability of $U_{2\mathbf{h}}$ being positive or negative from the values of $|U_{2\mathbf{h}}|$ and $|U_{\mathbf{h}}|$ (Hauptman & Karle, 1953; Cochran & Woolfson, 1955).

For equal resolved atoms the probability that $U_{2\mathbf{h}}$ is positive is

$$p_+(U_{2\mathbf{h}})=\tfrac{1}{2}+\tfrac{1}{2}\tanh\left\{\tfrac{1}{2}N|U_{2\mathbf{h}}|(U_{\mathbf{h}}^2-\frac{1}{N})\right\}.\qquad(17)$$

Applying equation (17) to our example we find

$$p_+(U_{2\mathbf{h}})=0\cdot473\quad\text{and}\quad p_+(U_{2\mathbf{h}'})=0\cdot475\,.$$

The probabilities of having the four sign combinations for $U_{2\mathbf{h}}$ and $U_{2\mathbf{h}'}$ are

$$\left.\begin{array}{ll}\text{(i) } 0\cdot225, & \text{(iii) } 0\cdot250\,,\\ \text{(ii) } 0\cdot248, & \text{(iv) } 0\cdot277\,.\end{array}\right\}\qquad(18)$$

Weighting the values of $\varphi(+)$ and $\varphi(-)$ given in list (16) by the probabilities of list (18) we find the average values of $\varphi(+)$ and $\varphi(-)$. These are

$$\overline{\varphi(+)}=0\cdot454\quad\text{and}\quad\overline{\varphi(-)}=0\cdot546\,,$$

which shows that there is a weak preference for $s(\mathbf{h}-\mathbf{h}')s(\mathbf{h}+\mathbf{h}')$ to be negative.

It is found that values of $\varphi(-)$ very much larger than $\frac{1}{2}$ do not occur although values of $\varphi(+)$ very nearly equal to unity may occur when the product $U_{\mathbf{h}}U_{\mathbf{h}'}$ is large. In the latter case it may be concluded that $s(\mathbf{h}-\mathbf{h}')s(\mathbf{h}+\mathbf{h}')$ is probably positive from the sign relationships

$$s(\mathbf{h}-\mathbf{h}')\approx s(\mathbf{h})s(\mathbf{h}')\approx s(\mathbf{h}+\mathbf{h}')\,.\qquad(19)$$

When $U_{\mathbf{h}}$ and $U_{\mathbf{h}'}$ are small then equation (17) shows that $U_{2\mathbf{h}}$ and $U_{2\mathbf{h}'}$ are both probably negative. The two sign relationships

$$s(\mathbf{h}-\mathbf{h}')s(\mathbf{h}+\mathbf{h}') \approx s(2\mathbf{h}) \qquad (20)$$

and

$$s(\mathbf{h}-\mathbf{h}')s(\mathbf{h}+\mathbf{h}') \approx s(2\mathbf{h}') \qquad (21)$$

will then each give an indication that $s(\mathbf{h}-\mathbf{h}')s(\mathbf{h}+\mathbf{h}')$ is probably negative. However, equation (17) will not generally indicate that $U_{2\mathbf{h}}$ and $U_{2\mathbf{h}'}$ are negative with probabilities much greater than $\frac{1}{2}$, and the overall probability that $s(\mathbf{h}-\mathbf{h}')s(\mathbf{h}+\mathbf{h}')$ is negative when equations (17), (20) and (21) are taken together can likewise not be very different from $\frac{1}{2}$. It is instructive to calculate $\varphi(+)$ and $\varphi(-)$ from equations (17), (20) and (21) for the example that we have already considered. From equation (17) we find

$$p_+(U_{2\mathbf{h}}) = 0{\cdot}473 \quad \text{and} \quad p_+(U_{2\mathbf{h}'}) = 0{\cdot}475 \, .$$

The probability that equation (20) holds is $\frac{1}{2}+\frac{1}{2}\tanh(N|U_{\mathbf{h}+\mathbf{h}'}U_{\mathbf{h}-\mathbf{h}'}U_{2\mathbf{h}}|)$ (Cochran & Woolfson, 1955). This probability equals 0·808 and in conjunction with the value of $p_+(U_{2\mathbf{h}})$ indicates the probability that $s(\mathbf{h}-\mathbf{h}')s(\mathbf{h}+\mathbf{h}')$ is positive as

$$\varphi_1(+) = (0{\cdot}808\times0{\cdot}473)+(0{\cdot}192\times0{\cdot}527) = 0{\cdot}483 \, .$$

Similarly from (17) and (21) we may find

$$\varphi_2(+) = 0{\cdot}483 \, .$$

The overall probability, $\varphi(+)$, obtained by combining these individual probabilities is found from

$$\frac{\varphi(+)}{\varphi(-)} = \frac{\varphi_1(+)}{\varphi_1(-)} \cdot \frac{\varphi_2(+)}{\varphi_2(-)}$$

(Cochran & Woolfson, 1955).

Thus

$$\frac{\varphi(+)}{\varphi(-)} = \frac{0{\cdot}483}{0{\cdot}517} \times \frac{0{\cdot}483}{0{\cdot}517} = 0{\cdot}873 \, ,$$

or

$$\varphi(+) = 0{\cdot}466, \quad \varphi(-) = 0{\cdot}534 \, .$$

This result differs from that obtained earlier from equation (15), which was

$$\varphi(+) = 0{\cdot}454, \quad \varphi(-) = 0{\cdot}546 \, .$$

The result from equation (15) is probably more reliable, especially when $U_{2\mathbf{h}}$ and $U_{2\mathbf{h}'}$ are small. For example, if $N = 50$, $|U_{\mathbf{h}+\mathbf{h}'}| = |U_{\mathbf{h}-\mathbf{h}'}| = 0{\cdot}3$, $|U_{\mathbf{h}}| = |U_{\mathbf{h}'}| = |U_{2\mathbf{h}}| = |U_{2\mathbf{h}'}| = 0$, then the application of equation (15) shows $\varphi(+) = 0{\cdot}456$. The repeated application of the sign relationships (17), (20) and (21) would show $\varphi(+) = \frac{1}{2}$. On general grounds one would expect $\varphi(+)$ to be less than $\frac{1}{2}$.

3. Conclusions

It has been found in the previous section that, in conformity with the author's observations, the theoretically calculated probabilities of relationship (4) never greatly exceed $\frac{1}{2}$. This would suggest that the use of (4) in the way suggested by Gillis is not likely to be very successful. The value of some test function depending on relationship (4) will not usually be significantly different for the correct set of signs as compared with the values for incorrect sets. The theoretical basis offered by Gillis for relationship (4) is also at fault. Equation (7), as given by Zachariasen (1952), is

$$(|U_{\mathbf{h}}|+|U_{\mathbf{h}'}|)^2 \approx s(\mathbf{h})s(\mathbf{h}')(U_{\mathbf{h}+\mathbf{h}'}+U_{\mathbf{h}-\mathbf{h}'})+U_{\mathbf{h}+\mathbf{h}'}U_{\mathbf{h}-\mathbf{h}'},$$

but should be

$$\begin{aligned}(|U_{\mathbf{h}}|+|U_{\mathbf{h}'}|)^2 \approx\ & s(\mathbf{h})s(\mathbf{h}')(U_{\mathbf{h}+\mathbf{h}'}+U_{\mathbf{h}-\mathbf{h}'})+U_{\mathbf{h}+\mathbf{h}'}U_{\mathbf{h}-\mathbf{h}'} \\ & -U_{2(\mathbf{h}+\mathbf{h}')}-U_{2(\mathbf{h}-\mathbf{h}')}-U_{2(\mathbf{h}+\mathbf{h}')}U_{2(\mathbf{h}-\mathbf{h}')} \\ & +4U^2_{\mathbf{h}+\mathbf{h}'}U^2_{\mathbf{h}-\mathbf{h}'} \, .\end{aligned}$$

The extra terms in the correct equation invalidate, or at least weaken, the conclusions which were drawn by Gillis from the faulty truncated equation.

The success of the criterion derived by Gillis from equation (4) in recognizing the correct set of signs from several sets for *p*-nitroaniline may be attributed to the simplicity of the structure for which condition (5) may have been realized or nearly realized in some cases. In a private communication Gillis has reported an unsuccessful application of equation (4) to a more complicated structure with lower unitary structure factors.

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