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Physical Significance of Triplets in Direct Methods

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Direct methods of phase determination frequently make use of the triplet formula, $\varphi(\mathbf{h}) \simeq \langle \varphi(\mathbf{h} - \mathbf{k}) + \varphi(\mathbf{k}) \rangle$. This expression is derived by a probability approach which has no easily visualized connection with an actual crystal structure. In this paper the positions of electron-dense planes are related to the positions of peaks in the two-term E map of $E(\mathbf{k})$ and $E(\mathbf{h} - \mathbf{k})$. The connection between $\varphi(\mathbf{h})$ and $[\varphi(\mathbf{k}) + \varphi(\mathbf{h} - \mathbf{k})]$ is then easily visualized. A consideration of spurious peaks in the two-term E map suggests that the probability that $\varphi(-\mathbf{h}) + \varphi(\mathbf{k}) + \varphi(\mathbf{h} - \mathbf{k})$ sums to zero is increased by a small value of $|E(2\mathbf{k} - \mathbf{h})/E(\mathbf{h})|$ and may be decreased by a large value of this ratio. The relation between symmetry and aberrancy is briefly considered.

I. Introduction

The major phase-determining equation of direct methods is

$$\varphi(\mathbf{h}) \simeq \langle \varphi(\mathbf{h} - \mathbf{k}) + \varphi(\mathbf{k}) \rangle_{Kr} \qquad (1)$$

(Karle & Karle, 1966) where Kr denotes that the average is restricted to the quasi-normalized structure factors $E(\mathbf{k})$, $E(\mathbf{h} - \mathbf{k})$ (Karle & Hauptman, 1959) with large magnitudes. (1), the triplet formula, is valid for both centrosymmetric and non-centrosymmetric structures. It can be obtained from Sayre's (1952) equation.

The mathematical derivation of (1) offers little insight into its physical significance. In this paper an intuitive approach is developed by considering the relation between the positions of atoms and the positions of peaks in the two-term Fourier synthesis of $E(\mathbf{k})$ and $E(\mathbf{h} - \mathbf{k})$. This two-term E map shows maximum amplitude of oscillation on the $\mathbf{h}$ and $(2\mathbf{k} - \mathbf{h})$ planes; high atom density on at least one of these planes is inferred.

With some simple structures as examples, it is argued that the value of $|E(2\mathbf{k} - \mathbf{h})/E(\mathbf{h})|$ is an aid to deciding if the triple

$$\varphi(-\mathbf{h}) + \varphi(\mathbf{k}) + \varphi(\mathbf{h} - \mathbf{k}) \qquad (2)$$

is normal (i.e. sums to near zero) or aberrant (i.e. sums to near π). This approach is used to identify the systematically aberrant triples of the benzene ring (Thiessen & Busing, 1974).

The relation between aberrancy and symmetry is briefly considered.

II. Visualizing the triplet formula

We shall use simple physical intuition to answer the question: given large values of $|E(\mathbf{k})|$, $|E(\mathbf{h} - \mathbf{k})|$, $|E(\mathbf{h})|$ and given $\varphi(\mathbf{k})$, $\varphi(\mathbf{h} - \mathbf{k})$ what is the most likely value of $\varphi(\mathbf{h})$?

Let us visualize the real part of the two-term Fourier synthesis of $E(\mathbf{k})$ and $E(\mathbf{h} - \mathbf{k})$ to give

$$|E(\mathbf{k})| \cos[-2\pi \mathbf{r} \cdot \mathbf{k} + \varphi(\mathbf{k})]$$
$$+ |E(\mathbf{h} - \mathbf{k})| \cos[-2\pi \mathbf{r} \cdot (\mathbf{h} - \mathbf{k}) + \varphi(\mathbf{h} - \mathbf{k})]. \quad (3)$$

On any plane in space the value of this sum oscillates. The amplitude of oscillation is a maximum on the planes defined by (4) and (5) since on these planes the maxima of the first and second terms of (3) coincide, and similarly for minima.

$$2l_1\pi - 2\pi \mathbf{r} \cdot \mathbf{k} + \varphi(\mathbf{k}) = 2\pi \cdot (\mathbf{h} - \mathbf{k}) - \varphi(\mathbf{h} - \mathbf{k}) \quad (4)$$

$$2l_2\pi - 2\pi \mathbf{r} \cdot \mathbf{k} + \varphi(\mathbf{k}) = -2\pi \cdot (\mathbf{h} - \mathbf{k}) + \varphi(\mathbf{h} - \mathbf{k}) \quad (5)$$

(l_1, l_2 are integers).

The planes defined by (4) and (5) will be called respectively A and B planes. If we regard (3) as representing a two-term E map, then the most likely position for atoms is on the A or B planes, since the amplitude of electron-density fluctuations in a real structure is greatest on atom-dense planes.

Initially we consider the A planes and write (4) as

$$2\pi \mathbf{r} \cdot \mathbf{h} = \varphi(\mathbf{k}) + \varphi(\mathbf{h} - \mathbf{k}) + 2l_1\pi. \quad (6)$$

(6) states that when the tip of the vector $\mathbf{r}$ lies in an A plane, the product $\mathbf{r} \cdot \mathbf{h}$ is independent of $\mathbf{r}$. Hence $\mathbf{h}$ must be perpendicular to the A planes which have a spacing $1/|\mathbf{h}|$. If the phase of $E(\mathbf{h})$ is dominated by large contributions from the atom-dense A planes, then the peaks of the $\mathbf{h}$ component in the Fourier synthesis, which lie in the planes

$$2m_3\pi - 2\pi \mathbf{r} \cdot \mathbf{h} + \varphi(\mathbf{h}) = 0 \quad (m_3 \text{ an integer}) \quad (7)$$

are likely to be close to the A planes. If the planes represented by (6) and (7) coincide, then we obtain

$$\varphi(\mathbf{h}) \simeq \varphi(\mathbf{k}) + \varphi(\mathbf{h} - \mathbf{k}) \quad (8)$$

which is a term of (1). Physically, (1) corresponds to the statement that the centre of gravity of the family of A planes generated by varying Kr is the most plausible position for the plane (7).

In summary, the two-term Fourier synthesis (3) implies that the plane wavefronts

$$2\pi m_1 - 2\pi \mathbf{r} \cdot \mathbf{k} + \varphi(\mathbf{k}) = 0 \quad (9a)$$

$$2\pi m_2 - 2\pi \mathbf{r} \cdot (\mathbf{h} - \mathbf{k}) + \varphi(\mathbf{h} - \mathbf{k}) = 0 \quad (9b)$$

$$2\pi m_3 - 2\pi \mathbf{r} \cdot \mathbf{h} + \varphi(\mathbf{h}) = 0 \quad (9c)$$

(m_1, m_2, m_3 are integers) should all intersect in a single line through the point D (Fig. 1), and thus (9) can be

solved for the unknown $\varphi(\mathbf{h})$. The triplet formula (1) follows. Points D, D', V, V' in Fig. 1 correspond to different values of m_1, m_2, m_3.

The case of $\mathbf{h}$ and $\mathbf{k}$ parallel [say $L\mathbf{k} = N(\mathbf{h} - \mathbf{k})$ where L and N are integers] is slightly different. (9) are not now linearly independent. (9a) and (9b) give

$$L\varphi(\mathbf{k}) = N\varphi(\mathbf{h} - \mathbf{k}). \quad (10)$$

If $\mathbf{h} = 2\mathbf{k}$ then (10) holds by definition and all the $\mathbf{k}$ planes coincide with the $(\mathbf{h} - \mathbf{k})$ planes. If $\mathbf{h} \neq 2\mathbf{k}$ and it is found that $\varphi(\mathbf{k})$ and $\varphi(\mathbf{h} - \mathbf{k})$ do not satisfy (10), then the premises on which (9) are based are contradicted, and there seems to be no physical reason why $\varphi(\mathbf{h})$ should satisfy (8).

(6) to (9) were obtained from (4), which defines the A planes. We can follow a similar argument based on (5) which defines the B planes. This is equivalent to replacing $(\mathbf{h} - \mathbf{k})$ and $\mathbf{h}$ by $-(\mathbf{h} - \mathbf{k})$ and $(2\mathbf{k} - \mathbf{h})$ respectively in (6) to (9). We then obtain

$$\varphi(2\mathbf{k} - \mathbf{h}) \simeq \varphi(\mathbf{k}) - \varphi(\mathbf{h} - \mathbf{k}) \quad (11)$$

in place of (8). The B planes are perpendicular to $(2\mathbf{k} - \mathbf{h})$ with a spacing $1/|(2\mathbf{k} - \mathbf{h})|$.

The two-term E map represented by (3) shows maximum fluctuation on the A and B planes, two quite different sets of planes. The large magnitudes of $E(\mathbf{k})$ and $E(\mathbf{h} - \mathbf{k})$ could be due to high atom density on the A planes, or the B planes or both. We would expect (8) to hold in the first case, (11) in the second, and both (8) and (11) in the third. Since we do not know whether the A planes or the B planes are the more atom dense, we do not know whether (8) or (11) is the more likely to be valid. This ambiguity is further discussed below.

III. The triplet formula for planar structures

In this section we obtain the exact relation between $\varphi(\mathbf{k})$, $\varphi(\mathbf{h} - \mathbf{k})$ and $\varphi(\mathbf{h})$ for some simple planar structures.
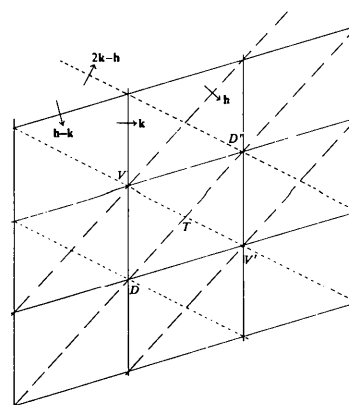

Fig. 1. The crests of the $\mathbf{h}$, $\mathbf{k}$, $(\mathbf{h} - \mathbf{k})$ and $(2\mathbf{k} - \mathbf{h})$ Fourier components are shown. These plane wavefronts are all perpendicular to the plane of the paper. The $\mathbf{h}$ and $(2\mathbf{k} - \mathbf{h})$ waves are positioned so that (8) and (11) are valid respectively.

Let us recall that the A and B planes were defined by the positions of peaks in the Fourier synthesis; we then hypothesized that these peaks indicated the presence of atoms. We now postulate a structure in which all atoms lie on planes (C planes) perpendicular to $\mathbf{h}$ with an interplanar spacing $1/|\mathbf{h}|$. From this definition the C planes are parallel to the A planes but not necessarily coincident with them. The position vectors $\mathbf{r}_j$ of the n atoms in the unit cell can be written

$$\mathbf{r}_j = \mathbf{R}_j + \mathbf{t} + m_j \mathbf{u} \quad (n \geq j \geq 1) \ (m_j \text{ an integer}) \quad (12)$$

where $\mathbf{t}$ and $\mathbf{u}$ are parallel to $\mathbf{h}$ and $|\mathbf{u}| = 1/|\mathbf{h}|$. Here $\mathbf{t}$ is a vector from the cell origin to the nearest C plane; $(\mathbf{t} + m_j \mathbf{u})$ is a vector to the C plane carrying the jth atom and $\mathbf{R}_j$ is a vector lying in this C plane.

Hence

$$\left. \begin{array}{c} \mathbf{h} \cdot \mathbf{R}_j \equiv 0 \quad (n \geq j \geq 1) \\[4pt] \mathbf{u} \cdot \mathbf{h} = 1. \end{array} \right\} \quad (13)$$

and

We write the quasi-normalized structure factors (Karle & Hauptman, 1959) as

$$E(\mathbf{k}) = \sigma_2^{-1/2} \sum_{j=1}^{n} Z_j \exp(2\pi i \mathbf{k} \cdot \mathbf{r}_j) \quad (14)$$

where $\sigma_2 = \sum_{j=1}^{n} Z_j^2$ and Z_j is the atomic number of the jth atom. We obtain, from (13),

$$E(\mathbf{k}) = \sigma_2^{-1/2} \sum_{j=1}^{n} Z_j \exp[2\pi i \mathbf{k} \cdot (\mathbf{R}_j + \mathbf{t} + m_j \mathbf{u})] \quad (15)$$

$$E(\mathbf{h} - \mathbf{k}) = \sigma_2^{-1/2} \exp(2\pi i \mathbf{h} \cdot \mathbf{t}) \sum_{j=1}^{n} Z_j$$
$$\times \exp[-2\pi i \mathbf{k} \cdot (\mathbf{R}_j + \mathbf{t} + m_j \mathbf{u})] \quad (16)$$

$$E(\mathbf{h}) = \sigma_2^{-1/2} \exp(2\pi i \mathbf{h} \cdot \mathbf{t}) \sum_{j=1}^{n} Z_j. \quad (17)$$

Thus $E(\mathbf{k}) E(\mathbf{h} - \mathbf{k}) = \alpha E(\mathbf{h})$ where α is a real number, and so

$$\varphi(\mathbf{k}) + \varphi(\mathbf{h} - \mathbf{k}) = \varphi(\mathbf{h}). \quad (18)$$

In this case (18) holds exactly, irrespective of the actual positions of atoms on the C planes, even if $E(\mathbf{k})$ and $E(\mathbf{h} - \mathbf{k})$ have small magnitudes (*postulate* I). It is easily shown that (18) is also exact if all atoms lie on planes perpendicular to $\mathbf{p}$ with a separation $1/|\mathbf{p}|$ for $\mathbf{p} = \mathbf{k}$ or $\mathbf{p} = (\mathbf{h} - \mathbf{k})$.

From (15)–(17) we note that, when all atoms lie on C planes,

$$|E(\mathbf{k})| = |E(\mathbf{h} - \mathbf{k})| \leq |E(\mathbf{h})| = E(000). \quad (19)$$

In this example we have assumed that all atoms lie in planes perpendicular to $\mathbf{h}$ with an interplanar spacing $1/|\mathbf{h}|$, yet the two-term Fourier synthesis of $E(\mathbf{k})$ and $E(\mathbf{h} - \mathbf{k})$ shows equal (maximum) amplitudes of oscillation on the two families of planes defined by (4)

and (5). The oscillations on the B planes defined by (5) are artefacts due to the small number of terms in the Fourier synthesis. Thus an ambiguity is introduced. Considering only the two-term E map, one might be tempted to assume that one could determine $\varphi(\mathbf{h})$ and $\varphi(2\mathbf{k} - \mathbf{h})$ with equal certainty, from (18) and (11) respectively. However, although (18) is exact for this example, (11) is not. We will verify this by means of a two-atom model structure.

IV.1. The two-atom structure

The model consists of two atoms lying in a C plane, a simple example of the planar structure discussed in § III. By varying the separation of the atoms we can determine the values of the sums

$$\varphi(-\mathbf{h}) + \varphi(\mathbf{k}) + \varphi(\mathbf{h} - \mathbf{k}) \quad (20)$$

and

$$\varphi(2\mathbf{k} - \mathbf{h}) + \varphi(-\mathbf{k}) + \varphi(\mathbf{h} - \mathbf{k}) \quad (21)$$

for all directions of $\mathbf{k}$ and all magnitudes of $\mathbf{h}$ and $\mathbf{k}$. Hence we can investigate the validity of (8) and (11) for all configurations of the two-atom structure.

The two moveable point atoms H, H' are positioned on the line GG' which lies in a C plane. $\vec{GG}'$ is not perpendicular to $\mathbf{k}$; otherwise the direction of $\vec{GG}'$ in the C plane is arbitrary. For a given $\mathbf{k}$, $|\vec{GG}'|$ is chosen such that

$$\mathbf{k} \cdot \vec{GG}' = 1.$$

H and H' are constrained to be equidistant from M, the midpoint of GG'. The Fourier transform of the structure relative to an origin at M is

$$T(\mathbf{k}) = \cos(2\pi \mathbf{k} \cdot \mathbf{M\vec{H}}) + \cos(2\pi \mathbf{k} \cdot \mathbf{M\vec{H}'}).$$

Since $\vec{GG}'$ is perpendicular to $\mathbf{h}$ we have

$$\left. \begin{array}{c} \mathbf{k} \cdot \vec{GG}' = -(\mathbf{h} - \mathbf{k}) \cdot \vec{GG}' = 1 \\[4pt] \mathbf{h} \cdot \vec{GG}' = 0. \end{array} \right\} \quad (22)$$

and

Using (22) we obtain

$$T(\mathbf{h} - \mathbf{k}) = 2 \cos(2\pi MH/GG') = T(\mathbf{k}) \quad (23)$$

$$T(\mathbf{h}) = 2 \quad (24)$$

$$T(2\mathbf{k} - \mathbf{h}) = 2 \cos(4\pi MH/GG'). \quad (25)$$

Hence

$$\varphi(\mathbf{k}) + \varphi(\mathbf{h} - \mathbf{k}) = 0 = \varphi(\mathbf{h}) \quad (\text{modulo } 2\pi) \quad (26)$$

for all values of MH. This is simply a restatement of (18), since the two atoms lie in a C plane.

From (23), (25) we have

$$\varphi(2\mathbf{k} - \mathbf{h}) + \varphi(-\mathbf{k}) + \varphi(\mathbf{h} - \mathbf{k})$$

$$= 0 \quad (0 < MH/GG' < \tfrac{1}{8} \text{ and } \tfrac{3}{8} < MH/GG' < \tfrac{1}{2})$$

$$= \pi \quad (\tfrac{1}{8} < MH/GG' < \tfrac{3}{8}). \quad (27)$$

Thus the triplet (21) is normal for only half the possible positions of H and H' on the line GG', whereas the triplet (20) is normal for all positions of H and H' on GG'. Fig. 2(a)–(d) shows the positions of the plane wavefronts in the four cases represented by (27). The plane wavefronts of the Fourier components of h, k and $(h - k)$ intersect in a line perpendicular to the plane of the paper in Fig. 2(a)–(d), whereas the $(2k - h)$, k, $(h - k)$ components have a common line of intersection only in Fig. 2(a)–(b). Hence Fig. 2(a)–(b) and (c)–(d) show respectively the normal and aberrant cases of the triplet (21). This result confirms that the two-term E map (3) is indeed ambiguous. If one had been guided only by this E map, one would have concluded that (8) and (11) were equally reliable.

IV.2. Acceptance criteria

Various criteria have been adopted to evaluate the reliability of a single phase-determining triplet (Karle &
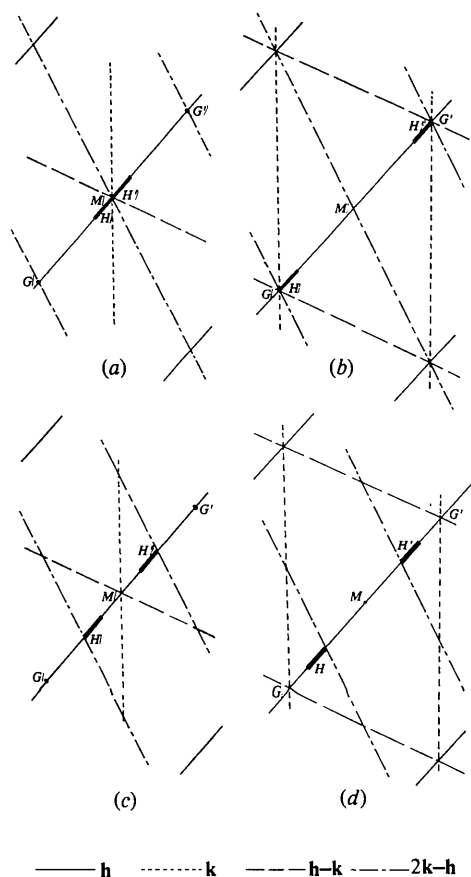
Karle, 1966). One criterion sets a lower limit on the $|E|$ values of each contributor, while another sets a lower limit on the product $|E(h)E(k)E(h - k)|$ for the contributors. Using the latter criterion, let us require that

$$|T(h)T(k)T(h - k)| > 1 \cdot 0 \qquad (28)$$

for (8) to be accepted, and

$$|T(2k - h)T(k)T(h - k)| > 1 \cdot 0 \qquad (29)$$

for (11) to be accepted. It is easily shown that, for $\frac{1}{8} < MH/GG' < \frac{3}{8}$, $|T(2k - h)T(k)T(h - k)| < 1 \cdot 0$. Hence with these criteria, no incorrect phase predictions will be made. $\varphi(h)$ is predicted for $0 \le MH/GG' \le 0 \cdot 192$, and $0 \cdot 308 \le MH/GG' \le 0 \cdot 5$, which represents 77% of the possible configurations of the two-atom system.

Additional criteria can be used to extend the range of MH/GG' over which phases are correctly predicted. Let us accept (8) if either (28) or (30) is satisfied, and accept (11) if either (29) or (31) is satisfied:

$$|T(2k - h)/T(h)| < 0 \cdot 95$$
$$and \quad |T(h)T(k)T(h - k)| > 0 \cdot 2 \qquad (30)$$

$$|T(h)/T(2k - h)| < 0 \cdot 95$$
$$and \quad |T(2k - h)T(k)T(h - k)| > 0 \cdot 2. \qquad (31)$$

Again no false phase predictions are made. Using the criteria (28)–(31), we can correctly predict $\varphi(h)$ for $0 \le MH/GG' \le 0 \cdot 225$ which represents 90% of the possible configurations of the two-atom model, a considerable improvement on the criteria (28)–(29). The range of MH/GG' over which $\varphi(2k - h)$ is predicted is unchanged since (31) is not satisfied.

Fig. 2. The crests of the h, k, $(h - k)$ and $(2k - h)$ Fourier components for the two-atom model. The atoms H, H' lie on the dense parts of the line GG'. MH/GG' is in the range (a) 0 to $\frac{1}{8}$ (b) $\frac{1}{8}$ to $\frac{1}{4}$ (c) $\frac{1}{8}$ to $\frac{1}{4}$ (d) $\frac{1}{4}$ to $\frac{3}{8}$. The triplet (20) is normal for (a)–(d) whereas (21) is normal for (a)–(b) and aberrant for (c)–(d).

IV.3. Physical significance of the ratio $|E(2k - h)/E(h)|$

Application of the criteria (30) and (31) to the two-atom model has shown that the ratio $|E(2k - h)/E(h)|$ is some guide to the validity of a single term [equation (8)] of the triplet formula. We now consider the physical significance of $|E(2k - h)/E(h)|$. In the two-atom model, both atoms lie in the same A plane. When the spacing of the atoms is such that each lies close to a B plane then $|\vec{HH'}.(2k - h)| \simeq 1$ and $|T(2k - h)/T(h)| \simeq 1$. When the separation of the two atoms is reduced so that $|\vec{HH'}.(2k - h)| \simeq \frac{1}{2}$ then the atom density of the B planes is a minimum and from (24), (25) we have $|T(2k - h)/T(h)| \simeq 0$. Hence the ratio $|T(2k - h)/T(h)|$ can be regarded as a measure of the relative atom densities of the B and A planes. In the extreme case where all atoms lie in A planes, postulate I states that (8) will be exact even if $|T(h)T(k)T(h - k)|$ is not large. Thus (30) is equivalent to the statement that provided $|T(h)T(k)T(h - k)|$ is not too small,

(20) is likely to be normal if the A planes are more atom dense than the B planes.

The planar model used in § II to obtain (18) requires only one set of atom-dense planes. To require that $|E(2k - h)/E(h)|$ be small for every permutation of the labels h, k, $(h - k)$ is to require three sets of atom-dense planes. Thus the relevant value of $|E(2k - h)/E(h)|$ to be tested in (30) is the smallest obtained by interchanging the labels h, k, $(h - k)$ among the three members of a given triplet.

V. Other model structures

Let us generalize from the two-atom structure to more realistic structures, with the following examples.

Case 1. Consider a structure in which atoms are fairly uniformly distributed over the C planes. $|E(k)|$, $|E(h - k)|$ and $|E(2k - h)|$ will be about unity [equation (14)] since the phases $(2\pi k . r_j)$ will be random. $|E(h)|$ will be large [equation (17)] since the C planes are atom dense. By postulate I, (18) is exact in this situation. If we consider only the separate magnitudes of $E(k)$, $E(h - k)$, $E(h)$ we would not expect (8) to give a reliable estimate of $\varphi(h)$. However, the small value of $|E(2k - h)/E(h)|$ suggests that the A planes are far more likely to be atom dense than the B planes, and so (8) is likely to be more reliable than one would expect from a consideration of $|E(k)|$, $|E(h - k)|$, $|E(h)|$ alone.

This reasoning can also be applied in reverse: a small value of $|E(2k - h)/E(h)|$ will reduce the probability that the triplet $\varphi(2k - h) + \varphi(h - k) + \varphi(-k)$ is normal even though, at first glance, $E(h)$ seems unconnected with this triplet. If a data set contains a few exceptionally large E values, the triplets whose probability is reduced by them should be identified.

Case 2. If the magnitudes of $E(h)$, $E(2k - h)$, $E(k)$, $E(h - k)$ are all large, then the A and B planes are probably both atom dense. Atoms could be concentrated around lines perpendicular to the paper through points D, D', V, V' (Fig. 1). (8) and (11) are likely to give reliable estimates of $\varphi(h)$ and $\varphi(2k - h)$ respectively.

Case 3. If atoms are concentrated about lines through D and T (Fig. 1) perpendicular to the plane of the paper then $|E(h)|$ and $|E(2k - h)|$ will be large (since the A and B planes are both atom dense). $|E(k)|$ and $|E(h - k)|$ will be small since the contributions from the atoms at D destructively interfere with those from T. The two-atom model illustrates this case when $MH/GG' \simeq 0.25$ and the very small values of $|T(h)T(k)T(h - k)|$ and $|T(2k - h)T(k)T(h - k)|$ show that it is unlikely that (20) and (21) will both be normal. Criteria analogous to (30) and (31) can be used to decide whether either (20) or (21) is likely to be normal. However, $|E(2k)|$ and $|E(2k - 2h)|$ will both

be large as the $2k$ and $(2k - 2h)$ planes are atom dense, and so the triplets

$$\varphi(h) + \varphi(2k - h) + \varphi(-2k)$$

$$\varphi(h) + \varphi(h - 2k) + \varphi(2k - 2h)$$

are both likely to be normal. These triplets could be used to determine $\varphi(h)$ and $\varphi(2k - h)$.

VI. Aberrant triples and the benzene transform

Let us consider the reliability of individual terms of the triplet formula when applied to the Fourier transform of a benzene ring. Actual cell dimensions are not important, so we can discuss reflections with non-integral indices.

Thiessen & Busing (1974) have pointed out that certain triplets of the benzene transform sum to π, and are therefore aberrant. They argued that in certain structures containing one or several six-membered rings certain triplets for the whole structure will be dominated by the corresponding triplets for the six-membered rings and so will be aberrant if the six-membered-ring triplet is aberrant.

In Fig. 3, the coordinates (relative to rectangular axes) of six point scatterers representing the C atoms of a benzene ring lying in the $z = 0$ plane are $(\pm 1,0)$, $(1/2,\pm\sqrt{3}/2)$, $(-1/2,\pm\sqrt{3}/2)$. The Fourier transform relative to an origin at $(0,0)$ is

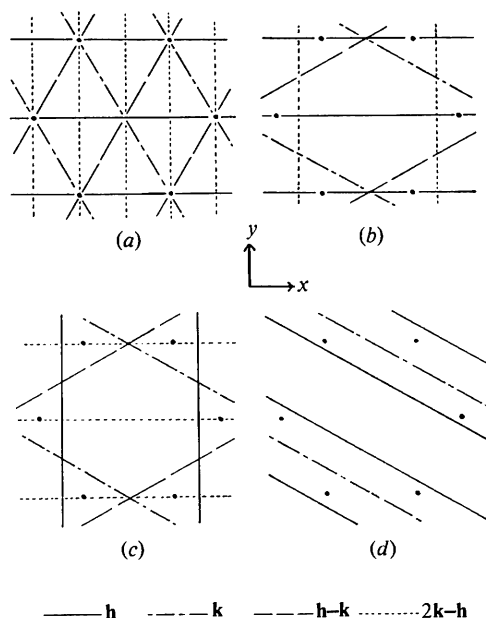Fig. 3. Six point C atoms of the benzene ring lie at $(\pm 1,0)$, $(\pm\frac{1}{2},\pm\sqrt{3}/2)$. (a) to (d) show the crests of the h, k, $(h - k)$ and $(2k - h)$ Fourier plane waves for triplets (36) to (39) respectively.

$$T(\mathbf{h}) = \sum_{j=1}^{n} \cos (2\pi \mathbf{h}.\mathbf{r}_j)$$

$$= 2 \cos (2\pi h_1) + 4 \cos (\pi h_1) \cos (\pi\sqrt{3}h_2) \quad (32)$$

where $\mathbf{h} = (h_1, h_2, h_3)$. Since the atoms lie in the $z = 0$ plane the value of the transform is independent of h_3.

Hence $T(\mathbf{h}) = T(h_1, h_2, h_3) = T(h_1, h_2, 0) \equiv T(h_1, h_2)$ where (h_1, h_2) indicates the two-dimensional vector $(h_1, h_2, 0)$. From (14) and (32) the E values are given by

$$E(\mathbf{h}) = T(\mathbf{h})/\sqrt{6}. \quad (33)$$

A section through the transform parallel to the $z = 0$ plane contains positive and negative extrema, with values of $+6$ and -3 respectively. Positive extrema exist at $\mathbf{h} = (0,0)$; $(0,\pm 2/\sqrt{3})$; $(1,\pm 1/\sqrt{3})$; $(-1,\pm 1/\sqrt{3})$ while negative extrema are found at $\mathbf{h} = (\pm 2/3, 0)$; $(1/3, \pm 1/\sqrt{3})$; $(-1/3, \pm 1/\sqrt{3})$. We initially consider triplets whose vectors $\mathbf{h}$, $\mathbf{k}$, $(\mathbf{h} - \mathbf{k})$ end in extrema of the transform and ask whether the value of $|E(2\mathbf{k} - \mathbf{h})/E(\mathbf{h})|$ will enable us to decide if a triplet $\mathbf{h}$, $\mathbf{k}$, $(\mathbf{h} - \mathbf{k})$ is normal or aberrant.

Before any triplet is accepted as normal it must be tested against a criterion which only accepts triplets with a high probability of normality. (34) is a common acceptance criterion (Karle & Karle, 1966); (35) is rather arbitrarily constructed to accept lower E values provided that the ratio $|E(2\mathbf{k} - \mathbf{h})/E(\mathbf{h})|$ is small for some permutation of the labels $\mathbf{h}$, $\mathbf{k}$, $(\mathbf{h} - \mathbf{k})$ among the members of the triplet.

$$|E(\mathbf{h})|, |E(\mathbf{k})|, |E(\mathbf{h} - \mathbf{k})| \geq 1\cdot 4 \quad (34)$$

$$|E(\mathbf{h})|, |E(\mathbf{k})|, |E(\mathbf{h} - \mathbf{k})| \geq 1\cdot 0$$

$$and \quad |E(2\mathbf{k} - \mathbf{h})/E(\mathbf{h})| \leq 1\cdot 0. \quad (35)$$

(35) is analogous to (30) used for the two-atom model. Both criteria are based on the hypothesis that $\varphi(-\mathbf{h}) + \varphi(\mathbf{k}) + \varphi(\mathbf{h} - \mathbf{k})$ is more likely to be normal if the $\mathbf{h}$ planes are more atom dense than the $(2\mathbf{k} - \mathbf{h})$ planes.
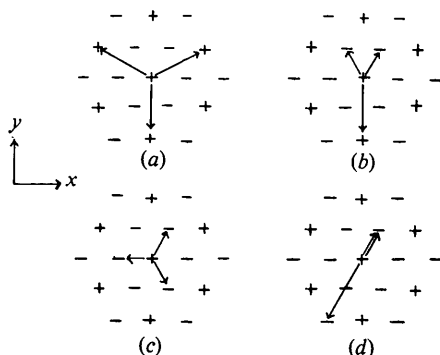

Fig. 4. Four triplets of vectors which sum to zero and which end in extrema of the benzene transform (Thiessen & Busing, 1974). (a)–(b) show normal triplets and (c)–(d) show aberrant ones. (a) to (d) correspond to triplets (36) to (39) respectively.

We apply the criteria (34) and (35) to the triplets (36) to (39) which correspond to Thiessen & Busing's (1974) examples of triplets of vectors which sum to zero. These triplets are illustrated in Fig. 4(a)–(d), together with the positions of extrema of the transform. In each of the triplets (36)–(39) the first, second and third terms represent $-\mathbf{h}$, $\mathbf{k}$ and $(\mathbf{h} - \mathbf{k})$ respectively.

$$\varphi(0,-2/\sqrt{3}) + \varphi(1,1/\sqrt{3}) + \varphi(-1,1/\sqrt{3}) \quad (36)$$

$$\varphi(0,-2/\sqrt{3}) + \varphi(1/3,1/\sqrt{3}) + \varphi(-1/3,1/\sqrt{3}) \quad (37)$$

$$\varphi(-2/3,0) + \varphi(1/3,1/\sqrt{3}) + \varphi(1/3,-1/\sqrt{3}) \quad (38)$$

$$\varphi(-2/3,-2/\sqrt{3}) + \varphi(1/3,1/\sqrt{3}) + \varphi(1/3,1/\sqrt{3}).(39)$$

The E values relating to (36) to (39) are given by (32) and (33).

$$|E(\pm 2/3, 0)| = |E(1/3, \pm 1/\sqrt{3})| = |E(-1/3, \pm 1/\sqrt{3})|$$

$$= |E(2/3, \pm 2/\sqrt{3})| = |E(-2/3, \pm 2/\sqrt{3})|$$

$$= \sqrt{6}/2$$

and

$$|E(0,0)| = |E(0, \pm 2/\sqrt{3})| = |E(1, \pm 1/\sqrt{3})|$$

$$= |E(-1, \pm 1/\sqrt{3})| = \sqrt{6}.$$

We now show in a pictorial manner, using Fig. 3, the relation between the ratio $|E(2\mathbf{k} - \mathbf{h})/E(\mathbf{h})|$ and the relative atom densities of the $(2\mathbf{k} - \mathbf{h})$ and $(\mathbf{h})$ planes.

The triplet (36) satisfies both (34) and (35). The ratio $|E(2\mathbf{k} - \mathbf{h})/E(\mathbf{h})|$ equals $1\cdot 0$ for all permutations of the labels $-\mathbf{h}$, $\mathbf{k}$, $(\mathbf{h} - \mathbf{k})$ among the members of (36). Hence we expect (36) to be normal. This triplet is an example of case 2, § V. Fig. 3(a) shows that the $\mathbf{h}$, $\mathbf{k}$, $(\mathbf{h} - \mathbf{k})$ and $(2\mathbf{k} - \mathbf{h})$ planes are all atom dense.

The triplet (37) does not satisfy (34) but does satisfy (35), since $|E(2\mathbf{k} - \mathbf{h})/E(\mathbf{h})|$ equals $1\cdot 0$ or $0\cdot 5$ depending on the permutation of the labels $-\mathbf{h}$, $\mathbf{k}$, $(\mathbf{h} - \mathbf{k})$ among the members of the triplet. Hence we expect (37) to be normal. This triplet is an example of case 1, § V. Putting $\mathbf{h} = (0, 2/\sqrt{3})$ and $\mathbf{k} = (1/3, 1/\sqrt{3})$, we see from Fig. 3(b) that the $\mathbf{h}$ planes are more atom dense than the $(2\mathbf{k} - \mathbf{h})$ planes.

The triplets (38) and (39) do not satisfy either (34) or (35). $|E(2\mathbf{k} - \mathbf{h})/E(\mathbf{h})|$ equals $2\cdot 0$ for all permutations of the labels $-\mathbf{h}$, $\mathbf{k}$, $(\mathbf{h} - \mathbf{k})$ among the members of (38) and (39). Hence we would expect that (38) and (39) are aberrant. Fig. 3(c) and (d) shows that the $(2\mathbf{k} - \mathbf{h})$ planes are more atom dense than the $\mathbf{h}$ planes for both of these triplets. For the triplet (39), $(2\mathbf{k} - \mathbf{h}) = (0,0)$.

From a knowledge of the magnitudes of the E values alone, we have predicted that the triplets (36)–(37) are normal, and (38)–(39) are aberrant. Fig. 4(a)–(d) shows that these predictions are correct and verify that the ratio $|E(2\mathbf{k} - \mathbf{h})/E(\mathbf{h})|$ can be a guide to the validity of (8). Fig. 3 illustrates the physical significance of $|E(2\mathbf{k} - \mathbf{h})/E(\mathbf{h})|$ in terms of the relative atom densities of the $(2\mathbf{k} - \mathbf{h})$ and $\mathbf{h}$ planes.

VII. Benzene ring as a planar structure

The benzene ring (Fig. 3) can be regarded as a planar structure in the sense that all atoms lie in $\mathbf{h}$ planes with an interplanar spacing $1/|\mathbf{h}|$ where $\mathbf{h} = (0,\pm 2/\sqrt{3})$ or $(1,\pm 1/\sqrt{3})$ or $(-1,\pm 1/\sqrt{3})$. Using postulate I, § III, we can say immediately that when $\mathbf{h}$ equals one of these vectors, then all triplets $\varphi(-\mathbf{h}) + \varphi(\mathbf{k}) + \varphi(\mathbf{h} - \mathbf{k})$ will be normal, irrespective of the magnitude of $E(\mathbf{k})$ or $E(\mathbf{h} - \mathbf{k})$. This result applies to any vector $\mathbf{h}$ which ends at a positive extremum of the benzene transform, even if $\mathbf{k}$ and $(\mathbf{h} - \mathbf{k})$ do not end in extrema.

VIII. Aberrancy and symmetry

Space-group symmetry can give rise to aberrancy in the same way as molecular symmetry. Consider a $P6$ structure with a unique atom at $(1/3,0,z)$. The six-fold axis generates a six-membered ring. The vectors $-\mathbf{h}$, $\mathbf{k}$, $(\mathbf{h} - \mathbf{k})$ which have the same relation to this six-membered ring as the vectors of the triplet (37) had to the benzene ring may be written, with hexagonal indexing,

$$(0,-3); \ (1,1); \ (-1,2).$$

Hence the triple analogous to (37) is

$$\varphi(0,-3,-h_3) + \varphi(1,1,k_3) + \varphi(-1,2,h_3 - k_3) \quad (40)$$

where h_3, k_3 are arbitrary since all atoms are in the $z = 0$ plane. The triplet (40) is normal, as it represents the same physical situation as (37). Similarly the triplet

$$\varphi(-2,1,-h_3) + \varphi(1,1,k_3) + \varphi(1,-2,h_3 - k_3) \quad (41)$$

with vectors defined relative to the $P6$ structure, is physically the same as the triplet (38). Thus (41) is aberrant. Depending on the actual position of atoms in the cell, a high proportion of triplets for a hexagonal structure could be aberrant.

In § III we showed that if a Fourier plane wave $\mathbf{h}$ can be positioned (by suitable choice of phase) so that all atoms of the structure lie on the peaks of the wave, then the triplet must be normal. Using (17), (19), we can make an equivalent statement: for a structure of identical atoms, any triplet containing a vector $\mathbf{h}$ such that

$$|E(\mathbf{h})| = E(000)$$

must be normal. We apply this criterion to two and three-fold axes.

Two two-fold rotation axes intersecting at right angles generate four atoms at the corners of a rectangle. For all extrema $\mathbf{h}$ of the transform, $|T(\mathbf{h})| = T(000) = 4$. Hence any triplet involving a vector ending at an extremum of the transform must be normal. This is also true for a single two-fold rotation axis (§ IV).

The transform of three atoms at the corners of an equilateral triangle contains two kinds of extrema, with magnitudes 3 and 1, the phases of the former being γ or $(\gamma + \pi)$ and of the latter γ or $(\gamma + \pi)$ or $(\gamma \pm \pi/2)$. γ depends on the choice of origin. For the larger extrema $|T(\mathbf{h})| = T(000)$ and so any triplets involving one of them will be normal. As for the benzene transform, some triplets involving only the smaller extrema are aberrant. However, the magnitudes of the smaller extrema are only $T(000)/3$ compared with $T(000)/2$ for the benzene transform, and so they are less likely to satisfy an acceptance criterion based on the magnitudes of the E values.

These results suggest that the members of aberrant triplets do not end in extrema of the transform unless three or six-fold symmetry is present.

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