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# The Calculation of Phases from the Patterson Function

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A formula expressing the values of the structure invariants in terms of the Patterson function has been derived. It has the advantage over previous phase determining formulas in that it appears to be insensitive to rational dependence and overlap in the Patterson function.

## 1. Introduction

The magnitudes of a sufficient number of structure factors determine the magnitudes of the structure seminvariants (Hauptman & Karle, 1953, 1956, 1959, 1961). Once the magnitudes of the structure seminvariants have been determined, the values of the individual phases may then be found by simple arithmetic manipulations. The program for these procedures has been described in the above references. Detailed procedures for the centrosymmetric space groups may be found in a recent series of papers (Karle & Hauptman, 1959, (referred to hereafter as 1P(1959)) ff.). The details for the non-centrosymmetric space groups will be published shortly.

The recent series of papers contain in addition explicit formulas (equations (3·1·2) and (3·2·2), 1P(1959)) for calculating the magnitudes of the seminvariants from the magnitudes of the structure factors. It is important to emphasize that although improved formulas for the seminvariants will be developed (e.g. equation (2·3·9) of this paper) the unified programs for going from the seminvariants to the individual phases, described in the recent series of papers (1P(1959), ff.), clearly retain their validity.

We have applied (3·1·2) and (3·2·2) of 1P(1959) to data which were available from the centrosymmetric crystals spurrite and N-benzyl-1,4-dihydronicotinamide. When only three-dimensional data were used (omitting one- and two-dimensional data) in applying these formulas to the spurrite data, excellent agreement was obtained. When the complete set of data was used, although the important signs were again correctly obtained, the quantitative agreement was poor. In the application to the N-benzyl-1,4-dihydronicotinamide, only the three-dimensional data were used. Again, the important signs were correctly obtained, but the quantitative agreement was only fair with some notable discrepancies (Karle, I., 1961). If the errors occurring in these applications are typical, (3·1·2) and (3·2·2) of 1P(1959) would be adequate for centrosymmetric structures. Clearly however, owing to the lack of quantitative agreement, attempts to use the analogous formulas in the non-centrosymmetric space groups would not, as a general rule, be likely to succeed. This is due to the fact that in the non-centrosymmetric space groups the phases may be anywhere between 0 and $2\pi$ while they must be 0 or $\pi$ in the centrosymmetric space groups.

The main reason for discrepancies lies in the fact that Patterson functions corresponding to actual crystal structures often contain many overlapping peaks. These give rise to correction terms which were not included in (3·1·2) and (3·2·2) of 1P(1959). It was therefore desirable to develop a formula from which the seminvariants could be found and which would automatically take into account the effects of the overlapping peaks in the Patterson function. It will be seen that the new formula which we shall call the vector-interaction formula, in contrast to (3·1·2) and (3·2·2) of 1P(1959), makes direct use of the Patterson function rather than the magnitudes of the structure factors. The existence of such an alternative formula is not unexpected since the Patterson function, being the Fourier transform of the magnitudes of the structure factors, contains the same information.

The new formula has additional advantages. Errors arising from limitations in both the number and accuracy of the observed data are reduced. In addition the one- and two-dimensional data may now be utilized, whereas previously their inclusion introduced errors.

## 2. Analysis for point atoms

### 2·1. *Notation*

We denote by $\mathbf{r}_j$ the position vector of the $j$th atom and by $Z_j$ the atomic number. The quasi-normalized structure factor $\mathscr{E}_\mathbf{h}$ is defined by means of

$$\mathscr{E}_\mathbf{h} = (1/\sigma_2^{1/2}) \sum_{j=1}^{N} Z_j \exp\left[2\pi i \mathbf{h}.\mathbf{r}_j\right], \qquad (2\cdot1\cdot1)$$

where

$$\sigma_n = \sum_{j=1}^{N} Z_j^n \qquad (2\cdot1\cdot2)$$

and $N$ is the number of atoms in the unit cell. It is evident from (2·1·1) that the phase $\varphi_\mathbf{h}$ of the quasi-normalized structure factor $\mathscr{E}_\mathbf{h}$ is the same as that of the crystal structure factor $F_\mathbf{h}$. Finally, we denote by $\mathbf{r}_{ij}$ the difference $\mathbf{r}_i - \mathbf{r}_j$, so that $\mathbf{r}_{ij} = -\mathbf{r}_{ji}$ and $\mathbf{r}_{ij} + \mathbf{r}_{jk} = \mathbf{r}_{ik}$.

Since (2·1·1) is the basis of our analysis, and no use is made of the crystal symmetry, it is clear that the final formula (2·3·9) is valid for every space group.

2·2. *Some preliminary results*

From (2·1·1) we find

$$|\mathscr{E}_{\mathbf{h}}| \cos \varphi_{\mathbf{h}} = (1/\sigma_2^{1/2}) \sum_{j=1}^{N} Z_j \cos 2\pi \mathbf{h}.\mathbf{r}_j\,, \quad (2\cdot2\cdot1)$$

$$|\mathscr{E}_{\mathbf{h}}| \sin \varphi_{\mathbf{h}} = (1/\sigma_2^{1/2}) \sum_{j=1}^{N} Z_j \sin 2\pi \mathbf{h}.\mathbf{r}_j\,, \quad (2\cdot2\cdot2)$$

and

$$|\mathscr{E}_{\mathbf{h}}|^2 = (1/\sigma_2) \sum_{j=1}^{N} Z_j^2 + (1/\sigma_2) \sum_{\substack{i,j=1 \\ i\neq j}}^{N} Z_i Z_j \exp[2\pi i \mathbf{h}.(\mathbf{r}_i - \mathbf{r}_j)], \quad (2\cdot2\cdot3)$$

or

$$|\mathscr{E}_{\mathbf{h}}|^2 - 1 = (2/\sigma_2) \sum_{\substack{i,j=1 \\ i<j}}^{N} Z_i Z_j \cos 2\pi \mathbf{h}.\mathbf{r}_{ij}\,. \quad (2\cdot2\cdot4)$$

Equation (2·2·4) yields

$$(|\mathscr{E}_{\mathbf{h}}|^2 - 1) \cos 2\pi \mathbf{h}.\mathbf{r} = (2/\sigma_2) \sum_{\substack{i,j=1 \\ i<j}}^{N} Z_i Z_j \cos 2\pi \mathbf{h}.\mathbf{r}_{ij} \cos 2\pi \mathbf{h}.\mathbf{r}\,, \quad (2\cdot2\cdot5)$$

or

$$\left.\begin{aligned} P(\mathbf{r}) &= \langle (|\mathscr{E}_{\mathbf{h}}|^2 - 1) \cos 2\pi \mathbf{h}.\mathbf{r} \rangle_{\mathbf{h}} \\ &= (Z_i Z_j/\sigma_2) \text{ if } \mathbf{r} = \pm \mathbf{r}_{ij} \\ &= \quad 0 \quad \text{ if } \mathbf{r} \neq \pm \mathbf{r}_{ij} \end{aligned}\right\}, \quad (2\cdot2\cdot6)$$

which is evidently the Patterson function. We assume that $P(\mathbf{r})$ is available, and the main formula will be seen to express the values of seminvariants in terms of $P(\mathbf{r})$.

From (2·2·4) we also obtain, since the value of $|\mathscr{E}_{\mathbf{h}}|^2 - 1$ is relatively insensitive to the substitution $Z \to Z^{3/2}$ (whence $\sigma_2 \to \sigma_3$) and since

$$(Z_i + Z_j)/2 \approx (Z_i Z_j)^{1/2},$$

the following approximate relationship:

$$(1/\sigma_3) \sum_{\substack{i,j=1 \\ i<j}}^{N} Z_i Z_j (Z_i + Z_j) \cos 2\pi \mathbf{h}.\mathbf{r}_{ij} \approx 2/\sigma_3 \sum_{\substack{i,j=1 \\ i<j}}^{N} (Z_i Z_j)^{3/2} \cos 2\pi \mathbf{h}.\mathbf{r}_{ij} \approx |\mathscr{E}_{\mathbf{h}}|^2 - 1\,; \quad (2\cdot2\cdot7)$$

and observe that (2·2·7) has exact validity if the structure consists of identical atoms. We note also that, since (2·2·7) will be used only in the derivation of the small correction term in the main formula (2·3·9), inaccuracies in (2·2·7) lead to negligible errors in the final result.

2·3. *The vector-interaction formula*

We assume throughout that

$$\mathbf{h}_1 + \mathbf{h}_2 + \mathbf{h}_3 = 0\,, \quad (2\cdot3\cdot1)$$

and introduce the abbreviations

$$\mathscr{E}_i = \mathscr{E}_{\mathbf{h}_i}, \quad i = 1, 2, 3; \quad (2\cdot3\cdot2)$$

$$\varphi_i = \varphi_{\mathbf{h}_i}, \quad i = 1, 2, 3. \quad (2\cdot3\cdot3)$$

Hence $\varphi_1 + \varphi_2 + \varphi_3$ is a structure invariant and it is natural to seek an expression for

$$|\mathscr{E}_1 \mathscr{E}_2 \mathscr{E}_3| \cos (\varphi_1 + \varphi_2 + \varphi_3)$$

in terms of the Patterson function $P(\mathbf{r})$.

Equations (2·2·1) and (2·2·2), together with the trigonometric identity

$$\begin{aligned} \cos (\varphi_1 + \varphi_2 + \varphi_3) = &\cos \varphi_1 \cos \varphi_2 \cos \varphi_3 \\ &- \cos \varphi_1 \sin \varphi_2 \sin \varphi_3 \\ &- \sin \varphi_1 \cos \varphi_2 \sin \varphi_3 \\ &- \sin \varphi_1 \sin \varphi_2 \cos \varphi_3\,, \end{aligned} \quad (2\cdot3\cdot4)$$

imply

$$|\mathscr{E}_1 \mathscr{E}_2 \mathscr{E}_3| \cos (\varphi_1 + \varphi_2 + \varphi_3) = (1/\sigma_2^{3/2}) \sum_{i,j,k=1}^{N} Z_i Z_j Z_k \cos 2\pi (\mathbf{h}_1.\mathbf{r}_i + \mathbf{h}_2.\mathbf{r}_j + \mathbf{h}_3.\mathbf{r}_k) \quad (2\cdot3\cdot5)$$

$$\begin{aligned} = (1/\sigma_2^{3/2}) &\sum_{i=1}^{N} Z_i^3 + (1/\sigma_2^{3/2}) \sum_{\substack{i,j=1 \\ i<j}}^{N} Z_i Z_j (Z_i + Z_j) (\cos 2\pi \mathbf{h}_1.\mathbf{r}_{ij} \\ &+ \cos 2\pi \mathbf{h}_2.\mathbf{r}_{ij} + \cos 2\pi \mathbf{h}_3.\mathbf{r}_{ij}) \\ &+ (1/\sigma_2^{3/2}) \sum_{\substack{i,j,k=1 \\ i\neq j\neq k}}^{N} Z_i Z_j Z_k \cos 2\pi (\mathbf{h}_1.\mathbf{r}_{ik} + \mathbf{h}_2.\mathbf{r}_{jk})\,. \end{aligned} \quad (2\cdot3\cdot6)$$

Making use of (2·1·2) and (2·2·7), we find, since $\mathbf{r}_{ij} = -\mathbf{r}_{ji}$,

$$\begin{aligned} &|\mathscr{E}_1 \mathscr{E}_2 \mathscr{E}_3| \cos (\varphi_1 + \varphi_2 + \varphi_3) \\ &\quad \approx (\sigma_3/\sigma_2^{3/2}) + (\sigma_3/\sigma_2^{3/2}) (|\mathscr{E}_1|^2 + |\mathscr{E}_2|^2 + |\mathscr{E}_3|^2 - 3) \\ &\quad + (1/\sigma_2^{3/2}) \sum_{\substack{i,j,k=1 \\ i\neq j\neq k}}^{N} Z_i Z_j Z_k \cos 2\pi (\mathbf{h}_1.\mathbf{r}_{ij} - \mathbf{h}_2.\mathbf{r}_{jk}) \end{aligned} \quad (2\cdot3\cdot7)$$

or

$$\begin{aligned} &|\mathscr{E}_1 \mathscr{E}_2 \mathscr{E}_3| \cos (\varphi_1 + \varphi_2 + \varphi_3) \\ &\quad \approx (\sigma_3/\sigma_2^{3/2}) (|\mathscr{E}_1|^2 + |\mathscr{E}_2|^2 + |\mathscr{E}_3|^2 - 2) \\ &\quad + \sum_{\substack{i,j,k=1 \\ i<j<k}}^{N} \{(Z_i Z_j/\sigma_2).(Z_j Z_k/\sigma_2).(Z_i Z_k/\sigma_2)\}^{1/2} \\ &\quad \times \{\cos 2\pi (\mathbf{h}_1.\mathbf{r}_{ij} - \mathbf{h}_2.\mathbf{r}_{jk}) + \cos 2\pi (\mathbf{h}_2.\mathbf{r}_{ij} - \mathbf{h}_1.\mathbf{r}_{jk}) \\ &\quad + \cos 2\pi (\mathbf{h}_2.\mathbf{r}_{ij} - \mathbf{h}_3.\mathbf{r}_{jk}) + \cos 2\pi (\mathbf{h}_3.\mathbf{r}_{ij} - \mathbf{h}_2.\mathbf{r}_{jk}) \\ &\quad + \cos 2\pi (\mathbf{h}_3.\mathbf{r}_{ij} - \mathbf{h}_1.\mathbf{r}_{jk}) + \cos 2\pi (\mathbf{h}_1.\mathbf{r}_{ij} - \mathbf{h}_3.\mathbf{r}_{jk})\}\,. \end{aligned} \quad (2\cdot3\cdot8)$$

Finally, utilizing the Patterson function (2·2·6) and the relation $\mathbf{r}_{ij} + \mathbf{r}_{jk} = \mathbf{r}_{ik}$, we obtain, if there is no overlap of Patterson peaks, the main formula (the vector-interaction formula)

$$\begin{aligned} &|\mathscr{E}_1 \mathscr{E}_2 \mathscr{E}_3| \cos (\varphi_1 + \varphi_2 + \varphi_3) \\ &\quad \approx (\sigma_3/\sigma_2^{3/2}) (|\mathscr{E}_1|^2 + |\mathscr{E}_2|^2 + |\mathscr{E}_3|^2 - 2) \\ &\quad + (1/2) \sum_{\mathbf{r},\mathbf{r}'} \{P(\mathbf{r}) P(\mathbf{r}') P(\mathbf{r}+\mathbf{r}')\}^{1/2} \{\cos 2\pi (\mathbf{h}_1.\mathbf{r} - \mathbf{h}_2.\mathbf{r}') \\ &\quad + \cos 2\pi (\mathbf{h}_2.\mathbf{r} - \mathbf{h}_1.\mathbf{r}') \\ &\quad + \cos 2\pi (\mathbf{h}_2.\mathbf{r} - \mathbf{h}_3.\mathbf{r}') + \cos 2\pi (\mathbf{h}_3.\mathbf{r} - \mathbf{h}_2.\mathbf{r}') \\ &\quad + \cos 2\pi (\mathbf{h}_3.\mathbf{r} - \mathbf{h}_1.\mathbf{r}') + \cos 2\pi (\mathbf{h}_1.\mathbf{r} - \mathbf{h}_3.\mathbf{r}')\}\,, \end{aligned} \quad (2\cdot3\cdot9)$$

where naturally the summation in (2·3·9) is extended over all Patterson peaks $\mathbf{r}$, $\mathbf{r}'$ such that $\mathbf{r}+\mathbf{r}'$ is also a Patterson peak. For exactness, only those $\mathbf{r}$ and $\mathbf{r}'$

would be used which involve the identification $\mathbf{r}=\mathbf{r}_{ij}$, $\mathbf{r}'=\mathbf{r}_{jk}$, $\mathbf{r}+\mathbf{r}'=\mathbf{r}_{ik}$. The factor 1/2 occurs on the right side because, together with the pair $\mathbf{r}$, $\mathbf{r}'$, for which $\mathbf{r}+\mathbf{r}'$ is also a Patterson peak, the Patterson function contains peaks at $-\mathbf{r}$, $-\mathbf{r}'$, and $(-\mathbf{r})+(-\mathbf{r}')$ is also a Patterson peak. Clearly this factor would be suppressed if the summation (2·3·9) were extended over only those vectors $\mathbf{r}$ in the asymmetric half of the unit cell. We note finally that the term

$$(\sigma_3/\sigma_2^{3/2})(|\mathscr{E}_1|^2+|\mathscr{E}_2|^2+|\mathscr{E}_3|^2-2)$$

appearing in (2·3·9) is a correction term which becomes negligibly small for large $N$. It should be emphasized that the only approximation used in the derivation of (2·3·9) involves this correction term.

In the case that the Patterson function contains many overlapping peaks, but the structure consists essentially of $N$ identical atoms, it is easy to show that the only modification required in (2·3·9) is to replace

$$\{P(\mathbf{r})P(\mathbf{r}')P(\mathbf{r}+\mathbf{r}')\}^{1/2} \text{ by } \{m(\mathbf{r},\mathbf{r}')\}^{3/2},$$

where $m(\mathbf{r},\mathbf{r}')$ is the minimum of $P(\mathbf{r})$, $P(\mathbf{r}')$, $P(\mathbf{r}+\mathbf{r}')$. In this case therefore

$$\begin{aligned}|\mathscr{E}_1\mathscr{E}_2\mathscr{E}_3|\cos(\varphi_1+\varphi_2+\varphi_3)&\\ \approx(\sigma_3/\sigma_2^{3/2})(|\mathscr{E}_1|^2+|\mathscr{E}_2|^2+|\mathscr{E}_3|^2-2)&\\ +(1/2)\sum_{\mathbf{r},\mathbf{r}'}\{m(\mathbf{r},\mathbf{r}')\}^{3/2}\{\cos 2\pi(\mathbf{h}_1.\mathbf{r}-\mathbf{h}_2.\mathbf{r}')&\\ +\cos 2\pi(\mathbf{h}_2.\mathbf{r}-\mathbf{h}_1.\mathbf{r}')+\cos 2\pi(\mathbf{h}_2.\mathbf{r}-\mathbf{h}_3.\mathbf{r}')&\\ +\cos 2\pi(\mathbf{h}_3.\mathbf{r}-\mathbf{h}_2.\mathbf{r}')+\cos 2\pi(\mathbf{h}_3.\mathbf{r}-\mathbf{h}_1.\mathbf{r}')&\\ +\cos 2\pi(\mathbf{h}_1.\mathbf{r}-\mathbf{h}_3.\mathbf{r}')\}\,. &\qquad(2\cdot3\cdot10)\end{aligned}$$

The extent to which unequal atom structures having considerable overlap in the Patterson function may be treated by (2·3·9) in an exact fashion depends upon the extent to which the nature of the overlap in the Patterson peaks can be interpreted. If a detailed analysis of the Patterson has not been, or cannot be, made, certain simple modifications of (2·3·9) may be introduced which, in general, are expected to cause only minor errors in the computation. For example, a weighting for the six cosines of (2·3·9) intermediate between those used in (2·3·9) and (2·3·10), would be proportional to $\{P(\mathbf{r})P(\mathbf{r}')P(\mathbf{r}+\mathbf{r}')\}^{1/3}$ and give rise to

$$\begin{aligned}|\mathscr{E}_1\mathscr{E}_2\mathscr{E}_3|\cos(\varphi_1+\varphi_2+\varphi_3)&\\ \approx(\sigma_3/\sigma_2^{3/2})(|\mathscr{E}_1|^2+|\mathscr{E}_2|^2+|\mathscr{E}_3|^2-2)&\\ +C\sum_{\mathbf{r},\mathbf{r}'}\{P(\mathbf{r})P(\mathbf{r}')P(\mathbf{r}+\mathbf{r}')\}^{1/3}\{\cos 2\pi(\mathbf{h}_1.\mathbf{r}-\mathbf{h}_2.\mathbf{r}')&\\ +\cos 2\pi(\mathbf{h}_2.\mathbf{r}-\mathbf{h}_1.\mathbf{r}')+\cos 2\pi(\mathbf{h}_2.\mathbf{r}-\mathbf{h}_3.\mathbf{r}')&\\ +\cos 2\pi(\mathbf{h}_3.\mathbf{r}-\mathbf{h}_2.\mathbf{r}')+\cos 2\pi(\mathbf{h}_3.\mathbf{r}-\mathbf{h}_1.\mathbf{r}')&\\ +\cos 2\pi(\mathbf{h}_1.\mathbf{r}-\mathbf{h}_3.\mathbf{r}')\}\,, &\qquad(2\cdot3\cdot11)\end{aligned}$$

where $C$ is a proportionality constant determined from the calculations in a manner to be discussed later. An alternative weighting would be the mid-value of $P(\mathbf{r})$, $P(\mathbf{r}')$, $P(\mathbf{r}+\mathbf{r}')$.

### 3. Analysis for electron distributions

Although (2·3·9) was derived on the basis of a point atom structure, it has the additional feature that it may be applied to Patterson functions obtainable from experiment. This would require a minor modification, namely the introduction of a scaling factor which is a function of the scattering angle. It is the purpose of this section to justify these statements.

If we denote by $\varrho(\mathbf{r})$ the electron density distribution function, the structure factor $F_{\mathbf{h}}$ is defined by means of

$$F_{\mathbf{h}}=\int_V \varrho(\mathbf{r})\exp[2\pi i\mathbf{h}.\mathbf{r}]d\mathbf{r}\,. \qquad(3\cdot1)$$

Just as (2·1·1) implies (2·3·5) we now find from (3·1)

$$\begin{aligned}|F_1F_2F_3|\cos(\varphi_1+\varphi_2+\varphi_3)=\iiint\varrho(\mathbf{r})\varrho(\mathbf{r}')\varrho(\mathbf{r}'')&\\ \times\cos 2\pi(\mathbf{h}_1.\mathbf{r}+\mathbf{h}_2.\mathbf{r}'+\mathbf{h}_3.\mathbf{r}'')d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{r}'', &\qquad(3\cdot2)\end{aligned}$$

where $\mathbf{h}_1+\mathbf{h}_2+\mathbf{h}_3=0$.

If we introduce for $\varrho(\mathbf{r})$ the sum of Gaussian distributions

$$\varrho(\mathbf{r})=\sum_{j=1}^{N}A_j\exp[-B_j|\mathbf{r}-\mathbf{r}_j|^2]\,, \qquad(3\cdot3)$$

the integral in (3·2) may be evaluated, leading to

$$\begin{aligned}|F_1F_2F_3|\cos(\varphi_1+\varphi_2+\varphi_3)&\\ =C'\sum_{i,j,k=1}^{N}\frac{A_iA_jA_k}{(B_iB_jB_k)^{3/2}}\exp\left[-\pi^2\left(\frac{h_1^2}{B_i}+\frac{h_2^2}{B_j}+\frac{h_3^2}{B_k}\right)\right]&\\ \times\cos 2\pi(\mathbf{h}_1.\mathbf{r}_i+\mathbf{h}_2.\mathbf{r}_j+\mathbf{h}_3.\mathbf{r}_k)\,, &\qquad(3\cdot4)\end{aligned}$$

where $h=|\mathbf{h}|$ and $C'$ is a constant. Equation (3·4) is to be compared with (2·3·5) in which $Z_i$ is replaced by $(A_i/B_i^{3/2})\exp[-\pi^2h_1^2/B_i]$, etc. The same analysis which led to (2·3·8) now gives rise to

$$\begin{aligned}|F_1F_2F_3|\cos(\varphi_1+\varphi_2+\varphi_3)&\\ \approx(\sigma_3/\sigma_2^{3/2})S(s_1,s_2,s_3)(|\mathscr{E}_1|^2+|\mathscr{E}_2|^2+|\mathscr{E}_3|^2-2)&\\ +C''\sum_{i<j<k=1}^{N}\left\{\frac{A_iA_j}{(B_i+B_j)^{3/2}}\cdot\frac{A_jA_k}{(B_j+B_k)^{3/2}}\cdot\frac{A_iA_k}{(B_i+B_k)^{3/2}}\right\}^{1/2}&\\ \times\left(\frac{1}{B_i}+\frac{1}{B_j}\right)^{3/4}\left(\frac{1}{B_j}+\frac{1}{B_k}\right)^{3/4}\left(\frac{1}{B_i}+\frac{1}{B_k}\right)^{3/4}&\\ \times\exp\left[-\pi^2\left(\frac{h_1^2}{B_i}+\frac{h_2^2}{B_j}+\frac{h_3^2}{B_k}\right)\right]&\\ \times\{\cos 2\pi(\mathbf{h}_1.\mathbf{r}_{ij}-\mathbf{h}_2.\mathbf{r}_{jk})+\cos 2\pi(\mathbf{h}_2.\mathbf{r}_{ij}-\mathbf{h}_1.\mathbf{r}_{jk})&\\ +\cos 2\pi(\mathbf{h}_2.\mathbf{r}_{ij}-\mathbf{h}_3.\mathbf{r}_{jk})+\cos 2\pi(\mathbf{h}_3.\mathbf{r}_{ij}-\mathbf{h}_2.\mathbf{r}_{jk})&\\ +\cos 2\pi(\mathbf{h}_3.\mathbf{r}_{ij}-\mathbf{h}_1\mathbf{r}_{jk})+\cos 2\pi(\mathbf{h}_1.\mathbf{r}_{ij}-\mathbf{h}_3.\mathbf{r}_{jk})\}\,, &\qquad(3\cdot5)\end{aligned}$$

where $S(s_1,s_2,s_3)$ in the correction term is some function of $s_i=\sin\theta_i/2$, $i=1,2,3$. If $\varrho(\mathbf{r})$ is given by (3·3), the Patterson function,

$$P(\mathbf{r})=\int\varrho(\mathbf{r})\varrho(\mathbf{r}+\mathbf{r}')d\mathbf{r}', \qquad(3\cdot6)$$

reduces to

$$P(\mathbf{r})=\pi^{3/2}\sum_{i,j=1}^{N}\frac{A_iA_j}{(B_i+B_j)^{3/2}}\exp\left[-\frac{B_iB_j}{B_i+B_j}|\mathbf{r}-(\mathbf{r}_i-\mathbf{r}_j)|^2\right]. \qquad(3\cdot7)$$

Since the $A_iA_j/(B_i+B_j)^{3/2}$ are proportional to the peak heights in the Patterson function, we may replace these by $P(\mathbf{r})$ in (3·5), thus obtaining the analogue of (2·3·9),

$$\begin{aligned}&|\mathscr{E}_1\mathscr{E}_2\mathscr{E}_3|\cos(\varphi_1+\varphi_2+\varphi_3)\\&\quad\approx(\sigma_3/\sigma_2^{3/2})(|\mathscr{E}_1|^2+|\mathscr{E}_2|^2+|\mathscr{E}_3|^2-2)\\&\quad+D(s_1s_2s_3)\sum_{\mathbf{r},\mathbf{r}'}\{P(\mathbf{r})P(\mathbf{r}')P(\mathbf{r}+\mathbf{r}')\}^{1/2}\\&\quad\times\{\cos 2\pi(\mathbf{h}_1.\mathbf{r}-\mathbf{h}_2.\mathbf{r}')+\cos 2\pi(\mathbf{h}_2.\mathbf{r}-\mathbf{h}_1.\mathbf{r}')\\&\quad+\cos 2\pi(\mathbf{h}_2.\mathbf{r}-\mathbf{h}_3.\mathbf{r}')+\cos 2\pi(\mathbf{h}_3.\mathbf{r}-\mathbf{h}_2.\mathbf{r}')\\&\quad+\cos 2\pi(\mathbf{h}_3.\mathbf{r}-\mathbf{h}_1.\mathbf{r}')+\cos 2\pi(\mathbf{h}_1.\mathbf{r}-\mathbf{h}_3.\mathbf{r}')\}\,.\end{aligned}\tag{3·8}$$

The same result follows if other electron distributions are used, e.g. if

$$\varrho(\mathbf{r})=\sum_{j=1}^{N}A_j/(1+B_j|\mathbf{r}-\mathbf{r}_j|^2)\,.\tag{3·9}$$

In short the same result holds for all electron distributions approximating a discrete atom structure.

It is clear that the sum in (3·8) is to be taken over all Patterson peaks $\mathbf{r}$, $\mathbf{r}'$. In application it is assumed that the function $D$ of the three variables $s_1$, $s_2$, $s_3$ is, to a good approximation, a function of $s_1.s_2.s_3$ alone. Hence $D(s_1s_2s_3)$ is found numerically by computing (3·8) for those invariants $\varphi_1+\varphi_2+\varphi_3$ which, as a consequence of the space group symmetry, are equal to 0 or $\pi$. In those instances the magnitudes of the left side of (3·8) would be known. Although this simple procedure would not be applicable in the space group $P1$, it is possible to treat this space group in a special way.

## 4. Numerical tests

At first two one-dimensional tests were carried out with structures having no symmetry. In one, identical atoms were placed at 0, 1/5, 1/4, 9/20. The true value of $|\mathscr{E}_1\mathscr{E}_4\mathscr{E}_5|\cos(\varphi_1+\varphi_4-\varphi_5)$ was 2·62; its value, as computed from (2·3·10), was 2·57. In the second example, identical atoms were placed at 0, 0·133, 0·289, 0·422, 0·639, 0·863. The expression

$$|\mathscr{E}_4\mathscr{E}_5\mathscr{E}_9|\cos(\varphi_4+\varphi_5-\varphi_9)\,,$$

with the true value 0·62, was computed to be 0·66 by (2·3·10). Since these examples were designed to exhibit the effect of rational dependence and overlap in the Patterson function, they afford preliminary indications of the fact that (2·3·10) is relatively insensitive to these effects.

A three-dimensional test in the space group $P2_12_12_1$ involved the placing of ten atoms, four carbon, two nitrogen, and four oxygen atoms in the asymmetric unit of the unit cell. The arrangement of the atoms was chosen to simulate a true structure and involved a considerable amount of overlap in the Patterson function. Interatomic vectors were computed to the nearest 1/30 in the $x$-direction and the nearest 1/60 in the $y$- and $z$-directions. Equation (2·3·10) then yielded the values of the eighteen expressions

$$|\mathscr{E}_\mathbf{h}\mathscr{E}_\mathbf{k}\mathscr{E}_{\mathbf{h}+\mathbf{k}}|\cos(\varphi_\mathbf{h}+\varphi_\mathbf{k}-\varphi_{\mathbf{h}+\mathbf{k}})$$

involving the invariants $\varphi_\mathbf{h}+\varphi_\mathbf{k}-\varphi_{\mathbf{h}+\mathbf{k}}$ listed in column 1 of Table 1. The true values of these expressions are shown in column 2.

Table 1. *Comparison of values of* $|\mathscr{E}_\mathbf{h}\mathscr{E}_\mathbf{k}\mathscr{E}_{\mathbf{h}+\mathbf{k}}|\cos(\varphi_\mathbf{h}+\varphi_\mathbf{k}-\varphi_{\mathbf{h}+\mathbf{k}})$ *with those computed from* (2·3·10) *for an artificial* 10 *atom structure in space group* $P2_12_12_1$

| h | k | h+k | Computed values | True values |
|---|---|---|---|---|
| 3 6 0 | 3 $\bar{6}$ 0 | 6 0 0 | −3·51 | −7·23 |
| 3 0 4 | 3 0 $\bar{4}$ | 6 0 0 | 5·44 | 4·85 |
| 3 0 7 | 3 0 $\bar{7}$ | 6 0 0 | −7·21 | −7·15 |
| 3 0 8 | 3 0 $\bar{8}$ | 6 0 0 | 15·81 | 15·49 |
| 1 0 2 | 1 0 2 | 2 0 4 | 9·68 | 10·37 |
| 1 2 2 | 1 $\bar{2}$ 2 | 2 0 4 | 3·27 | 3·89 |
| 1 4 2 | 1 $\bar{4}$ 2 | 2 0 4 | 4·00 | 3·63 |
| 2 0 4 | $\bar{2}$ 0 4 | 0 0 8 | −4·02 | −9·75 |
| 3 0 4 | $\bar{3}$ 0 4 | 0 0 8 | 7·77 | 7·61 |
| 0 7 4 | 0 $\bar{7}$ 4 | 0 0 8 | 10·09 | 6·16 |
| 3 0 4 | 3 0 4 | 6 0 8 | 6·77 | 4·47 |
| 3 2 4 | 3 $\bar{2}$ 4 | 6 0 8 | 4·18 | 3·37 |
| 3 3 3 | $\bar{3}$ 3 3 | 0 6 6 | 3·98 | 3·19 |
| 2 4 3 | $\bar{2}$ 4 3 | 0 8 6 | −2·40 | −2·85 |
| 5 4 3 | $\bar{5}$ 4 3 | 0 8 6 | 3·43 | 4·04 |
| $\bar{6}$ 1 0 | 3 $\bar{7}$ 0 | $\bar{3}$ $\bar{6}$ 0 | 14·80 | 17·05 |
| 6 1 0 | 0 $\bar{1}$ 1 | 6 0 1 | 23·82 | 21·17 |
| $\bar{3}$ $\bar{7}$ 0 | 0 1 $\bar{1}$ | $\bar{3}$ $\bar{6}$ $\bar{1}$ | 15·83 | 13·76 |

The invariants of Table 1 are composed of phases associated with one-, two- and three-dimensional structure factors. In spite of considerable overlap in the Patterson function, the quantitative agreement shown in Table 1 is satisfactory. In particular, those

$$|\mathscr{E}_\mathbf{h}\mathscr{E}_\mathbf{k}\mathscr{E}_{\mathbf{h}+\mathbf{k}}|\cos(\varphi_\mathbf{h}+\varphi_\mathbf{k}-\varphi_{\mathbf{h}+\mathbf{k}})$$

having negative values are correctly computed. It is known from the probability theory that the value of $\cos(\varphi_\mathbf{h}+\varphi_\mathbf{k}-\varphi_{\mathbf{h}+\mathbf{k}})$ is generally positive if $|\mathscr{E}_\mathbf{h}\mathscr{E}_\mathbf{k}\mathscr{E}_{\mathbf{h}+\mathbf{k}}|$ is large. Clearly it is important to determine the invariants $\varphi_\mathbf{h}+\varphi_\mathbf{k}-\varphi_{\mathbf{h}+\mathbf{k}}$ for which $\cos(\varphi_\mathbf{h}+\varphi_\mathbf{k}-\varphi_{\mathbf{h}+\mathbf{k}})$ is negative.

It is apparent from the nature of the formulas described here that the accuracy with which phases may be determined depends upon the quality of the Patterson function. In a forthcoming paper a procedure for obtaining high quality Patterson maps will be described.

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