

where x_q is determined from equation (6) at $z_3 = -z_1$ and equals $x_{A2} + z_1 \tan \theta$; the value $\Delta_o = \Delta_o(T)$ is determined in equations (A.5) and (9).

In calculating the amplitudes of fields E_h^I and E_h^{II} we omitted the time dependence. If the phase difference arises when a phase object is put into the path of one of the beams, then fields E_h^I and E_h^{II} reach the point r_{A2} at different moments of time τ and $\Delta\tau$. In this case an additional phase difference $\Phi(\Delta\tau) = \omega\Delta\tau$ appears. Let us express ω through x_q , then:

$$\Phi(\Delta\tau) = \bar{\omega}\Delta\tau(1 + x_q \cos^3 \theta/z_3 \sin \theta), \quad (A.19)$$

where $\bar{\omega}$ is the mean value of the cyclic frequency of waves reaching the observation point within the variation range $|x_q| \lesssim \Delta_o$.

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Derivation of Three-Phase Invariants from the Patterson Function

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Abstract

The idea of Anzenhofer & Hoppe [*Phys. Verh.* (1962), **13**, 119] that all the Fourier coefficients of the function $\rho(\mathbf{r}) \cdot \rho(\mathbf{r} + \mathbf{u})$ are zero if the Patterson function is zero at vector point \mathbf{u} is first developed; it is shown that the three-phase cosine and sine invariants may be derived jointly by solving two sets of linear equations. A least-squares method exploiting the entire Patterson function is then presented; this may allow the three-phase cosine and sine invariants to be determined and/or refined. As expected, the low-valued Patterson regions contribute most to the least-squares procedure.

Introduction

Anzenhofer & Hoppe (1962) first pointed out that, if the Patterson function $P(\mathbf{u})$ of any structure is zero at some vector point \mathbf{u} , exact equations among structure factors may be derived. In fact, the shift-product function $\rho(\mathbf{r}) \cdot \rho(\mathbf{r} + \mathbf{u})$ must be zero for any \mathbf{r} ; consequently, all its Fourier components must vanish, thus producing a set of linear equations among products of structure factor pairs (Anzenhofer & Hoppe, 1962; Hoppe, 1962, 1963). More recently, Dideberg (1977) also discussed applications of the same idea. It is interesting to recall that Main & Woolfson (1962, 1963)

proposed a different method which also makes use of the zero points in the Patterson function (the 'M-function' method). Unlike Anzenhofer & Hoppe, they exploit the information that, if $P(\mathbf{u})$ is zero and the structure is centrosymmetric, no electron density can exist at $\pm\mathbf{u}/2$ from any inversion centre. As a consequence, they obtain exact linear equations among the structure factors.

In the first part of the present paper we develop Anzenhofer & Hoppe's idea showing that the three-phase cosine and sine invariants may be derived from two sets of linear equations obtained from the vector points with $P(\mathbf{u}) = 0$. In the second part, a general least-squares procedure exploiting the knowledge of the Patterson function at every vector point is discussed; this may allow the three-phase cosine and sine invariants to be determined and/or refined. Since no practical application of these methods has been carried out as yet, this is to be regarded as a preliminary theoretical investigation.

Linear equations among cosine and sine invariants

Let $P(\mathbf{u})$ be zero. This means that

$$\int_V \rho(\mathbf{r}) \cdot \rho(\mathbf{r} + \mathbf{u}) d^3 \mathbf{r} = 0. \quad (1)$$

Since $\rho(\mathbf{r})$ is everywhere either positive or zero, the same applies to the shift-product function

$$\rho^{(p)}(\mathbf{r}/\mathbf{u}) = \rho(\mathbf{r} - \frac{1}{2}\mathbf{u}) \cdot \rho(\mathbf{r} + \frac{1}{2}\mathbf{u}), \quad (2)$$

which is zero for every \mathbf{r} in view of equation (1). [A $-\frac{1}{2}\mathbf{u}$ origin shift has been applied to the ρ 's of equation (1) for symmetry reasons.] A vanishing function has vanishing Fourier components, so that, remembering

$$\rho(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{H}} F_{\mathbf{H}} \exp(2\pi i \mathbf{H} \cdot \mathbf{r}), \quad (3)$$

we may write

$$\begin{aligned} \mathcal{F}_{\mathbf{H}}(\mathbf{u}) &= \int_V \rho^{(p)}(\mathbf{r}/\mathbf{u}) \exp(-2\pi i \mathbf{H} \cdot \mathbf{r}) d^3 \mathbf{r} \\ &= \frac{1}{V^2} \int_V \left\{ \sum_{\mathbf{K}} \sum_{\mathbf{L}} F_{\mathbf{K}} F_{\mathbf{L}} \exp[2\pi i (\mathbf{K} + \mathbf{L} - \mathbf{H}) \cdot \mathbf{r}] \right. \\ &\quad \left. \times \exp[2\pi i (-\mathbf{K} + \mathbf{L}) \cdot \mathbf{u}/2] \right\} d^3 \mathbf{r} \\ &= \frac{1}{V} \sum_{\mathbf{K}} F_{\mathbf{K}} F_{\mathbf{H}-\mathbf{K}} \exp[2\pi i (\mathbf{H} - 2\mathbf{K}) \cdot \mathbf{u}/2] = 0. \quad (4) \end{aligned}$$

Adding together the pairs of terms with $(\mathbf{K} = \bar{\mathbf{K}}, \mathbf{K} = \mathbf{H} - \bar{\mathbf{K}})$ and remembering that there may be only one such term for $\mathbf{K} = \mathbf{H}/2$, the above equation reduces to

$$V \cdot \mathcal{F}_{\mathbf{H}}(\mathbf{u}) = \sum_{\mathbf{K}} [2 - \delta(\mathbf{H} - 2\mathbf{K})] F_{\mathbf{K}} F_{\mathbf{H}-\mathbf{K}} \times \cos[2\pi(\mathbf{H} - 2\mathbf{K}) \cdot \mathbf{u}/2] = 0, \quad (5)$$

where δ stands for the Kronecker delta, and the bar over the summation symbol means that the terms with $F_{\mathbf{K}} F_{\mathbf{H}-\mathbf{K}}$ and $F_{\mathbf{H}-\mathbf{K}} F_{\mathbf{K}}$ are taken once only.

Unlike Anzenhofer & Hoppe (1962), we do not deem it useful to start from a shift-product function of the type

$$\rho_1^{(p)}(\mathbf{r}/\mathbf{u}) = \rho(\mathbf{r}) \cdot [\rho(\mathbf{r} - \mathbf{u}) + \rho(\mathbf{r} + \mathbf{u})]. \quad (6)$$

The reason is that, as it is easy to show, the Fourier components of the above function are given by

$$\mathcal{F}_{\mathbf{H}}(\mathbf{u}) \cdot 2 \cos \pi \mathbf{H} \cdot \mathbf{u}, \quad (7)$$

and they may vanish when $\cos \pi \mathbf{H} \cdot \mathbf{u}$ is zero, independently of the value of $\mathcal{F}_{\mathbf{H}}(\mathbf{u})$, thus introducing spurious information.

It is now convenient to multiply equation (5) by $\exp(-i\varphi_{\mathbf{H}})$, with the substitution

$$F_{\mathbf{H}} = |F_{\mathbf{H}}| \exp(i\varphi_{\mathbf{H}}), \quad (8)$$

so that, after separating the real and the imaginary components equation (5) becomes

$$\sum_{\mathbf{K}} [2 - \delta(\mathbf{H} - 2\mathbf{K})] |F_{\mathbf{K}} F_{\mathbf{H}-\mathbf{K}}| \cos[2\pi(\mathbf{H} - 2\mathbf{K}) \cdot \mathbf{u}/2] \times \cos(-\varphi_{\mathbf{H}} + \varphi_{\mathbf{K}} + \varphi_{\mathbf{H}-\mathbf{K}}) = 0, \quad (9a)$$

$$\sum_{\mathbf{K}} [2 - \delta(\mathbf{H} - 2\mathbf{K})] |F_{\mathbf{K}} F_{\mathbf{H}-\mathbf{K}}| \cos[2\pi(\mathbf{H} - 2\mathbf{K}) \cdot \mathbf{u}/2] \times \sin(-\varphi_{\mathbf{H}} + \varphi_{\mathbf{K}} + \varphi_{\mathbf{H}-\mathbf{K}}) = 0, \quad (9b)$$

giving a set of linear equations in the three-phase cosine and sine invariants. It is easy to see that equation (9a) reduces to $V \cdot P(\mathbf{u}) = 0$ for $\mathbf{H} = 0$, as expected. It should be pointed out that at least the term with $\mathbf{K} = 0$ has a known value in equation (9a), *i.e.*

$$2|F_{\mathbf{H}} F_0| \cos(\pi \mathbf{H} \cdot \mathbf{u}),$$

which is different from zero in general. (Of course, only the case $|F_{\mathbf{H}}| \neq 0$ will be considered, since $\varphi_{\mathbf{H}}$ is undetermined otherwise.) Consequently, equation (9a) represents a linear inhomogeneous system where the cosine invariants represent the unknowns. The system given by equation (9b) is also linear although homogeneous; it has a different set of unknowns (the sine invariants), but it is important to remark that the matrix of the coefficients of the unknowns is the same as for system (9a).

It is apparent that the above result may be utilized in several ways. Leaving aside at present the question of how close to zero the Patterson function must be in order for the above equations to have practical

validity, let us analyse a possible application of equations (9).

For a given \mathbf{u} there are as many equations of either type (a) or (b) as there are observed reflections, say N . Unfortunately, the total number of three-phase invariants is of the order N^2 . However, let us suppose there are \mathcal{N} vectors within the unit cell for which $P(\mathbf{u}) = 0$, sufficiently distinct from one another for the corresponding equations to be not virtually identical. Further, let us assume that \mathcal{N} is equal to, or larger than, the number of (non-zero) three-phase invariants that a given reflection with a large $|F_{\mathbf{H}}|$ contributes to. Then for that particular \mathbf{H} it is possible to create at least as many different equations of either type (9) as there are Sayre triples with $|F_{\mathbf{K}}F_{\mathbf{H}-\mathbf{K}}| \neq 0$. Let us suppose that the number of these distinct triples is $\mathcal{N}' (\leq \mathcal{N}$ by assumption).

In the centric case, all the sine invariants must be zero and it is possible, at least in principle, to select \mathcal{N}' vector points with $P(\mathbf{u}) = 0$ so that the determinant of the coefficient matrix is (sufficiently) different from zero; under this assumption, the cosine invariants may be directly calculated with the usual methods of linear algebra. It is worth pointing out that the above-mentioned matrix may be written as a product of two matrices, one of which does not depend on the observed amplitudes. In fact, let us first write equations (9) in the following form

$$\mathbf{A}_{\mathbf{H}} \cdot \mathbf{c}_{\mathbf{H}} = \mathbf{p}_{\mathbf{H}}; \quad \mathbf{A}_{\mathbf{H}} \cdot \mathbf{s}_{\mathbf{H}} = \mathbf{0}, \quad (10)$$

where $\mathbf{A}_{\mathbf{H}}$ is a square matrix while $\mathbf{c}_{\mathbf{H}}$, $\mathbf{s}_{\mathbf{H}}$ and $\mathbf{p}_{\mathbf{H}}$ are column vectors, all of order \mathcal{N}' , with

$$A_{\mathbf{H}}(j, i) = [2 - \delta(\mathbf{H} - 2\mathbf{K}_i)] |F_{\mathbf{K}_i} F_{\mathbf{H}-\mathbf{K}_i}| \times \cos [2\pi(\mathbf{H} - 2\mathbf{K}_i) \cdot \mathbf{u}_j / 2], \quad (11a)$$

$$c_{\mathbf{H}}(j) = \cos(-\varphi_{\mathbf{H}} + \varphi_{\mathbf{K}_j} + \varphi_{\mathbf{H}-\mathbf{K}_j}), \quad (11b)$$

$$s_{\mathbf{H}}(j) = \sin(-\varphi_{\mathbf{H}} + \varphi_{\mathbf{K}_j} + \varphi_{\mathbf{H}-\mathbf{K}_j}), \quad (11c)$$

$$p_{\mathbf{H}}(j) = -2|F_{\mathbf{H}} F_0| \cos(\pi \mathbf{H} \cdot \mathbf{u}_j). \quad (11d)$$

It is easy to see that $\mathbf{A}_{\mathbf{H}}$ may be factorized as

$$\mathbf{A}_{\mathbf{H}} = \boldsymbol{\alpha}_{\mathbf{H}} \cdot \boldsymbol{\beta}_{\mathbf{H}}, \quad (12)$$

where

$$\alpha_{\mathbf{H}}(j, i) = \cos [2\pi(\mathbf{H} - 2\mathbf{K}_i) \cdot \mathbf{u}_j / 2], \quad (12')$$

$$\boldsymbol{\beta}_{\mathbf{H}} = \text{Diag} \{ [2 - \delta(\mathbf{H} - 2\mathbf{K}_i)] \cdot |F_{\mathbf{K}_i} F_{\mathbf{H}-\mathbf{K}_i}| \},$$

so that $\text{Det } \mathbf{A}_{\mathbf{H}} = \text{Det } \boldsymbol{\alpha}_{\mathbf{H}} \cdot \text{Det } \boldsymbol{\beta}_{\mathbf{H}}$, and the determinant of $\boldsymbol{\alpha}_{\mathbf{H}}$ does not depend on the amplitudes.

In the acentric case, the above procedure cannot be followed, rigorously speaking. In fact, the sine invariants are not zero, in general, and any selection of \mathcal{N}' vector points with $P(\mathbf{u}) = 0$ must imply $\text{Det } \mathbf{A}_{\mathbf{H}} = 0$ [see equations (10)], otherwise $\mathbf{s}_{\mathbf{H}} = \mathbf{0}$ is the only possible solution. Incidentally, from the above it turns

out that $\text{Det } \mathbf{A}_{\mathbf{H}} = 0$ means $\text{Det } \boldsymbol{\alpha}_{\mathbf{H}} = 0$, *i.e.* annihilation of the determinant only depends on the scalar products $(\mathbf{H} - 2\mathbf{K}_i) \cdot \mathbf{u}_j / 2$, while the observed amplitudes are unimportant.

This difficulty may be overcome if it is possible to select the \mathcal{N}' vector points in such a way that the rank of the $\mathbf{A}_{\mathbf{H}}$ is $\mathcal{N}' - 1$, *i.e.* if there is at least a coefficient matrix pertaining to $\mathcal{N}' - 1$ invariants whose determinant is (sufficiently) different from zero. In this case both systems can be solved in terms of one cosine and sine invariant and proper use of the identity $\cos^2 x + \sin^2 x = 1$ may lead to a full solution of the problem.

By changing \mathbf{H} to \mathbf{H}' , other systems of equations (9) may be obtained, and more cosine and sine invariants derived. Of course, in general any of them should be obtained at least three times, namely solving each of the systems corresponding to \mathbf{H} , \mathbf{K} and $\mathbf{H} - \mathbf{K}$. The agreement among the three values should represent an internal consistency check. The same consideration applies to any different choice of the zero-values Patterson vectors.

A general least-squares approach

We shall consider first the general properties of the shift-product function $\rho^{(p)}(\mathbf{r}/\mathbf{u})$ [see equation (2)] for any \mathbf{u} [*i.e.* $P(\mathbf{u}) \neq 0$ in general] under the following assumptions: (i) the electron density of the general q th atom of the real structure has the following Gaussian shape:

$$\rho_q(r) = \frac{1}{(2\pi\sigma^2)^{3/2}} Z_q \exp -\frac{r^2}{2\sigma^2};$$

$$\int \rho_q(r) dV = Z_q, \quad (13)$$

where r is the distance from the centre and σ is the same for all the atoms; (ii) there are many atoms in the unit cell; (iii) the electron numbers (*i.e.* Z_q) of the large majority of the atoms differ only slightly.

As a consequence, the electron density $\rho(x, y, z)$ of the real structure may be expressed as

$$\rho(x, y, z) = \sum_{q=1}^{n_o} (2\pi\sigma^2)^{-3/2} Z_q \exp \{ -[(x - x_q)^2 + (y - y_q)^2 + (z - z_q)^2] / 2\sigma^2 \}, \quad (14)$$

where (x, y, z) and (x_q, y_q, z_q) are the respective coordinates of the general point and of the general atomic centre, referred to orthogonal axes for simplicity, although with no loss of generality. Since the Gaussian distribution [equation (13)] does not rigorously vanish anywhere, strictly speaking the above sum must be extended to all the n_o atoms within the crystal. Con-

sequently, any shift-product function [see equation (2)] may be expressed as a sum of pairwise products of the Gaussian functions belonging to all the n_0^2 pairs of atoms of the crystal. Each product is of the type

$$\begin{aligned} & (2\pi\sigma^2)^{-3} Z_q Z_s \\ & \times \exp \left[-\frac{x^2 + y^2 + z^2}{2\sigma^2} - \frac{(x - \Delta)^2 + y^2 + z^2}{2\sigma^2} \right] \\ & = (2\pi\sigma^2)^{-3} Z_q Z_s \exp \left(-\frac{\Delta^2}{4\sigma^2} \right) \\ & \times \exp \left[-\frac{(x - \Delta/2)^2 + y^2 + z^2}{\sigma^2} \right], \quad (15) \end{aligned}$$

where (again for the sake of simplicity although with no loss of generality) one of the atoms is placed at the origin of the coordinates while the other is shifted by a distance Δ along the x axis. (Obviously enough, the distribution of the shifts between the atom pairs will depend both on the actual structure and on the Patterson vector \mathbf{u} from which the shift-product function is obtained.) The above expression shows that each pair of atoms gives rise to a pseudo-atom in the shift-product function (we shall denote it as a *product atom*) that is still spherically Gaussian and is centred exactly half-way between the two interacting atoms. Although the product atoms have different weights, they are all represented by the same Gaussian function having a square half-peak width equal to one-half that of the real atoms. Consequently, it is easy to show from equations (14) and (15) that the ideal scattering factor $\psi_k(\mathbf{H})$ of the k th product atoms depends on the reciprocal vector \mathbf{H} according to the following law:

$$\psi_k(\mathbf{H}) = \psi_k^0 \cdot (\bar{f}_H)^{1/2}, \quad (16)$$

where \bar{f}_H is the unitary scattering factor of the real atoms ($\bar{f}_0 = 1$). Although strictly speaking the overall number of product atoms is n_0^2 , it is possible to prove that each pair of atoms contained in the unit cell (including the self-pairs, *i.e.* one atom and itself) originates only eight distinct product atoms, if the unit-cell translation symmetry is taken into consideration. In fact, let \mathbf{r}_1 be the position vector of atom 1 in the real structure $\rho(\mathbf{r} - \mathbf{u}/2)$ and $\mathbf{r}_2 = \mathbf{r}_1 + \Delta$ the position vector of atom 2 in the shifted structure $\rho(\mathbf{r} + \mathbf{u}/2)$ [see equation (2)]. From equation (15) we know that a product atom will appear in $\rho^{(p)}(\mathbf{r}/\mathbf{u})$ at $\mathbf{r}_0 = (\mathbf{r}_1 + \mathbf{r}_2)/2 = \mathbf{r}_1 + \Delta/2$. But, since atom 2 also appears at $\mathbf{r}_2(n, m, p) = \mathbf{r}_2 + n\mathbf{a} + m\mathbf{b} + p\mathbf{c}$ (n, m, p any integral numbers, $\mathbf{a}, \mathbf{b}, \mathbf{c}$ unit-cell vectors), we shall also have product atoms at $\mathbf{r} = [\mathbf{r}_1 + \mathbf{r}_2(n, m, p)]/2 = \mathbf{r}_1 + \Delta/2 + (n\mathbf{a} + m\mathbf{b} + p\mathbf{c})/2$. It is not difficult to see that these vectors define only eight distinct positions in the unit cell, *i.e.* those obtained by \mathbf{r}_0 after a shift equal to

$\frac{1}{2} \times$ (translation vector) in all directions. Although the weights of the eight product atoms may be quite different and most will be vanishingly small, strictly speaking they can never be zero, in view of equation (15). Consequently, if there are N real atoms within the unit cell, we shall have $\nu = 8N^2$ product atoms in the shift-product structure. In view of equations (2) and (4), the sum of the scattering factors ψ_k^0 over the product atoms contained in the unit cell is given by $\mathcal{F}_0(\mathbf{u}) = P(\mathbf{u})$; consequently, it should be clear that the exact value of $P(\mathbf{u})$ is bound to be >0 . Therefore, the assumption that $P(\mathbf{u}) = 0$ for some vectors \mathbf{u} , made in the preceding section, must be necessarily considered as an approximation. Incidentally, since the modulus of any Fourier component \mathcal{F}_H of a positive function can never exceed the value of \mathcal{F}_0 , we may write for any \mathbf{u} (neglecting experimental errors)

$$|\mathcal{F}_H(\mathbf{u})|^2 = \mathcal{R}_H^2(\mathbf{u}) + \mathcal{I}_H^2(\mathbf{u}) \leq \mathcal{F}_0^2(\mathbf{u}) = P^2(\mathbf{u}), \quad (17)$$

where $\mathcal{R}_H(\mathbf{u})$ and $\mathcal{I}_H(\mathbf{u})$ are the real and imaginary components of $\mathcal{F}_H(\mathbf{u})$ [see equation (4)].

We shall now proceed to evaluate the statistical distribution of $\mathcal{R}_H(\mathbf{u})$ and $\mathcal{I}_H(\mathbf{u})$ in the general case. We shall consider all possible distributions of product atoms of given weights within the unit cell. At first, for the sake of simplicity, we shall confine our considerations to the space group $P1$. In view of the above, we may apply the usual statistical distribution of the structure factor components of many-atom structures (Wilson, 1949):

$$\begin{aligned} W[\mathcal{R}_H(\mathbf{u})] &= [2\pi \langle \mathcal{R}_H^2(\mathbf{u}) \rangle]^{-1/2} \\ & \times \exp \{ -\mathcal{R}_H^2(\mathbf{u}) / [2 \langle \mathcal{R}_H^2(\mathbf{u}) \rangle] \}, \quad (18) \end{aligned}$$

with an analogous expression for $W[\mathcal{I}_H(\mathbf{u})]$, where [see equation (16)]

$$\begin{aligned} \langle \mathcal{R}_H^2(\mathbf{u}) \rangle &= \langle \mathcal{I}_H^2(\mathbf{u}) \rangle = \frac{1}{2} \sum_{k=1}^{\nu} \psi_k^2(\mathbf{H}, \mathbf{u}) \\ &= \frac{\nu}{2} \langle \psi_k^2(\mathbf{u}) \rangle_k \cdot \bar{f}_H. \quad (19) \end{aligned}$$

In the above equations, the argument \mathbf{u} has been added to ψ_k in order to specify that the k th product atom corresponds to the product structure with a vector shift equal to \mathbf{u} . We shall now proceed to evaluate the last average in the above equations.

We will assume that $\psi_k^0(\mathbf{u})$ may have any value with the same *a priori* probability, under the constraint

$$\sum_{k=1}^{\nu} \psi_k^0(\mathbf{u}) = \nu \langle \psi_k^0(\mathbf{u}) \rangle_k = \bar{\mathcal{F}}_0(\mathbf{u}) = \bar{P}(\mathbf{u}), \quad (20)$$

where the bars over $\bar{\mathcal{F}}_0$ and \bar{P} stand for 'exact value

of², and the last equality may be easily verified upon inspection of equations (2) and (4). This assumption may appear arbitrary on first thought, because the largest weight of the product atoms is limited by the largest weight of the real atoms. However, it will be apparent in the following that the low-valued Patterson regions are by far the most important in the present context. In the corresponding shift-product structures light product atoms must predominate [in view of equation (20)], their weight distribution having essentially a random character, reminiscent of the kinetic energy distribution among the molecules of a gas. We may in fact reduce our problem to that of the kinetic energy in a perfect gas (microcanonical ensemble), provided we state the correspondence:

- $\nu \leftrightarrow$ total number of molecules;
- $\psi_k^o(\mathbf{u}) \leftrightarrow$ kinetic energy of the k th molecule for one degree of freedom;
- $\bar{P}(\mathbf{u}) \leftrightarrow$ total energy of the system for the same degree of freedom.

It is therefore immediately possible to write the probability distribution of the ψ_k^o 's as

$$W[\psi^o(\mathbf{u})] = \beta(\mathbf{u}) \exp[-\beta(\mathbf{u}) \cdot \psi^o(\mathbf{u})], \quad (21)$$

where $\beta(\mathbf{u})$ may be obtained from equations (20) as follows:

$$\begin{aligned} \nu \langle \psi_k^o(\mathbf{u}) \rangle_k &= \nu \int_0^{\infty} \psi^o(\mathbf{u}) \cdot W[\psi^o(\mathbf{u})] d\psi^o(\mathbf{u}) \\ &= \nu / \beta(\mathbf{u}) = \bar{P}(\mathbf{u}), \end{aligned} \quad (22)$$

whence

$$\beta(\mathbf{u}) = \nu / \bar{P}(\mathbf{u}). \quad (22')$$

Proceeding analogously to the above, it is now easy to solve equation (19), obtaining:

$$\begin{aligned} \langle \mathcal{R}_{\mathbf{H}}^2(\mathbf{u}) \rangle &= \langle \mathcal{F}_{\mathbf{H}}^2(\mathbf{u}) \rangle = \frac{\nu}{2} \langle \psi_k^{o2}(\mathbf{u}) \rangle_k \cdot \bar{f}_{\mathbf{H}} = \bar{f}_{\mathbf{H}} \nu / \beta^2(\mathbf{u}) \\ &= \bar{f}_{\mathbf{H}} \cdot \bar{P}^2(\mathbf{u}) / \nu. \end{aligned} \quad (23)$$

Although we do not know the exact value $\bar{P}^2(\mathbf{u})$, we may obtain its most probable value as follows:

$$\bar{P}^2(\mathbf{u}) \approx \langle \bar{P}^2(\mathbf{u}) \rangle = \langle [P(\mathbf{u}) + \Delta P(\mathbf{u})]^2 \rangle, \quad (24)$$

where ΔP is the random error of the Patterson function, and the average is to be performed over all possible random errors. Its formal evaluation will be obtained under the simplest approximation that $\bar{P}(\mathbf{u}) = P(\mathbf{u}) + \Delta P(\mathbf{u})$ may assume in principle any positive value with the same probability and that [for a given $\bar{P}(\mathbf{u})$] the observed value $P(\mathbf{u})$ is normally distributed around

$\bar{P}(\mathbf{u})$ with a variance σ_p^2 . In fact, in this case we must have [putting $\Delta P(\mathbf{u}) = \Delta$]:

$$\begin{aligned} \langle \bar{P}^2(\mathbf{u}) \rangle &= \int_{-P(\mathbf{u})}^{\infty} [P(\mathbf{u}) + \Delta]^2 \exp(-\Delta^2/2\sigma_p^2) d\Delta \\ &\times \left[\int_{-P(\mathbf{u})}^{\infty} \exp(-\Delta^2/2\sigma_p^2) d\Delta \right]^{-1}. \end{aligned} \quad (25)$$

Fig. 1 shows the plot of $y = \langle \bar{P}^2(\mathbf{u}) \rangle / \sigma_p^2$ vs $x = P(\mathbf{u}) / \sigma_p$; it can be seen that $y \simeq x^2 + 1$ if $x < 2.0$. The error variance σ_p^2 originates from several conceptually distinct sources, *i.e.* the random errors in the intensity measurements, the scaling error, the series truncation and the absorption/extinction effects. Owing to the large number of independent terms $|F_{\mathbf{H}}^2| \cos 2\pi \mathbf{H} \cdot \mathbf{u}$ contributing to $P(\mathbf{u})$ we may reasonably assume that σ_p^2 is independent of \mathbf{u} .

An important point should be noted in this connection. In principle, the inaccuracies affecting equation (18) not only involve $\langle \mathcal{R}_{\mathbf{H}}^2(\mathbf{u}) \rangle$ but $\mathcal{R}_{\mathbf{H}}^2(\mathbf{u})$ as well [$\mathcal{R}_{\mathbf{H}}(\mathbf{u})$ is the real part of $\mathcal{F}_{\mathbf{H}}(\mathbf{u})$, see equation (4)]. However, as will be apparent in the following, the smallest values of $\langle \mathcal{R}_{\mathbf{H}}^2(\mathbf{u}) \rangle$ [and therefore of $P(\mathbf{u})$, see equation (23)] are especially important in the present approach because they appear in the denominator, so that explicit consideration of their random error can by no means be avoided. Otherwise, the whole theory would break down if $P(\mathbf{u})$ happened to be zero or negative even at a single point of the unit cell.

We shall now stipulate a further assumption: *The product-atom distributions within the unit cell, belonging to two shift-product structures with different shifts \mathbf{u}_1 and \mathbf{u}_2 , may be regarded as statistically uncorrelated if $|\mathbf{u}_2 - \mathbf{u}_1|$ is sufficiently large.*

No doubt the above assumption is incorrect if the two shifts are very close and/or if $P(\mathbf{u}_1)$ and $P(\mathbf{u}_2)$ are large.

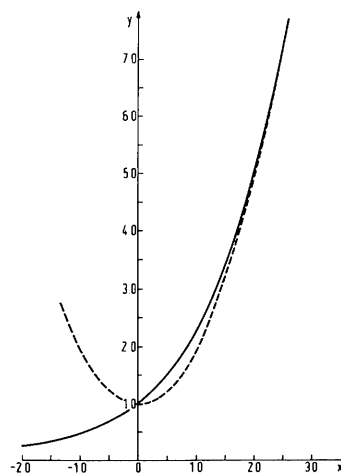


Fig. 1. Plot of $y = \langle \bar{P}^2(\mathbf{u}) \rangle / \sigma_p^2$ vs $x = P(\mathbf{u}) / \sigma_p$ [see equation (25)]. The function $y = x^2 + 1$ is also reported as a dashed line.

In fact, in the former case the two product structures are very similar, while in the latter they must bear some resemblance to the real structure. However, we believe the assumption to be essentially valid because the large Patterson values are virtually unimportant in the present context, as we shall see; as for the product structures with sufficiently different \mathbf{u} 's and small $P(\mathbf{u})$'s, they are certainly very poorly correlated. Let \mathbf{u}_q be any among the M Patterson vectors evenly distributed over the points of a regular lattice covering the unit cell ($q = 1, 2, \dots, M$), the smallest lattice interval being larger than some suitable value. We have from the above [cf. equations (18)–(25)]:

$$\begin{aligned} W[\mathcal{R}_H(\mathbf{u}_1), \mathcal{R}_H(\mathbf{u}_2) \dots \mathcal{R}_H(\mathbf{u}_M)] &= \prod_{q=1}^M W[\mathcal{R}_H(\mathbf{u}_q)] \\ &= (2\pi \tilde{f}_H/v)^{-M/2} \cdot \prod_{q=1}^M \langle \tilde{P}^2(\mathbf{u}_q) \rangle^{-1/2} \\ &\quad \times \exp\left(-\sum_{q=1}^M \left\{ \mathcal{R}_H^2(\mathbf{u}_q) / [2\tilde{f}_H/v \cdot \langle \tilde{P}^2(\mathbf{u}_q) \rangle] \right\}\right), \end{aligned} \quad (26)$$

with an analogous expression for the $\mathcal{I}_H(\mathbf{u}_q)$. If M is large enough the above probability distribution will be largest for the correct set of phases $\{\varphi_H\}$, bearing in mind that they determine the values of the $\mathcal{R}_H(\mathbf{u})$'s for given amplitudes. The largest probability is obtained when the exponent with reversed sign is lowest, *i.e.*

$$\sum_{q=1}^M \frac{\mathcal{R}_H^2(\mathbf{u}_q)}{\langle \tilde{P}^2(\mathbf{u}_q) \rangle} = \text{minimum}. \quad (27)$$

It is now easy to convert the above sum into an integral extended to the unit-cell volume, if one considers that the three-dimensional lattice of the Patterson points may be given any translation shift. For each lattice translation equation (27) must hold, and it is apparent that the best minimizing function is the sum of the left-hand sides over all possible translations, *i.e.*

$$\int_V \frac{\mathcal{R}_H^2(\mathbf{u})}{\langle \tilde{P}^2(\mathbf{u}) \rangle} d^3\mathbf{u} = \text{minimum}. \quad (27')$$

This result clearly shows that the real (or the imaginary) square components of $\mathcal{F}_H(\mathbf{u})$ [see equation (4)] have the largest weights in the minimizing function when $P(\mathbf{u})$ is closest to zero, as expected. However, it is remarkable that the *entire* Patterson function contributes to the result.

It is now important to point out that the above result is not strictly subject to the assumption leading to equation (21) (*i.e.* the gas-kinetic-energy analogue). In fact, it is easy to see that the much wider class of probability distributions of the form

$$W[\psi^0(\mathbf{u})] = \frac{1}{\tilde{P}(\mathbf{u})} \cdot f[\psi^0(\mathbf{u})/\tilde{P}(\mathbf{u})], \quad (28)$$

satisfying the normalizing conditions

$$\begin{aligned} \int_0^\infty f(x) dx &= 1; \quad \int_0^\infty x \cdot f(x) dx = v^{-1}; \\ \int_0^\infty x^2 f(x) dx &= \text{any finite value}, \end{aligned} \quad (29)$$

leads to equations (23), except for a factor independent of $\tilde{P}(\mathbf{u})$. Then equation (27) is still valid. The above assumption may be summarized as follows: *The relative probability density of having a product atom with weight $\psi^0(\mathbf{u})$ depends only on the ratio $\psi^0(\mathbf{u})/\tilde{P}(\mathbf{u})$.*

Furthermore, the result reported in equations (23) appears to be supported by a comparison with inequality (17). In fact, disregarding as a first approximation the difference between $P(\mathbf{u})$ and $\tilde{P}(\mathbf{u})$, we see that the upper limit for either $|\mathcal{R}_H(\mathbf{u})|$ or $|\mathcal{I}_H(\mathbf{u})|$ is proportional to its standard deviation, a result which is frequently encountered in comparing the inequality with the probability theory of direct methods (see, for example, Karle, 1972).

Let us now take a further step in our assumptions, stating that φ_H is essentially uncorrelated with the phase angle of $\mathcal{F}_H(\mathbf{u})$, the more so if $P(\mathbf{u})$ is small. Then we may conclude that probability distribution (26) also applies to the real and imaginary components of $\mathcal{F}_H \exp(-i\varphi_H)$ [say $\mathcal{R}'_H(\mathbf{u})$ and $\mathcal{I}'_H(\mathbf{u})$], given in the first members of equations (9). Then expression (27'), after substitution of $\mathcal{R}_H(\mathbf{u}_q)$ for $\mathcal{R}'_H(\mathbf{u}_q)$, is a quadratic form of the three-phase cosine invariants, which may be especially suitable for a minimization procedure (the same applies to the sine invariants). As an example, in the favourable event that all the non-zero three-phase invariants ($-\varphi_H + \varphi_K + \varphi_{H-K}$) with fixed \mathbf{H} are linearly independent, the corresponding cosines (or sines) may be regarded as independent variables. Let us define, from equation (27),

$$\Psi_H(c_{H_1}, c_{H_2}, \dots) = \int_V \frac{\mathcal{R}'_H(\mathbf{u})}{\langle \tilde{P}^2(\mathbf{u}) \rangle} d^3\mathbf{u} = \text{minimum}, \quad (30)$$

where [cf. equations (9a) and (11b)]

$$\begin{aligned} \mathcal{R}'_H(\mathbf{u}) &= \sum_i [2 - \delta(\mathbf{H} - 2\mathbf{K}_i)] |F_{\mathbf{K}_i} F_{\mathbf{H}-\mathbf{K}_i}| \\ &\quad \times \cos[2\pi(\mathbf{H} - 2\mathbf{K}_i) \cdot \mathbf{u}/2] \cdot c_{H_i}, \end{aligned} \quad (31)$$

and

$$c_{H_i} = \cos(-\varphi_H + \varphi_{\mathbf{K}_i} + \varphi_{\mathbf{H}-\mathbf{K}_i}).$$

If the c_{H_i} 's are all independent, we have from the above:

$$\frac{\partial \Psi_H}{\partial c_{H_i}} = 2 \int_V \frac{\partial \mathcal{R}'_H(\mathbf{u})}{\partial c_{H_i}} \cdot \frac{\mathcal{R}'_H(\mathbf{u})}{\langle \tilde{P}^2(\mathbf{u}) \rangle} d^3\mathbf{u} = 0, \quad (32)$$

giving an inhomogeneous set of linear equations with as many unknowns c_{H_j} , which in an explicit form reads:

$$\begin{aligned} & \sum_i [2 - \delta(\mathbf{H} - 2\mathbf{K}_i)] |F_{\mathbf{K}_i} F_{\mathbf{H}-\mathbf{K}_i}| \\ & \times \int_V \frac{\cos[2\pi(\mathbf{H} - \mathbf{K}_i - \mathbf{K}_j) \cdot \mathbf{u}] + \cos[2\pi(\mathbf{K}_i - \mathbf{K}_j) \cdot \mathbf{u}]}{\langle \bar{P}^2(\mathbf{u}) \rangle} \\ & \times d^3 \mathbf{u} c_{H_j} \\ & = -2 |F_0 F_H| \\ & \times \int_V \frac{\cos[2\pi(\mathbf{H} - \mathbf{K}_j) \cdot \mathbf{u}] + \cos(2\pi \mathbf{K}_j \cdot \mathbf{u})}{\langle \bar{P}^2(\mathbf{u}) \rangle} d^3 \mathbf{u}, \quad (33) \end{aligned}$$

after use of the identity $\cos \alpha \cos \beta = \frac{1}{2}[\cos(\alpha + \beta) + \cos(\alpha - \beta)]$.

It is interesting to analyse the structure of the above system in some detail. Let us first define

$$\Phi(\mathbf{u}) = \frac{1}{\langle \bar{P}^2(\mathbf{u}) \rangle}, \quad (34)$$

which is a positive function with the same symmetry as the Patterson function itself. The general Fourier component of $\Phi(\mathbf{u})$ may be defined as

$$Q_H = \int_V \Phi(\mathbf{u}) \cos(2\pi \mathbf{H} \cdot \mathbf{u}) d^3 \mathbf{u}, \quad (35)$$

while the corresponding component of $P(\mathbf{u})$ is $|F_H|^2$. Since $\Phi(\mathbf{u})$ is large when $P(\mathbf{u})$ is small, and *vice versa*, it is not difficult to see that Q_H is probably large and negative for large $|F_H|^2$. In fact, as may be seen from the above equation written in terms of $|F_H|^2$, $P(\mathbf{u})$ is larger on average when $\cos(2\pi \mathbf{H} \cdot \mathbf{u})$ is positive than when it is negative; the reverse applies to $\Phi(\mathbf{u})$, so that the probable value of Q_H is negative. [It should be clearly pointed out that this conclusion is only statistically valid; in fact, it may well happen that both the largest peaks and the deepest minima of $P(\mathbf{u})$ are contained in regions with $\cos(2\pi \mathbf{H} \cdot \mathbf{u})$ positive, with the consequence that Q_H is positive.] It is now convenient to write equation (33) in terms of Q_H , giving (for the j th equation)

$$\begin{aligned} & \sum_i [2 - \delta(\mathbf{H} - 2\mathbf{K}_i)] |F_{\mathbf{K}_i} F_{\mathbf{H}-\mathbf{K}_i}| (Q_{\mathbf{H}-\mathbf{K}_i-\mathbf{K}_i} \\ & + Q_{\mathbf{K}_i-\mathbf{K}_i}) c_{H_j} = -2 |F_0 F_H| (Q_{\mathbf{H}-\mathbf{K}_j} + Q_{\mathbf{K}_j}). \quad (36) \end{aligned}$$

Let us suppose that $|F_H|$, $|F_{\mathbf{K}_j}|$ and $|F_{\mathbf{H}-\mathbf{K}_j}|$ are all large, so that we have a 'strong' triple $|F_{-\mathbf{H}} F_{\mathbf{K}_j} F_{\mathbf{H}-\mathbf{K}_j}|$. In equation (36) any product of the type $|F_1 F_2| (Q + Q')$ may be large for either of the following reasons: (i) $|F_1 F_2|$ is large; (ii) either Q or Q' is large. Since F_0 is usually much larger than any other structure factor,

requirement (i) is best satisfied by the term on the right-hand side, which is probably positive for what is said above. As for requirement (ii), it is best satisfied by taking $\mathbf{K}_i = \mathbf{K}_j$ on the left-hand side, which produces the factor $(Q_{\mathbf{H}-2\mathbf{K}_j} + Q_0)$; in fact, we may reasonably assume Q_0 to be much larger than most Q_H 's. Since Q_0 does not appear in any other element, the equation is (probably) dominated by the term containing $c_{H_j} = \cos(\varphi_{-\mathbf{H}} + \varphi_{\mathbf{K}_j} + \varphi_{\mathbf{H}-\mathbf{K}_j})$ on the left-hand side, with a positive coefficient, and by the (probably positive) right-hand side itself. The conclusion that the cosine invariant is probably positive under the above hypotheses is immediate. It seems a promising feature of the present approach that this result, more accurately expressed as

$$\varphi_{-\mathbf{H}} + \varphi_{\mathbf{K}} + \varphi_{\mathbf{H}-\mathbf{K}} \approx 0, \quad \text{for } |F_{-\mathbf{H}} F_{\mathbf{K}} F_{\mathbf{H}-\mathbf{K}}| \text{ large,} \quad (37)$$

in the classical probability theory, can be qualitatively derived in this completely different logical context. But perhaps the most important implication of the above considerations is the realization that the diagonal elements of the coefficient matrix are dominant, if $|F_{\mathbf{K}_j} F_{\mathbf{H}-\mathbf{K}_j}|$ are all large enough. Since the existence of large diagonal elements is usually taken as an indication of a well conditioned system of equations, we may expect that the solution of our problem should not be intrinsically difficult to obtain, as long as the small terms $|F_{\mathbf{K}_j} F_{\mathbf{H}-\mathbf{K}_j}|$ may be omitted from $\mathcal{R}'_H(\mathbf{u})$ [see equation (31)] without destroying the validity of equation (30).

The corresponding procedure may be followed for S_H , and it is easy to check that the overall result is formally identical to equations (10).

If the phase invariants are not independent, the minimization of the Ψ_H function [equation (30)] must be performed differently. As an example, a step-wise procedure analogous to that utilized in the least-squares refinement of the atomic coordinates may be followed, starting from a rough set of phases obtained from the zero-valued Patterson vectors. However, it is possible to show that for the triclinic space groups the linear independence is always automatically guaranteed.

Although the above least-squares approach was followed with specific reference to the $P1$ case, it is not difficult to show that the essential results shown in equations (27') and (30) (or their analogues with the sine invariants) are valid for any space group. In fact, although the existence of particular space-group symmetries may change by a factor the averages $\langle \mathcal{R}_H^2(\mathbf{u}) \rangle$ and $\langle \mathcal{S}_H^2(\mathbf{u}) \rangle$ [see equations (19)], this factor is obviously constant for all \mathbf{u} 's, so that the minimizing function turns out to be the same.

As a final comment, we wish to point out that the above least-squares approach seems to exploit in quite a complete way the physical information contained in the observed amplitudes, to derive the corresponding phases. The equal-atoms assumption is not strictly re-

quired. Needless to say, practical testing of both methods indicated in the present paper is needed. In our laboratory, a computing program for the least-squares approach to triclinic space groups is under preparation.

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A New Monte Carlo Method for Phase Determination

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Abstract

An extended version of the multi-solution method has been devised by introducing a Monte Carlo technique. This Monte Carlo direct method differs from the ordinary multi-solution procedure in two respects: (1) The starting set usually consists of as many as 10–50 phases; (2) Tentative phase values assigned to the members of the starting set are derived from successively generated random numbers. The application of the new method to several unknown structures has shown that it can be used as an effective means of phase determination.

Introduction

The direct methods of phase determination have now made it possible to determine unknown structures of complicated organic compounds without converting them into heavy-atom derivatives. These excellent results may give one a false impression that the phase problem would have been completely solved. However, especially in noncentrosymmetric cases, there seem to be a good many structures whose analyses end in failure. It has been pointed out that the probable cause of such a failure is that some phase relationships produce grave errors early in the phase determination (Karle, Karle & Estlin, 1967; Karle, Gibson & Karle, 1969).* If this is the case, it is very hard to overcome the difficulty, because it is practically impossible to find

the serious trouble-makers among the many phase relationships at the early stage of the analysis. Although a promising way of doing this is to add some additional phases to the starting set, it causes a great increase in the number of phase sets to be treated. A method which has been developed to surmount this new obstacle is the magic-integer technique (White & Woolfson, 1975; Declercq, Germain & Woolfson, 1975).

When applying the multi-solution method (Germain & Woolfson, 1968), one sometimes finds that two or more phase sets appearing in succession lead to the correct solution. In this case, generally speaking, one will be able to reach the correct solution earlier by making the phase sets appear in completely random order rather than in systematic order, because the dispersion of the successive, essentially correct phase sets remarkably decreases the average number of trials necessary for finding the correct solution. The larger the starting set, the more frequently such a case must be met. Accordingly, the introduction of a Monte Carlo technique seems to afford a new method for solving the difficulty in phase determination.

Although the use of a Monte Carlo method for X-ray structure analysis was proposed by Vand, Niggli & Pepinsky (1960), the idea now appears to have been given up. One of the main causes of the failure is probably that the optimal-shift method (Niggli, Vand & Pepinsky, 1960) cannot refine random structures sufficiently well. On the other hand, the tangent formula (Karle & Hauptman, 1956) often shows remarkable ability in the refinement of phases. This suggests that it may be more promising to use generated random

* It has recently been reported that there exist structures which the tangent formula itself is inadequate to solve (Lessinger, 1976).