Acta Cryst. (1995). A**51**, 754–763

Twin Variables and Determinants in Direct Methods

By A. Hountas

Physics Laboratory, Agricultural University of Athens, 75 *Iera Odos, Votanicos, Athens* 118-55, *Greece*

and G. Tsoucaris

Laboratoire de Physique, Tour B, Centre Pharmaceutique, Université Paris Sud, 92290 *Châtenay-Malabry, France*

(*Received* 26 *July* 1994; *accepted* 3 *April* 1995)

Abstract

In most algorithms of direct methods, the variables are the normalized structure factors (SF) $E_{\mathbf{H}}$. An alternative set of variables is proposed which provides more flexibility for handling, in a single algorithm, phase relationships and direct-space constraints, as well as the complete set of diffraction data. This set of variables $\Psi_{\mathbf{H}}$ consists of SF associated with a complex periodic function $\psi(r)$ such that $\rho(r) = |\psi(r)|^2$. The pair of variables $\{E_{\mathbf{H}}, \Psi_{\mathbf{H}}\}$, called twin variables, play a crucial role in the subsequent theory. The phase relations are enhanced by using pairs of non-negative 'twin determinants' $\{D_m, D'_{m+1}\}$; D_m is a classical Karle–Hauptman (K-H) determinant involving E and D'_{m+1} is generated by bordering D_m with an $(m+1)$th row and column containing Ψ. The associated regression equation establishes a relation between E and Ψ. Furthermore, a remarkable expression is obtained for the gradient of the phase given by the classical tangent formula, as well as for the gradients involved in the related formulae pertaining to the Ψ set. The flexibility of the algorithm is illustrated by the *ab initio* transferring to the Ψ set of the *a priori* known information (such as the whole set of the observed moduli), before starting the sequential phase determination of the unknown phases. All constraints are included in a global minimization function. Analytical formulae are given for the gradient of this function with respect to the Ψ set of variables. In the final result, the Ψ set is simultaneously compatible in the least-squares sense with the whole set of observed SF and with various other constraints and phase relations. Application to two known structures permitted testing the different parts of the algorithm.

1. Introduction and general scope

In direct methods, the simultaneous use of a large number of phases in a single mathematical expression is a major subject of research. The introduction, in the very first stages of phase determination, of the complete set of observed structure-factor moduli is also a problem without an easy solution. Similar problems arise in the course of phase extension by direct methods. In most existing algorithms, the unknown variables are the SF or, for fixed moduli, their phases. We propose in this paper an alternative set of variables which provide more flexibility in handling, in a single algorithm, phase relationships and direct-space constraints, as well as the complete set of diffraction data. In particular, novel mathematical expressions (§§2.3–2.6) will allow the *ab initio* imprinting into the algorithm of *a priori* known information (§§1.2, 3*a*, 6). This set of variables, called the Ψ set, is introduced in two ways: by using a Sayre-type squaring equation (Sayre, 1952) or by defining a modified Karle–Hauptman (K-H) determinant (Karle & Hauptman, 1950).

1.1. *The Ψ set as elements of twin determinants*

It is classically known that the non-negative character of a complete set of K-H determinants is a necessary and sufficient condition for the associated scattering density to be non-negative. For point atoms with positive atomic scattering factors, their definition is

$$D_m = \det(U_{pq}) \geq 0,$$

where $U_{pq} = U_{\mathbf{H}_p-\mathbf{H}_q} = E_{\mathbf{H}_p-\mathbf{H}_q}/E_0$ is the unitary SF [equation (1.3)]. As an example taken from experimental diffraction data where the above K-H inequality does not hold, we mention neutron diffraction SF where the atomic scattering factor may be positive or negative as well.

Even after introducing a distribution of point atoms with negative or non-real scattering factors, however, one could seek the construction of non-negative determinants based upon a different definition. Such a determinant has been proposed for 'isomorphous pairs' of X-ray and neutron diffraction SF, both associated with the same set of atomic coordinates and denoted, respectively, by $E^{xR}_{\mathbf{H}}$ and $\Psi^n_{\mathbf{H}}$ [see equations 9–10 in Tsoucaris (1970*b*) for proper scaling of the SF]. For example,

$$D_3^n = \begin{vmatrix} 1 & E^{xR}_{\mathbf{H}} & \Psi^n_{\mathbf{K}} \\ (E^{xR}_{\mathbf{H}})^* & 1 & \Psi^n_{\mathbf{K}-\mathbf{H}} \\ (\Psi^n_{\mathbf{K}})^* & (\Psi^n_{\mathbf{K}-\mathbf{H}})^* & 1 \end{vmatrix} \geq 0. \qquad (1.1)$$

Acta Crystallographica Section A
ISSN 0108-7673 ©1995

In these determinants, neutron SF $\Psi^n_{\mathbf{K}}$ are the elements of the last row and column, whereas the elements of all other rows and columns are X-ray SF $E^{xR}_{\mathbf{H}}$. It is this particular construction that restores the non-negative character of the determinants.

We note that the phase dependence of D^n_3 involves only the 'mixed type triplet invariants':

$$T_{\mathbf{HK}} = E^{xR}_{-\mathbf{H}}\Psi^n_{\mathbf{K}}(\Psi^n_{\mathbf{K-H}})^*. \tag{1.2}$$

The definition of the mixed X-ray/neutron determinants [(1.1)] involved the expression $+g_j^{1/2}$, *i.e.* the square root of the normalized X-ray scattering factor $g_j \geq 0$ derived from the experimental scattering factor f_j [(1.3*a*)]. By analogy with the physical isomorphous X-ray/neutron SF pair ($E^{xR}_{\mathbf{H}}$, $\Psi^n_{\mathbf{H}}$), this mathematical formulation will now be transposed to the present purpose by considering an isomorphous pair of X-ray SF $E_{\mathbf{H}}$, equation (1.3), and a novel set of SF $\Psi_{\mathbf{H}}$, equation (1.4), defined as follows. For both $E_{\mathbf{H}}$ and $\Psi_{\mathbf{H}}$, the atomic coordinates are identical; for $\Psi_{\mathbf{H}}$, the scattering factor γ_j is a complex number with a modulus equal to the X-ray scattering factor $+g_j^{1/2}$ but with an arbitrary phase taking any value between $-\pi$ and $+\pi$. It is to be noted that the physical anomalous-dispersion expressions involve such complex scattering factors but their phase is rather closer to 0. Hence, the theory of twin determinants also applies to anomalous dispersion. We write

$$E_{\mathbf{H}} = \sum_{j=1}^{N} g_j \exp(2\pi i\mathbf{H}\cdot\mathbf{r}_j) \tag{1.3}$$

with the usual definition for normalized SF:

$$g_j = f_j \Big/ \left(\sum_{j=1}^{N} f_j^2\right)^{1/2} \tag{1.3a}$$

under the condition

$$\sum_{j=1}^{N} g_j^2 = 1$$

and

$$\Psi_{\mathbf{H}} = (1/E_0^{1/2})\sum_{j=1}^{N} \gamma_j \exp(2\pi i\mathbf{H}\cdot\mathbf{r}_j) \tag{1.4}$$

$$|\gamma_j|^2 = g_j \geq 0, \tag{1.4a}$$

where N is the number of atoms in the unit cell. The scaling of (1.4) is such that Ψ are normalized SF, in the same sense as normalized E values [special case of (2.5)]:

$$\langle|\Psi_{\mathbf{H}}|^2\rangle = \sum_{j=1}^{N} |\gamma_j|^2/E_0 = 1. \tag{1.4b}$$

It is important to emphasize that the phase of γ_j is not directly provided by experimental data, whereas its modulus is precisely given *a priori* from the known values g_j, (1.4*a*). Clearly, the Ψ set (1.4) is purposely designed as an alternative auxiliary set of primitive variables in the process of phase determination or phase extension. A prerequisite for their use is obtaining the explicit expressions linking the classical variables E to the new set of variables Ψ [(1.6) and §§2.3–2.6]. As a particular case, we can consider only real values $\gamma_j = \pm g_j^{1/2}$. Here also the signs can be provided by a random-number-generator subroutine.

The mathematical formalism leading to the general non-negative determinant (1.5) is given in §2.1. The novel D'_{m+1} will be obtained from a classical K-H determinant D_m by bordering it with an $(m+1)$th row and column containing only Ψ. With the usual notation $U_{pq} = E_{pq}/E_0$ and Ψ_q given by (1.4):

$$D'_{m+1} = \left|\begin{array}{ccc|c} 1 & \cdots & U_{1m} & \Psi_1 \\ & \ddots & & \vdots \\ & U_{pq} & & \Psi_p \\ & & \ddots & \vdots \\ U_{m1} & \cdots & 1 & \Psi_m \\ \hline (\Psi_1)^* \;\cdots & (\Psi_q)^* & \cdots\; (\Psi_m)^* & N \end{array}\right| \geq 0 \tag{1.5}$$

where the single index p stands for the vector $\mathbf{H}_p$ and the double index pq for $\mathbf{H}_p{-}\mathbf{H}_q$. Note, however, that $(\Psi_{\mathbf{H}_q})^* \neq \Psi_{-\mathbf{H}_q}$.

The pair of 'isomorphous sets' $E_{\mathbf{H}}$ and $\Psi_{\mathbf{H}}$ of (1.3) and (1.4) will be called twin variables. Pairs of determinants involving twin variables, such as D_m and D'_{m+1} in (1.5), are called twin determinants. Further developments (§2.2) lead to a still different type of twin determinant where the Ψ set is involved not only in the last row and column of D'_{m+1} but also in a novel definition of all elements of D_m.

1.2. *The Ψ set of variables and its self convolution*

Another way of introducing the Ψ set is a convolution-type equation:

$$E_{\mathbf{H}} = \sum_{\mathbf{K}} w_{\mathbf{HK}}\Psi_{\mathbf{K}}(\Psi_{\mathbf{K-H}})^*, \tag{1.6}$$

which arises, except for the weighting factor $w_{\mathbf{HK}}$, from Fourier transformation (FT) of the following modelization function $\rho(r)$ for a positive electron-density function:

$$\rho(r) = |\psi(r)|^2 \begin{cases} E_{\mathbf{H}} = \mathrm{FC}[\rho(r)] \\ \Psi_{\mathbf{H}} = \mathrm{FC}[\psi(r)], \end{cases} \tag{1.7}$$

where FC stands for Fourier coefficient.

Anticipating the results of §§3 and 4, we indicate that an advantage of the new set of variables is that it allows at any stage the whole set of the observed moduli to be incorporated into the phase-determining algorithm; this is achieved by constraining the Ψ set to fulfil the modulus part of (1.6), in the sense of least squares (LS), equation (4.3). This constraint is applied from the very beginning at the usual sequential determination of phases; the phase-determination process, carried on by varying the Ψ set, is then confined to that subset of Ψ that satisfies the modulus constraints.

A similar formalism has been proposed by Davies & Rollet (1976) for phase extension in the special case of real $\pm\rho^{1/2}$. The present algorithm, in addition to the constraint (1.6), introduces several other direct-space or reciprocal-space constraints and provides a further strengthening of the phase relations with high-order determinants. Furthermore, the complex character of $\psi(r)$ or γ_j leads to the breakdown of Friedel's law in the Ψ set and subsequently to doubling the number of variables within a given reciprocal sphere. These facts contribute to using the algorithm in the *ab initio* problem.

As a first step in practical applications, we develop in §§3 and 4 an algorithm mainly based on the convolution equation (1.6) and the results of §§2.3–2.6. Numerical results are given in §5 and a short discussion in §6.

2. The theoretical foundation

2.1. *Twin determinants*

By analogy with the theory of the maximum-determinant method (MDM), we consider $m+1$ vectors $(\tilde{\mathbf{V}}_1, \ldots, \tilde{\mathbf{V}}_m, \tilde{\mathbf{V}}_{m+1})$ in $\mathbb{C}^N$; this $\mathbb{C}$-vector space is equipped with its orthonormal canonical basis $\{\tilde{\mathbf{e}}_i, i = 1, \ldots, N\}$ [Tsoucaris, 1970*a*, equations (*B*.1)–(*B*.6)]. However, the scattering factors involved in the vector coordinates are replaced as follows:

$$\tilde{\mathbf{V}}_p = (1/E_0^{1/2}) \sum_{j=1}^{N} [\gamma_j \exp(2\pi i \mathbf{H}_p \cdot \mathbf{r}_j)] \tilde{\mathbf{e}}_j \quad (p = 1, \ldots, m) \tag{2.1}$$

$$\tilde{\mathbf{W}}_{m+1} = \sum_{j=1}^{N} \tilde{\mathbf{e}}_j. \tag{2.2}$$

The elements of the principal minor D_m, (1.5), are generated as scalar products:

$$U_{pq} = \langle \tilde{\mathbf{V}}_p | \tilde{\mathbf{V}}_q \rangle = E_{\mathbf{H}_p - \mathbf{H}_q} / E_0. \tag{2.3}$$

The element at the $(m+1)$th column and qth row is

$$\Psi_{\mathbf{H}} = \langle \tilde{\mathbf{V}}_q | \tilde{\mathbf{V}}_{m+1} \rangle = (1/E_0^{1/2}) \sum_{j=1}^{N} \gamma_j \exp(2\pi i \mathbf{H}_p \cdot \mathbf{r}_j). \tag{2.4}$$

The element $\langle \tilde{\mathbf{V}}_{m+1} | \tilde{\mathbf{V}}_q \rangle$ at the $(m+1)$th row and qth column is the complex conjugate of (2.4).

Standard mathematics then lead to the twin determinants and the inequality (1.5). The positive definite character of the underlying matrices is a necessary condition for the validity of the probability relations which will be studied in §§2.3–2.4.

The last row and column elements in D'_{m+1} do not obey the Friedel law, in contrast to the principal minor D_m. It follows that, in the mixed-type phase invariants involved in the expansion of D'_{m+1}, the sum of the reciprocal vectors is not equal to 0, as it is for the classical invariants:

$$T_{pq} = (\Psi_{\mathbf{H}_p})^* \Psi_{\mathbf{H}_q} E_{\mathbf{H}_p - \mathbf{H}_q}. \tag{2.4a}$$

Note that whereas the triplets (1.2) or (2.4*a*) are real numbers, the triplet $\Psi_{-\mathbf{H}_p} \Psi_{\mathbf{H}_q} E_{\mathbf{H}_p - \mathbf{H}_q}$ is not. Interestingly, the expected value of the mixed triplets (2.4*a*) is equal to $1/E_0$, an expression that differs from that of the classical triplets $E_{-\mathbf{H}} E_{\mathbf{K}} E_{\mathbf{H}-\mathbf{K}}$ but similarly reduces to $1/N^{1/2}$ for equal atoms.

The elements of D_m can be considered as correlation coefficients between Ψ values; indeed, with the usual notation we have

$$U_{\mathbf{H}_p - \mathbf{H}_q} = \langle \Psi_{\mathbf{H}_p - \mathbf{L}} (\Psi_{\mathbf{H}_q - \mathbf{L}})^* \rangle_{\mathbf{L}}. \tag{2.5}$$

This formula is obtained, by analogy with the Sayre–Hughes equation, by introducing (1.4) in the right-hand member of (2.5) and allowing $\mathbf{L}$ to sweep all reciprocal space in the averaging process denoted by the bracket.

It is to be noticed that, in equation (*B*.2) of Tsoucaris (1970*a*), the elements of D_m were the SF G_{pq} associated with the squared structure ρ^2; only the last row and column contained the usual E values, *i.e.* associated with the ρ structure. In contrast, all elements U_{pq} of D_m of (1.5), calculated by (2.5), are associated with the ρ structure itself.

The behavior of the determinants (1.5) as a function of the order m is similar to that of the classical ones. Two ranges of m are of particular interest: (*a*) for values of m considerably less than N (order of magnitude less than $N/3$), the MDM rule applies; (*b*) for $m \geq N$, we have $D'_{m+1} = 0$. The N-rank matrix theory (Navaza & Navaza, 1992; Altomare, Giacovazzo, Guagliardi & Siliqi, 1994) also applies to D'_{m+1} and the lowest eigenvalue of D'_{N+1} tends to a minimum value for decreasing phase errors.

2.2. *Construction of twin determinants associated with matrices of given rank n*

Equation (2.5) strictly holds only for an infinite number of terms in the averaging operation. It suggests, however, for a limited number of terms n, a new way of defining matrices which are by construction (*a*) positive definite and (*b*) identically null for an order m higher than a given value n. The theory outlined below has not been used in the subsequent sections of this paper.

We consider here not only a single last row and column of elements of the form (1.4), as in (1.5), but a set of n distinct reciprocal vectors $\mathbf{H}_p - \mathbf{H}_l$, with

$l = 1, \ldots, n$ and $p = 1, \ldots, m$. The corresponding Ψ set, namely $\Psi_{\mathbf{H}_p-\mathbf{H}_l} = \Psi_{pl}$ compose an $(m \times n)$ rectangular matrix. This will be the basis of a novel definition of an n-dimensional vector space $\boldsymbol{C}^n$ and of a set of $m+1$ vectors; the latter involves Ψ values as coordinates instead of the classical atomic contributions in (2.1):

$$\tilde{\mathbf{V}}'_p = (1/c_p^{1/2}) \sum_{i=1}^{n} \{\Psi_{pi}\} \tilde{\mathbf{e}}_i \quad (p = 1, \ldots, m) \tag{2.6}$$

$$\tilde{\mathbf{W}}'_l = \tilde{\mathbf{e}}_l \quad (l = 1, \ldots, n), \tag{2.7}$$

where c_p is a normalizing factor:

$$c_p = \sum_{i=1}^{n} |\Psi_{pi}|^2. \tag{2.7a}$$

We form the scalar products

$$C_{pq} = \langle \tilde{\mathbf{V}}'_p | \tilde{\mathbf{V}}'_q \rangle = [1/(c_p c_q)^{1/2}] \sum_{i=1}^{n} \Psi_{\mathbf{H}_p-\mathbf{H}_i} (\Psi_{\mathbf{H}_q-\mathbf{H}_i})^* \quad (p, q = 1, \ldots m) \tag{2.8}$$

$$\langle \tilde{\mathbf{W}}'_p | \tilde{\mathbf{V}}'_l \rangle = \Psi_{pl}/c_p^{1/2}, \quad \langle \tilde{\mathbf{W}}'_l | \tilde{\mathbf{V}}'_p \rangle = (\Psi_{pl})^*/c_p^{1/2}. \tag{2.9}$$

Thus, we obtain by construction an mth-order positive definite matrix $\mathbf{C}$, (2.8), of maximum rank n, no matter what are the values (correct or not) of Ψ. The value of n is arbitrary, *a priori* unrelated to the number of atoms N; it plays, however, a role similar to that of N in classical K-H determinants. The behavior of $D_m^{(n)}$ as a function of m is governed by the following 'steady decrease inequality' and 'n-rank equality':

$$D_m^{(n)} = \det(C_{pq}) \geq 0 \tag{2.10}$$

$$D_m^{(n)} \begin{cases} \geq D_{m+1}^{(n)} & \text{for } m \leq n \\ = 0 & \text{for } m > n \end{cases}. \tag{2.10a}$$

Clearly, apart from accidental coincidence, the maximum rank of the associated matrix $\mathbf{C}$ is equal to n. As in (1.5), the twin pair $[D_m^{(n)}, D'^{(n)}_{m+1}]$[†] is generated by bordering (2.10) with an $(m+1)$th row and column chosen in the above rectangular matrix Ψ_{pl}.

A characteristic of the K-H determinant is that the value of an element U_{pq} depends solely on the reciprocal-vector difference $\mathbf{H}_p$–$\mathbf{H}_q$; this property may be called stationarity, a usual term in signal theory. The counterpart of the limited number of terms in (2.8) is the lack of strict stationarity: the elements C_{pq} are not bound to depend solely on the difference $\mathbf{H}_p$–$\mathbf{H}_q$, and $\mathbf{C}$ is not a Töplitz-type matrix. However, stationarity can constitute a new constraint to be fulfilled by an acceptable Ψ set. In fact, this means that we will impose a new type of constraint:

$$C_{pq} = C_{p'q'} \quad (\mathbf{H}_p - \mathbf{H}_q = \mathbf{H}_{p'} - \mathbf{H}_{q'}), \tag{2.11}$$

which are to be treated by the LS algorithms developed in §4. The interest of the determinants (2.10) will be enhanced if the value of n used in practical applications is equal to or smaller than N (maximum rank for K-H determinants) but still large enough to ensure an acceptable level of discrepancy in (2.11). Thus, the search for the unknown phases will be confined to a subspace of variables such that two fundamental conditions are automatically fulfilled, namely the positive definiteness and the finite rank of matrices (2.10).

2.3. *The regression and the '$\rho\psi$' equation*

The positive definite character of the matrices of §2 allows the extension of the probability expressions established for the classical E values to the Ψ set (Gaussian laws, MDM rule). We write here the Ψ-set regression equation:

$$\Psi_{(m+1)p} = -(1/D_{pp}) \sum_{q=1}^{m} D_{pq} \Psi_{(m+1)q}, \tag{2.12}$$

where D_{pq} are inverse matrix elements arising from the principal minor D_m. In practice, (2.12) can be used to transfer the phase information of the usual SF E values towards the Ψ set of variables. It can be shown that the precision of the determination of new Ψ values from (2.12) increases with increasing order m. A remarkable fact is that the regression equation becomes an exact equality for $m = N + 1$ (de Rango, Tsoucaris & Zelwer, 1974) with the N-rank determinants (1.5), and for $m = n + 1$ with the n-rank determinants (2.10).

Furthermore, by expanding D_{pq} in power series and keeping only the first term, we obtain an approximation to (2.12), called the '$\rho\psi$ equation':

$$\text{phase of } \{\Psi_{\mathbf{K}}\} \simeq \text{phase of } \left\{ \sum_{\mathbf{K}} E_{\mathbf{H}} \Psi_{\mathbf{K}-\mathbf{H}} \right\}. \tag{2.13}$$

It is worthwhile stressing that the counterpart in direct space of the last expression has a quite clear meaning: it is a sort of 3/2 power of $\rho(r)$, the bracket in the right hand member being the FT of $\rho\psi$. Therefore, it may not suffer to the same extent the well known problem of the Sayre equation for non-atomic resolution or unequal atoms. Equation (2.13) will routinely be used in the subsequent numerical calculations in order to extend the Ψ set as soon as the development of the phasing process of E values requires a larger Ψ set to achieve the fulfilment of the several constraints described in §4.

2.4. *Mixed-type invariants and probability relations*

Generalizing the mixed triplets (2.4a), we note that the expansion of D'_{m+1} (1.5) contains high-order mixed-type

---

[†] The upper index (n) must not be confused with the superscript n appearing in (1.1) for neutron diffraction.

invariants of the form

$$T_{pqr}\ldots = E_{pq}E_{qr}\ldots E_{st}\Psi_t(\Psi_p)^*, \qquad (2.14)$$

where $\Psi_t = \Psi_{\mathbf{H}_t}$.

From the non-negative character of D'_{m+1}, one can foresee several other relations. In particular, the mixed-type triplet phase invariants Ω_3 [see (2.4*a*)] are biased around the value 0:

$$\Omega_3 = -\varphi_{\mathbf{H}} + \omega_{\mathbf{K}} - \omega_{\mathbf{K}-\mathbf{H}}, \qquad (2.15)$$

where $\varphi_{\mathbf{H}}$ and $\omega_{\mathbf{K}}$ are the phases of $E_{\mathbf{H}}$ and $\Psi_{\mathbf{K}}$, respectively. Furthermore, the associated probability law is given by the expression

$$P(\Omega_3) \propto \exp(A'\cos\Omega_3), \qquad (2.16)$$

where $A' = 2|E_{-\mathbf{H}}\Psi_{\mathbf{K}}\Psi_{\mathbf{K}-\mathbf{H}}|/E_0(1-|U_{\mathbf{H}}|^2)$. For equal atoms and large N, A' reduces to $2|E_{-\mathbf{H}}\Psi_{\mathbf{K}}\Psi_{\mathbf{K}-\mathbf{H}}|/N^{1/2}$. We note that higher approximations for the above coefficient A' involving Ψ can be adapted from the recent bibliography for classical triplets (see Altomare *et al.*, 1994, and related questions in §§4.3–4.4).

2.5. *The calculation of a LS gradient with respect to the Ψ set*

The actual problem involves tractable calculations of LS functions of the general form $\mathsf{M}(\ldots\Psi_{\mathbf{L}}\ldots)$ developed in §4. The calculations are greatly based on the use of general expressions given below (Navaza, Castellano & Tsoucaris, 1983). First we wish to clarify the notation for gradients and derivatives used throughout this paper. For n complex variables $\Psi_{\mathbf{L}}$, the function M: $\mathcal{R}^{2n} \to \mathcal{R}$ merely depends on the real variables $A_{\mathbf{L}}$, $B_{\mathbf{L}}$. The expression $(\operatorname{grad}\mathsf{M})_{\Psi_{\mathbf{L}}}$ will represent the pair of partial derivatives with respect to the two real variables $(\partial\mathsf{M}/\partial A_{\mathbf{L}}, \partial\mathsf{M}/\partial B_{\mathbf{L}})$ and is written with the complex notation:

$$(\operatorname{grad}\mathsf{M})_{\Psi_{\mathbf{L}}} = \partial\mathsf{M}/\partial A_{\mathbf{L}} + i\partial\mathsf{M}/\partial B_{\mathbf{L}} \qquad \Psi_{\mathbf{L}} = A_{\mathbf{L}} + iB_{\mathbf{L}},$$

keeping in mind that the gradient component $(\operatorname{grad}\mathsf{M})_{\Psi_{\mathbf{L}}}$ is a vector of $\mathcal{R}^2$. This pair is conveniently obtained as the real and imaginary parts of the complex derivative of M with respect to $(\Psi_{\mathbf{L}})^*$:

$$(\operatorname{grad}\mathsf{M})_{\Psi_{\mathbf{L}}} = 2\partial\mathsf{M}/\partial(\Psi_{\mathbf{L}})^* = \begin{cases} \partial\mathsf{M}/\partial A_{\mathbf{L}} = 2\Re[\partial\mathsf{M}/\partial(\Psi_{\mathbf{L}})^*] \\ \partial\mathsf{M}/\partial B_{\mathbf{L}} = 2\Im[\partial\mathsf{M}/\partial(\Psi_{\mathbf{L}})^*] \end{cases} \qquad (2.17)$$

2.6. *General expressions of phase derivatives*

We consider first a question pertaining to the pair of SF $(E_{\mathbf{H}}, E_{\mathbf{H}'})$ in the classical squaring equation (4.9): for a given small variation of the phase $\varphi_{\mathbf{H}'}$ of $E_{\mathbf{H}'}$ involved in one contributor in the tangent formula, what is the resulting variation of the phase $\Phi_{\mathbf{H}}$ of $G_{\mathbf{H}}$? The calculation yields

$$\partial\Phi_{\mathbf{H}}/\partial\varphi_{\mathbf{H}'} = (|E_{\mathbf{H}'}E_{\mathbf{H}-\mathbf{H}'}|/|G_{\mathbf{H}}|)\cos\Phi_3 \qquad (2.18)$$

$$\Phi_3 = -\Phi_{\mathbf{H}} + \varphi_{\mathbf{H}'} + \varphi_{\mathbf{H}-\mathbf{H}'}. \qquad (2.18a)$$

One could expect to observe that the derivative of the phase of a SF, with respect to the phase of another SF, is itself an origin-invariant quantity. The remarkable fact in the above expression is that this phase invariant involves solely, except for moduli, the cosine triplet invariants (2.18*a*). Similarly, the derivative of the phase $\varphi_{\mathbf{H}}$ of $E_{\mathbf{H}}$ in (1.6), with respect to the phase $\omega_{\mathbf{K}}$ of $\Psi_{\mathbf{K}}$, depends solely on the mixed-type cosine invariants:

$$\partial\varphi_{\mathbf{H}}/\partial\omega_{\mathbf{L}} = (|\Psi_{\mathbf{L}}\Psi_{\mathbf{L}-\mathbf{H}}|/|E_{\mathbf{H}}|)\cos\Omega_3, \qquad (2.19)$$

where Ω_3 is given by (2.15).

A related useful formula provides an answer to a similar question, pertaining to the twin variable pair $(E_{\mathbf{H}}, \Psi_{\mathbf{L}})$. It provides, *via* (2.17), the partial derivatives of the phase $\varphi_{\mathbf{H}}$ of $E_{\mathbf{H}}$ with respect to the pair of variables $A_{\mathbf{L}}$ and $B_{\mathbf{L}}$:

$$(\operatorname{grad}\varphi_{\mathbf{H}})_{\Psi_{\mathbf{L}}} = i(E_{\mathbf{H}}\Psi_{\mathbf{L}-\mathbf{H}} - E_{-\mathbf{H}}\Psi_{\mathbf{L}+\mathbf{H}})/|E_{\mathbf{H}}|^2. \qquad (2.20)$$

We note that the second term is obtained, with a sign inversion, from the first by replacing **H** by −**H**. Thus, for summations comprising Friedel pairs such as (4.8), calculations with only one of the two terms lead to the correct result.

A proof of (2.20) is obtained by applying (2.17) to the real function $\varphi_{\mathbf{H}} = \arg(E_{\mathbf{H}})$. We have:

$$i\varphi_{\mathbf{H}} = \ln(E_{\mathbf{H}}) - \ln(|E_{\mathbf{H}}|) \qquad (2.21)$$

$$i\partial\varphi_{\mathbf{H}}/\partial(\Psi_{\mathbf{L}})^* = [\partial E_{\mathbf{H}}/\partial(\Psi_{\mathbf{L}})^*]/E_{\mathbf{H}} - \{\partial[E_{\mathbf{H}}(E_{\mathbf{H}})^*]^{1/2}/\partial(\Psi_{\mathbf{L}})^*\}/|E_{\mathbf{H}}|. \qquad (2.22)$$

The complex derivatives of the right-hand member are immediately obtained from (1.6) where, for simplicity, the relative weighting factors have been omitted and the general scale factor has been incorporated in the Ψ set (see §4.3*c*).

3. The phase-extension algorithm

The algorithm is based on alternately transferring the phase information between the twin variable sets of E and Ψ values. Each cycle of calculations comprises three steps.

(*a*) *Preliminary step. Transfer of information from E to Ψ.* An initial set of phased SF $E_{\mathbf{H}}$ is introduced in the following minimization function and kept constant, in moduli and phases, throughout this step:

$$\mathsf{M}_{\mathrm{SF}} = \sum_{\mathbf{H}} |E_{\mathbf{H}} - \sum_{\mathbf{K}} \Psi_{\mathbf{K}}(\Psi_{\mathbf{K}-\mathbf{H}})^*|^2. \qquad (3.1)$$

Then the initial Ψ values are varied until a set is found that minimizes (3.1).

The convergence is greatly accelerated by using in the first cycles the '$\rho\psi$' equation (2.13). Thus, the phase and modulus information conveyed by the initial set of E values is now transferred and capitalized into the set of Ψ values. Other data can be introduced as well at this first step before starting the sequential phase determination of the unknown phases in the steps (*b*) and (*c*) below. Among them, we mention the whole set or a subset of the observed SF moduli and empty or solvent regions in direct space. The significance of this important aspect is further considered in §6.

(*b*) *Phase extension. Transfer of information from* Ψ *to* E. An additional set of non-phased E values will now be considered. The set of Ψ values obtained in (*a*) is introduced in (1.6) in order to approximately determine the phases of this additional set of E values. We achieve, thus, an inverse transfer of information, *i.e.* from Ψ to E.

(*c*) *Phase refinement via a set of minimization functions of both* E *and* Ψ. The approximate phases of the additional set, along with the phases of the 'initial set', will be introduced as a starting point of iterative calculations in the refinement step. This is achieved *via* minimization functions described in §4. In these calculations, the values of the Ψ set are further varied so as to best satisfy the corresponding constraints. During this variation, it is possible that the new values of the Ψ set no longer fit with sufficient precision the given SF of the initial set. This is taken care of by introducing the expression (3.1) of $\mathsf{M}_{\rm SF}$ into the global sum of minimization functions (4.1).

After convergence in the phase-refinement step is reached, the last two steps are iterated with a new additional set of non-phased E values introduced in (*b*) at each new cycle.

4. The M-minimization functions and their gradient components

The sum of the minimization functions, with appropriate weights (and eventually negative sign for maximization functions), enters a global minimization function:

$$\mathsf{M}_{\rm global} = \mathsf{M}_{\rm SF} + \mathsf{M}_{\rm mod} + \mathsf{M}_{\rm phase}, \qquad (4.1)$$

where $\mathsf{M}_{\rm SF}$ involves only phased SF given by (3.1) and

$$\mathsf{M}_{\rm phase} = \mathsf{M}_{\rm class\,tripl} + \mathsf{M}_{\rm mix\,tripl} + \mathsf{M}_{\rm quartet} + \ldots . \qquad (4.2)$$

4.1. *The observed moduli* $\mathsf{M}_{\rm mod}$ *function*

This function is associated with the usual reliability R factor:

$$\mathsf{M}_{\rm mod} = \sum_{\mathbf{H}} (|E_{\mathbf{H}}| - |E^{\rm obs}_{\mathbf{H}}|)^2 \qquad (4.3)$$

and will provide an explicit example of the calculations.

After writing (4.3) in the form

$$\mathsf{M}_{\rm mod} = \sum_{\mathbf{H}} (E_{\mathbf{H}} - E^{\rm obs}_{\mathbf{H}})(E_{\mathbf{H}} - E^{\rm obs}_{\mathbf{H}})^* \qquad (4.3a)$$

with

$$E^{\rm obs}_{\mathbf{H}} = |E^{\rm obs}_{\mathbf{H}}| \exp(i\varphi_{\mathbf{H}}),$$

we replace $E_{\mathbf{H}}$ and $(E_{\mathbf{H}})^*$ in (4.3*a*) by their simplified expression:

$$E_{\mathbf{H}} = \sum_{\mathbf{K}} \Psi_{\mathbf{K}} (\Psi_{\mathbf{K}-\mathbf{H}})^* = \sum_{\mathbf{K}} \Psi_{\mathbf{K}+\mathbf{H}} (\Psi_{\mathbf{K}})^* \qquad (4.3b)$$

$$\partial (E_{\mathbf{H}})^* / \partial (\Psi_{\mathbf{L}})^* = \Psi_{\mathbf{L}-\mathbf{H}}$$

and (4.3*c*)

$$\partial E_{\mathbf{H}} / \partial (\Psi_{\mathbf{L}})^* = \Psi_{\mathbf{L}+\mathbf{H}}.$$

Then, (2.17) yields

$$(\mathrm{grad}\,\mathsf{M}_{\rm mod})_{\Psi_{\mathbf{L}}} = 2 \sum_{\mathbf{H}} [(E_{\mathbf{H}} - E^{\rm obs}_{\mathbf{H}}) \Psi_{\mathbf{L}-\mathbf{H}} + (E_{\mathbf{H}} - E^{\rm obs}_{\mathbf{H}})^* \Psi_{\mathbf{L}+\mathbf{H}}], \qquad (4.4)$$

which, for $\mathbf{H}$ sweeping all Friedel pairs in reciprocal space, amounts to

$$(\mathrm{grad}\,\mathsf{M}_{\rm mod})_{\Psi_{\mathbf{L}}} = 4 \sum_{\mathbf{H}} (E_{\mathbf{H}} - E^{\rm obs}_{\mathbf{H}}) \Psi_{\mathbf{L}-\mathbf{H}}. \qquad (4.4a)$$

The last remark applies to all subsequent results involving Friedel pairs.

4.2. *Phase constraints associated with mixed-type phase invariants*

One of the simplest expressions suitable for analytical calculations of the gradient components is the following maximization function arising from a sum of D'_3 determinants (1.5):

$$\begin{aligned} \mathsf{M}_{\rm mix\,tripl} &= \sum_{\mathbf{H}} \sum_{\mathbf{K}} \Re[E_{-\mathbf{H}} \Psi_{\mathbf{K}} (\Psi_{\mathbf{K}-\mathbf{H}})^*] \\ &= \sum_{\mathbf{H}} \sum_{\mathbf{K}} |E_{-\mathbf{H}} \Psi_{\mathbf{K}} \Psi_{\mathbf{K}-\mathbf{H}}| \cos \Omega_3, \end{aligned} \qquad (4.5)$$

where Ω_3 is given by (2.15). It has been found in practice that the gradient of (4.5) with respect to the phases $\omega_{\mathbf{L}}$ is most efficient for quick convergence. Thus, if the Ψ-set moduli are kept constant throughout a single iteration, the gradient expression is greatly simplified. This gradient involves the remarkable expression (2.19):

$$\begin{aligned} (\mathrm{grad}\,\mathsf{M}_{\rm mix\,tripl})_{\omega_{\mathbf{L}}} = &- \sum_{\mathbf{H}} \sum_{\mathbf{K}} |E_{-\mathbf{H}} \Psi_{\mathbf{K}} \Psi_{\mathbf{H}-\mathbf{K}}| \sin \Omega_3 \\ &\times (-\partial \varphi_{\mathbf{H}} / \partial \omega_{\mathbf{L}} + \delta_{\mathbf{KL}} + \delta_{(\mathbf{K}-\mathbf{H})\mathbf{L}}), \end{aligned} \qquad (4.6)$$

where the Kronecker symbol $\delta_{\mathbf{KL}} = 0$ if $\mathbf{K} \neq \mathbf{L}$ and $\delta_{\mathbf{KL}} = 1$ if $\mathbf{K} = \mathbf{L}$.

4.3. *Phase constraints associated with classical triplet invariants*

For $\mathsf{M}_{\text{triplet}}$, two different forms have been used in the present work. The first, denoted by $\mathsf{M}_{\text{Bessel}}$, involves the information contained in the Cochran distribution (Cochran, 1955) and the connected formula for the expected cosine invariants (Hauptman, 1976):

$$\mathsf{M}_{\text{Bessel}} = \sum_{\mathbf{H}} \left\{ \sum_{\mathbf{H}'} E_3[\cos \Phi_3 - I_1(A)/I_0(A)] \right\}^2 \qquad (4.7)$$

with the usual notations: $E_3 = |E^{\text{obs}}_{-\mathbf{H}} E^{\text{obs}}_{\mathbf{H}'} E^{\text{obs}}_{\mathbf{H}-\mathbf{H}'}|$, $A = 2E_3/N^{1/2}$, $\Phi_3 = -\varphi_{\mathbf{H}} + \varphi_{\mathbf{H}'} + \varphi_{\mathbf{H}-\mathbf{H}'}$; $I_0(A)$ and $I_1(A)$ are the modified Bessel functions. The final gradient expression is obtained by introducing (2.20) in each of the three terms arising from $\partial\Phi_3/\partial\Psi_{\mathrm{L}}$:

$$\begin{aligned}(\operatorname{grad} \mathsf{M}_{\text{Bessel}})_{\Psi_{\mathrm{L}}} = -2\sum_{\mathbf{H}} \Bigg\{ \sum_{\mathbf{H}'} E_3[\cos \Phi_3 \\ - I_1(A)/I_0(A)] \Bigg\} \sin \Phi_3[-(\operatorname{grad} \varphi_{\mathbf{H}})_{\Psi_{\mathrm{L}}} \\ + (\operatorname{grad} \varphi_{\mathbf{H}'})_{\Psi_{\mathrm{L}}} + (\operatorname{grad} \varphi_{\mathbf{H}-\mathbf{H}'})_{\Psi_{\mathrm{L}}}].\end{aligned} \qquad (4.8)$$

The second minimization function, denoted by $\mathsf{M}_{\text{tangent}}$, pertains to the usual agreement between a set of phases $\varphi_{\mathbf{H}}$ and the phases $\Phi_{\mathbf{H}}$ of the tangent formula, *i.e.* the phase of $G_{\mathbf{H}}$:

$$G_{\mathbf{H}} = \sum_{\mathbf{H}'} E_{\mathbf{H}'} E_{\mathbf{H}-\mathbf{H}'}. \qquad (4.9)$$

A convenient way of avoiding the 2π ambiguity and expressing explicitly this agreement is the following maximization function:

$$\mathsf{M}_{\text{tangent}} = \sum_{\mathbf{H}} w_{\mathbf{H}} \cos(\varphi_{\mathbf{H}} - \Phi_{\mathbf{H}}). \qquad (4.10)$$

The gradient of (4.10) is

$$\begin{aligned}(\operatorname{grad} \mathsf{M}_{\text{tangent}})_{\Psi_{\mathrm{L}}} = -\sum_{\mathbf{H}} w_{\mathbf{H}} \sin(\varphi_{\mathbf{H}} - \Phi_{\mathbf{H}})[(\operatorname{grad} \varphi_{\mathbf{H}})_{\Psi_{\mathrm{L}}} \\ - (\operatorname{grad} \Phi_{\mathbf{H}})_{\Psi_{\mathrm{L}}}].\end{aligned} \qquad (4.11)$$

The first term within square brackets is given by (2.20), while the second involves a summation over $\mathbf{H}'$, subsequent use of (2.18), and then (2.20).

4.4. *Quartet refinement*

The minimal function of Hauptman has been introduced for the quartets (Hauptman, 1991; Hauptman, Velmurugan & Han, 1991; Miller *et al.*, 1993; DeTitta, Weeks, Thuman, Miller & Hauptman, 1994; Weeks, DeTitta, Hauptman, Thuman & Miller, 1994):

$$\mathsf{M}_{\text{quartet}} = \sum_{\mathbf{H}} \sum_{\mathbf{H}'} \sum_{\mathbf{H}''} E_4[\cos \Phi_4 - I_1(B)/I_0(B)]^2, \qquad (4.12)$$

where $E_4 = |E_{\mathbf{H}} E_{\mathbf{H}'} E_{\mathbf{H}''} E_{-(\mathbf{H}+\mathbf{H}'+\mathbf{H}'')}|$ and $\Phi_4 = \varphi_{\mathbf{H}} + \varphi_{\mathbf{H}'} + \varphi_{\mathbf{H}''} + \varphi_{-(\mathbf{H}+\mathbf{H}'+\mathbf{H}'')}$.

In the present calculations, we considered for the Bessel functions the simplified argument $B = 4E_4/N$. Higher approximations are given by the above authors and by Giacovazzo (1976). The corresponding gradient is

$$\begin{aligned}(\operatorname{grad} \mathsf{M}_{\text{quartet}})_{\Psi_{\mathrm{L}}} = -2\sum_{\mathbf{H}} \sum_{\mathbf{H}'} \sum_{\mathbf{H}''} E_4[\cos \Phi_4 - I_1(B)/I_0(B)] \\ \times \sin \Phi_4 (\operatorname{grad} \Phi_4)_{\Psi_{\mathrm{L}}}.\end{aligned} \qquad (4.13)$$

The gradient in the right-hand member is given by (2.20).

4.5. *Direct-space constraints: solvent flattening, non-crystallographic symmetry and origin atom problem*

The solvent flattening, a procedure helpful in macromolecules, can also be formulated as a Ψ-set minimization problem by writing the integral of ρ over the solvent region:

$$\mathsf{M}_{\text{solv}} = \int_{\text{solv}} \rho(r) \mathrm{d}v = \int_{\text{solv}} \left[\sum_{\mathbf{H}} E_{\mathbf{H}} \exp(-2\pi i \mathbf{H} \cdot \mathbf{r}) \right] \mathrm{d}v. \qquad (4.14)$$

The corresponding gradient is

$$\begin{aligned}(\operatorname{grad} \mathsf{M}_{\text{solv}})_{\Psi_{\mathrm{L}}} &= 4 \int_{\text{solv}} \left[\sum_{\mathbf{H}} \Psi_{\mathrm{L}-\mathbf{H}} \exp(2\pi i \mathbf{H} \cdot \mathbf{r}) \right] \mathrm{d}v \\ &= 4 \sum_{\mathbf{H}} S_{\mathbf{H}} \Psi_{\mathrm{L}-\mathbf{H}},\end{aligned} \qquad (4.15)$$

where $S_{\mathbf{H}}$ is the FT at $\mathbf{H}$ of ρ over the solvent region.

A usual problem in $P1$ and other low-symmetry space groups is the occurrence of a false solution with a heavy atom at the origin. This can be readily avoided in the present algorithm by introducing an appropriate $\mathsf{M}_{\text{origin}}$ minimization function; its gradient is obtained from the special case of (4.15) for $r = 0$.

Non-crystallographic symmetry can be introduced through additional terms in the global minimization expression (4.1). Their general form is similar to (4.14) and (4.15), replacing $\rho(r)$ by differences $[\rho(r) - \rho(\mathbf{A}r)]^2$ at equivalent points related by a symmetry element $\mathbf{A}$:

$$\mathsf{M}_{\text{noncrs sym}} = \int_{\text{subunit}} [\rho(r) - \rho(\mathbf{A}r)]^2 \, \mathrm{d}v. \qquad (4.16)$$

5. General scheme of the twin determinant algorithm and numerical calculations

All the above parts of the algorithm have been thoroughly tested with a Fortran program applied to the following known structures: (*a*) 4,5-bis(methylthio)-1,3-dithiol-2-ylium–bis(TCNQ), $C_{29}H_{15}N_8S_4$ (Psycharis, Mentzafos & Terzis, unpublished data), and β-CD–(*Z*)-7-tetradecemal (CD = cyclodextrin), $C_{98}H_{196}O_{97}$ (Mavri-

Table 1. *Data, results and indications for the structures of* (*a*) 4,5-*bis*(*methylthio*)-1,3-*dithiol*-2-*ylium*–*bis*(*TCNQ*) *and* (*b*) *β-CD*–(*Z*)-7-*tetradecemal*

	(*a*)	(*b*)
Space group	$P1$ ($Z = 1$)	$P1$ ($Z = 1$)
Unit cell: a (Å)/α (°)	8.029/96.8	15.645/101.7
b (Å)/β (°)	7.323/79.1	15.645/101.7
c (Å)/γ (°)	13.565/114.8	15.935/103.6
Number of unique data	2106	7073
Number of non-H atoms in the unit cell	41	195
Minimum E ($E_{\min}$)	1.3	1.7
Number of E values $> E_{\min}$	354	432
Number of assigned phases	6	8
Number of calculated phases	354	132
Final phase error (°)	25	38

dis & Papaioannou, 1995). Data information and the most important results and indications are summarized in Table 1. The program includes the construction of a high-order K-H matrix from which several submatrices are extracted, appropriate to the various calculations. An interesting feature is the easy choice of an efficient Ψ set among the matrix elements of the form $\Psi_{\mathbf{L}-\mathbf{H}_p}$.

In a first stage, we tested the ability of a Ψ set of variables to faithfully reproduce a set of given E values, either in moduli only or in moduli and phase. Starting with totally arbitrary values of Ψ, the usual crystallographic R factors corresponding, respectively, to $\mathsf{M}_{\rm SF}$ (3.1) and $\mathsf{M}_{\rm mod}$ (4.3) are computed at each cycle:

$$R_{\rm SF} = \sum_{\mathbf{H}} |E_{\mathbf{H}} - E^{\rm obs}_{\mathbf{H}}| \Big/ \sum_{\mathbf{H}} |E^{\rm obs}_{\mathbf{H}}| \qquad (5.1)$$

and

$$R_{\rm mod} = \sum_{\mathbf{H}} ||E_{\mathbf{H}}| - |E^{\rm obs}_{\mathbf{H}}|| \Big/ \sum_{\mathbf{H}} |E^{\rm obs}_{\mathbf{H}}|. \qquad (5.2)$$

They can reach values as low as 1% after a few tens of iterations by the simple gradient method. Similarly, for other minimization functions, the convergence is appreciated by the correponding R factors; for example, that corresponding to (4.7) is

$$R_{\rm triplet} = \sum_{\mathbf{H}} \left| \sum_{\mathbf{H}'} E_3[\cos \Phi_3 - I_1(A)/I_0(A)] \right| \times \left[\sum_{\mathbf{H}} \sum_{\mathbf{H}'} E_3 I_1(A)/I_0(A) \right]^{-1}. \qquad (5.3)$$

The convergence for combined M functions has been tested in a few cases among the various combinations. The results of Table 1 have been achieved by using mainly three M functions of (3.1), (4.3) and (4.5).

The above programs permit the investigation of the role of the various parameters involved in the phase determination. In each cycle of the Ψ-extension algorithm, an additional set of SF are introduced; their number varies from 1 to 50 depending on the particular values of various parameters controlling the selection of the new set. The minimum accepted value for the mixed triplet moduli of (2.4*a*), and that for the mixed invariants $\cos \Omega_3$, (2.15), are among the most important parameters. We also have to consider: the minimum value of $|E^{\rm obs}|$ for introducing a reflection into the phasing process; the minimum values for the moduli of classical triplets and quartets introduced in the minimization functions (4.7) and (4.12); the minimum value of $\Psi_{\mathbf{K}}$, and others.

An important feature of the algorithm is the very large range of the ratio "number of Ψ's/number of E's". Values as low as 1/5 still allow an acceptable fit for several M-minimization functions. With further algorithmic and computational improvements, it is likely to reach even lower values of the above ratio. This leads to the important question of the minimum number of independent parameters presiding over the actual values of a given set of phased SF. A related question is the adequacy of a Ψ set obeying or not the Friedel law (real or complex ψ function, respectively). The tests carried out so far show that both cases can be considered with certain advantages for each of them. We emphasize the fact that, in all calculations presented in Table 1, the initial Ψ set issues from the computer random-number-generator subroutine.

Among other aspects illustrating the algorithmic flexibility, we mention the timing for successive transferring of the information between E and Ψ, *i.e.* the time of alternate transferring of information into the Ψ set and of subsequent retrieval to E through (1.6). We also mention the choice between sequential phase determination or global determination techniques.

From the preliminary examination of various parameters, it appears that their optimum value varies in the course of the phase-expansion process. In particular, several cut-off values are to be adjusted as a function of the number of already phased E values and of their figures of merit. Clearly, if the cut-off values are kept at too low levels at a later stage of phase expansion, we expect a general decrease of the quality of the new phases. On the other hand, if these values are too high, very few new phases will be obtained at each cycle and the total calculation time considerably increases.

The smaller number of acceptable phases in the larger structure (*b*) is largely due to the lack in the present computing program of interactively controlled evolution of the various parameters; this will be the object of a forthcoming paper. Such problems have been closely studied and improved over the years for classical direct methods. The present method involves more parameters and more correlation between them. This arises from the nature of the method which is based on the simultaneous examination of the physical structure, expressed by the electron density $\rho(r)$ and its companion structure, expressed by the auxiliary function $\psi(r)$. Thus, in adition to the usual parameters used in direct methods, we also have new parameters of a mixed type to be interactively optimized.

6. Discussion

The methods and theoretical approaches which are related to or compared with the present algorithm can be divided in two categories. The first is based on reciprocal-space algorithms, while an underlying model in direct space provides an insight into the physical meaning. Prototypes for this category are the tangent formula and the Sayre equation, especially in the LS form (Sayre, 1974). Recently, a method called *SAYTAN* (Debaerdemaeker, Tate & Woolfson, 1985, 1988) introduced a Sayre-type LS function to be minimized with respect to the phases of E. The minimal-functions method of Hauptman (1991) is closely related to the minimization functions (4.7) and (4.12). Similarly, the idea of simultaneously minimizing two functions, one for positive triplets and the other for negative quartets is also related to maximizing the first two phased terms of a K-H determinant by the MDM rule. We note, however, that the methods based upon a minimization with respect to the phases of E do not lead necessarily to a model compatible with the whole set of observed diffraction data and with the non-negative electron-density criterion.

The methods of the second category are based on the idea of explicitly exploiting the structure information at all stages through an auxiliary function in direct space. In this category belongs the probability for an atomic presence 'MDM $\tau(r)$' function, which allows the transfer to direct space of the phase information conveyed by a high-order determinant (Mauguen, 1979; Knossow, de Rango, Mauguen, Sarrazin & Tsoucaris, 1977; de Rango *et al.*, 1985). This function is defined as a Fourier series where the FC are elements of the inverse K-H matrix. The maximum-entropy method (MEM) also proceeds through the explicit calculation of a maximum-entropy function in direct space, which exploits the available information (Collins, 1978; Bricogne, 1984; Navaza, 1985); its relationship with MDM has been investigated by Britten & Collins (1982), Narayan & Nityananda (1982) and Bricogne (1984).

The present algorithm, although entirely built, in its present version, in reciprocal space, bears common features with both categories. Indeed, the squaring process in (1.7) underlies the reciprocal-space Ψ set of variables. One should note, however, that the weighting factor $w_{\mathbf{HK}}$ introduced in (1.6) results in a loss of the convolution character of the right-hand expression. The direct-space exact equivalent of (1.6) would be a complicated expression involving $\psi(r)$ and the FT in six dimensions of $w_{\mathbf{HK}}$. The importance of the underlying model in direct space is also reflected in the convolution form of the gradient expressions, such as (4.4) and (4.15), which corresponds to multiplicative operations in direct space. We note the well known relation between difference Fourier and classical LS refinement. On the other hand, an essential feature of the present algorithm is associated with methods of the second category, the process of alternate storing and retrieval of information through the Ψ set playing the role of an auxiliary discrete function.

A main advantage of the present approach is the decoupling of the phase relations, such as (4.5)–(4.13), from the observed moduli constraint (4.3) and from the direct-space constraints (4.14)–(4.16). The observed moduli set, as well as the direct-space constraints at a given stage of calculations, can be considered as *a priori* information for the phase-determining process. The search aiming at the fulfilment of the phase relationships is then confined to the subset of Ψ that already satisfies the above *a priori* constraint. In particular, the algorithm allows a systematic use of the whole set of unobserved reflections within the observed sphere, which may play an important role by avoiding the introduction of a phase error at the early stages of the phase determination.

The ability of the present algorithm to convey information other than LS constraints is illustrated by the possibility of an appropriate choice of the Ψ set. Indeed, the number and location in reciprocal space of the chosen primitive variables $\Psi_{\mathbf{K}}$ is arbitrary. This choice [*i.e.* lattice vectors, moduli and phases of the starting Ψ set, real or complex nature of the function ψ, (1.7)] can be adapted to the information one wishes to emphasize and to the characteristics of the diffraction data.

Two types of this choice will be briefly examined. The first, emphasizing the information pertaining to the observed diffraction data, suggests to select for the reciprocal vectors $\mathbf{K}$ of $\Psi_{\mathbf{K}}$ those corresponding to the largest observed SF ($|E|$'s). As a further step, one could take the values of $|E^{\text{obs}}|$ as initial assignment for the moduli of the Ψ set. We recall, however, that this possibility concerns only the initial moduli of the Ψ set: starting from these values of the moduli and arbitrary phases, the Ψ values are allowed to vary, in modulus and phase, so as to fulfil the minimization constraints. The second type, on the contrary, consists of totally decoupling Ψ and E. For instance, part of the Ψ set can be located outside the observed sphere. This amounts to modeling lower-resolution data with a higher-resolution Ψ set and thus introducing a bias towards atomicity.

The above considerations illustrate the flexibility offered by the use of the Ψ set and by the novel phase gradient expressions developed in §2.

The authors are indebted to Professor H. Hauptman and Dr J. Navaza for illuminating discussions.

References

Altomare, A., Giacovazzo, C., Guagliardi, A. & Siliqi, D. (1994). *Acta Cryst.* A**50**, 311–317.
Bricogne, G. (1984). *Acta Cryst.* A**40**, 410–445.
Britten, P. L. & Collins, D. M. (1982). *Acta Cryst.* A**38**, 129–132.
Cochran, W. (1955). *Acta Cryst.* **8**, 473–478.

Collins, D. M. (1978). *Acta Cryst.* A**34**, 533–541.

Davies, A. R. & Rollett, J. S. (1976). *Acta Cryst.* A**32**, 17–23.

Debaerdemaeker, T., Tate, C. & Woolfson, M. M. (1985). *Acta Cryst.* A**41**, 286–290.

Debaerdemaeker, T., Tate, C. & Woolfson, M. M. (1988). *Acta Cryst.* A**44**, 353–357.

DeTitta, G. T., Weeks, C. M., Thuman, P., Miller, R. & Hauptman, H. A. (1994). *Acta Cryst.* A**50**, 203–210.

Giacovazzo, C. (1976). *Acta Cryst.* A**32**, 958–966.

Hauptman, H. (1976). *Acta Cryst.* A**32**, 877–882.

Hauptman, H. (1991). *Crystallographic Computing* 5: *from Chemistry to Biology*, edited by D. Moras, A. D. Podjarny & J. C. Thierry, pp. 324–332. IUCr/Oxford Univ. Press.

Hauptman, H., Velmurugan, D. & Han, F. (1991). *Direct Methods of Solving Crystal Structures*, edited by H. Shenk, pp. 403–406. New York: NATO ASI/Plenum Press.

Karle, J. & Hauptman, H. (1950). *Acta Cryst.* **3**, 181–187.

Knossow, M., de Rango, C., Mauguen, Y., Sarrazin, M. & Tsoucaris, G. (1977). *Acta Cryst.* A**33**, 119–125.

Mauguen, Y. (1979). Thèse, Univ. de Paris VI, France.

Mavridis, I. & Papaioannou, G. (1995). In preparation.

Miller, R., DeTitta, G., Jones, R., Langs, D. A., Weeks, C. M. & Hauptman, H. A. (1993). *Science*, **295**, 1430–1433.

Narayan, R. & Nityananda, R. (1982). *Acta Cryst.* A**38**, 122–128.

Navaza, A. & Navaza, J. (1992). *Acta Cryst.* A**48**, 695–700.

Navaza, J. (1985). *Acta Cryst.* A**41**, 232–244.

Navaza, J., Castellano, E. E. & Tsoucaris, G. (1983). *Acta Cryst.* A**39**, 622–631.

Rango, C. de, Mauguen, Y., Tsoucaris, G., Dodson, E. J., Dodson, G. G. & Taylor, D. J. (1985). *Acta Cryst.* A**41**, 3–17.

Rango, C. de, Tsoucaris, G. & Zelwer, C. (1974). *Acta Cryst.* A**30**, 342–353.

Sayre, D. (1952). *Acta Cryst.* **5**, 60–65.

Sayre, D. (1974). *Acta Cryst.* A**30**, 180–184.

Tsoucaris, G. (1970*a*). *Acta Cryst.* A**26**, 492–499.

Tsoucaris, G. (1970*b*). *Acta Cryst.* A**26**, 499–501.

Weeks, C. M., DeTitta, G. T., Hauptman, H. A., Thuman, P. & Miller, R. (1994). *Acta Cryst.* A**50**, 210–220.

Acta Cryst. (1995). A**51**, 763–771

The Interpretation of Single-Crystal Diffuse Scattering using Reverse Monte Carlo Modelling

By V. M. Nield*

*School of Physics and Space Research, University of Birmingham, Edgbaston, Birmingham B*15 *2TT, England*

D. A. Keen

*ISIS Science Division, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX*11 *0QX, England*

and R. L. McGreevy

Studsvik Neutron Research Laboratory, S-611 82 *Nyköping, Sweden*

(*Received* 25 *October* 1994; *accepted* 27 *March* 1995)

Abstract

The scattering from crystals has two components, Bragg and diffuse. In the case of disordered crystalline materials, or those at high temperature, the latter contribution is considerable and contains a great deal of information about any static or thermal disorder in the system. However, interpretation of this diffuse scattering is in general difficult. A new and widely applicable technique for modelling single-crystal diffuse scattering has been developed, which is most useful for the study of disordered crystalline materials. The algorithm, based on the reverse Monte Carlo method, is described in detail, and the information that can be obtained using it is discussed with reference to a study on ice *Ih*.

1. Introduction

The reverse Monte Carlo (RMC) modelling technique, first developed by McGreevy & Pusztai (1988), enables detailed short-range structural information to be obtained from neutron, X-ray and extended X-ray absorption fine structure (EXAFS) measurements (McGreevy & Howe, 1992). A wide variety of different systems has been studied, as diverse as expanded caesium near the critical point (Nield, Howe & McGreevy, 1991) and disordered crystalline solids (Nield, Keen, Hayes & McGreevy, 1992, 1993). The latter group of materials was studied using powder neutron diffraction. There are many recently developed techniques for producing models of crystalline materials, including refinement using simulated annealing in conjunction with both molecular dynamics (Brünger, Kuriyan & Karplus, 1987) and Monte Carlo methods (Newsam, Deem & Freeman,

---

* Present address: Physics Laboratory, University of Kent, Canterbury, Kent CT2 7NR, England.

Acta Crystallographica Section A
ISSN 0108-7673 ©1995