Then one obtains

$$P_+(E_{2\mathbf{h}}||E_{\mathbf{h}}|) = \left\{1+\left[\frac{a_+(E_1,E_2)}{a_-(E_1,E_2)}\right]^{1/2}\exp\left(-|U_1|E_2^2\right)\right\}^{-1}. \quad (20)$$

Let us compare this with the classical tangent formula (Cochran & Woolfson, 1955) for $E_2^2=1$. It then follows from (20) that (if N is high enough)

$$P_+(E_{2\mathbf{h}}||E_{\mathbf{h}}|=1)=\left[1+\left(\frac{1+|U_1|-\frac{3}{2}U_1^2}{1-|U_1|-\frac{3}{2}U_1^2}\right)^{1/2}\right]^{-1}. \quad (21)$$

This gives $P_+=0{\cdot}41$ for $|U_1|=0{\cdot}3$ whereas the classical formula would have given $P_+=0{\cdot}5$.

5. Concluding remarks

Besides the problem of proving that the m equations (2) always give a solution for acceptable values of $E_1, \ldots, E_m$ it also remains to investigate the term δ_N. We believe that δ_N can be approximated very well by 1 (and some heuristic arguments point to that direction), but a lot of research has still to be done.

APPENDIX
Some useful relations

$$\frac{\mathrm{d}}{\mathrm{d}x}I_n(x)=\tfrac{1}{2}I_{n-1}(x)+\tfrac{1}{2}I_{n+1}(x). \quad (A1)$$

$$\frac{\mathrm{d}^2}{\mathrm{d}x^2}I_n(x)=\tfrac{1}{4}I_{n-2}(x)+\tfrac{1}{2}I_n(x)+\tfrac{1}{4}I_{n+2}(x). \quad (A2)$$

$$J_n(ix)=i^nI_n(x); \quad J_{-n}(x)=(-1)^nJ_n(x); \quad I_{-n}(x)=(-1)^nI_n(x). \quad (A3)$$

$$\exp(iz\cos\varphi)=J_0(z)+2\sum_{k=1}^{\infty}i^kJ_k(z)\cos(k\varphi). \quad (A4)$$

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The Direct Method Based on a Fitting of Distributions of Semi-Invariants

BY VÁCLAV KŘÍŽ

Institute of Physics, Czechoslovak Academy of Sciences, Na Slovance 2, 180 40 *Prague* 8, *Czechoslovakia*

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Abstract

A new direct method (called *TRYMIN*) for phase-problem solution is described. At first a methodical procedure is presented for the construction of a direct method. The aim of the calculation is formulated as a consistency between theoretical and calculated distributions of invariants. A minimized function is obtained and an algorithm for its minimization is proposed. The algorithm is based on the partial decomposition of phases into three subsets and on the cyclical improvement of the estimate of local minima. The efficiency of the method has been tested on 23 structures and a short evaluation of the results of computer experiments with test structures is presented.

Definition of the problem

The direct method for the solution of the phase problem is based on a theory that gives for a great number of functions Y_i of phases φ a forecast of their values for the correct phases φ^*. For arbitrary values l_i, u_i the theory affords the probability that the theoretically correct value $Y_i^*=Y_i(\varphi^*)$ satisfies

$$l_i<Y_i^*<u_i.$$

Implementing this theory we can formulate the following task: to construct an algorithm for the generation of a limited number of sets $\bar{\varphi}$ for which the values $\bar{Y}_i=Y_i(\bar{\varphi})$ will satisfy inequalities $l_i<\bar{Y}_i<u_i$ (for *a priori* given l_i, u_i) with frequency in correspondence with the theory.

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We can presume that some of the sets $\bar{\varphi}$ will be close to the correct value φ^*. This assumption is acceptable, because the power of direct methods resides in the fact that the problem is overdetermined. For some number of unknown phases the theory gives typically a twenty times greater number of functions Y_i.

We shall use only functions Y_i of the form

$$Y_i(\varphi) = \text{rsd}\left(\sum_j^m k_{ij}\varphi_j - p_i\right),$$

where k_{ij} are equal to 1, −1 or 0, and most of them are zero; p_i is chosen so that the theoretical probability density function of the absolute values of Y_i has a maximum at zero; and rsd is the real function of the real argument defined as

$$\text{rsd}(x) = z \text{ if and only if } -\pi \le z < \pi,$$

and an integer value $j(x)$ exists that satisfies $x = z + 2\pi j(x)$.

We shall use the symbol K for the matrix (k_{ij}), n for the number of functions Y_i and m for the number of unknown phases. Phases are chosen to fix the origin and their values projected into terms p_i. Now we can suppose that K^TK is a non-singular matrix.

In the examples we shall use only the triple-phase relationships as they are generated by the *MULTAN*80 *SIGMA*2 routine (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) for phase determination. We shall use the symbol κ_i for the parameter of their distribution functions. If Y_i is derived from triple-phase relationships then at most three coefficients k_{ij} for each $i = 1, \ldots, m$ are non-zero and p_i contains the phase shift and the values of the phases fixing the origin.

Fitting the distribution

The principle of crystal structure solution using distribution fitting methods was used by Hašek (1974). However, a general description of these methods was presented later (Hašek, 1984).

The theoretical distribution functions for Y_i may differ for different i. To overcome this problem Hašek (1984) proposes a division of semi-invariants into groups with approximately the same one-dimensional distribution. A similar solution to this problem is given in Appendix 1. The method may be simply explained: For each function Y_i we divide the interval $\langle 0, \pi\rangle$ of possible values of $|\bar{Y}_i|$ into k subintervals (*e.g.* $k = 15$) so that the probability

$$\text{prob}(|Y_i^*| \text{ is element of } j\text{th subinterval})$$

is independent of the serial number of the subinterval and equals $1/k$. Now we can link an integer vector $\bar{J}$ to any calculated vector $\bar{Y}$ so that $\bar{J}_i$ is the serial number of the subinterval containing the value $|\bar{Y}_i|$. For the theoretically correct vector Y^* each number $1, 2, \ldots, k$ must be contained in the linked vector J^* with the same frequency.

Let n be the total number of elements $\bar{J}$ and let n_j be the number of such $\bar{J}_i$ for which $\bar{J}_i = j$ $(j = 1, \ldots, k)$. We can express the measure of the consistency of $\bar{Y}$ (and $\bar{\varphi}$) with the theory as a function (chi-square test)

$$G(\bar{\varphi}) = \sum_j^k (n/k - n_j)^2 k/n.$$

Imitative function

The previous expression transforms the solution of the phase problem into a function minimization problem.

The properties of G are very bad for the application of some minimization technique: G is not a continuous function, the regions of continuity are very small and G is constant in these regions. In some stages of the minimization process it may be useful to replace G by an imitative function F. This function must have the following two features: one of the best minima of F must be close to φ^*; and effective tools must be available for searching for 'good' minima of F.

The first demand can be satisfied if the expected value $\langle F(\varphi^*)\rangle$ is small in comparison with the other values of F. It may be expressed by the condition

$$D(F) \text{ must be minimum,}$$

where $D(F) = (\langle F\rangle - \min(F))/(\|F\| - \min(F))$; $\langle F\rangle$ denotes the estimated value of F, $\min(F)$ is the value of the global minimum of F, and $\|F\|$ is the value of F expected from random phases:

$$\|F\| = \int_V F(\varphi)\,\mathrm{d}\varphi \Big/ \int_V \mathrm{d}\varphi,$$

where

$$V = \langle -\pi, \pi\rangle \times \cdots \times \langle -\pi, \pi\rangle.$$

For the function F to be simply minimized we shall consider only the form

$$F(\varphi) = \sum_i^n f_i[Y_i(\varphi)].$$

Functions f_i must contribute uniformly to the sum function F. This may be expressed by the normalization conditions

expected values $\langle f_i\rangle = 1$ and minimum values $\min(f_i) = 0$. For simple f_i it is easy to express $\langle F\rangle$ and $\|F\|$ analytically:

$$\langle F\rangle = \sum_i^n \langle f_i\rangle = n \text{ and } \|F\| = \sum_i^n \|f_i\|,$$

where

$$\|f_i\| = \left[\int_{-\pi}^{\pi} f_i(x)\,\mathrm{d}x\right] \Big/ 2\pi.$$

Table 1. *Coefficients u_i, v_i, u_i' as a function of κ_i*

κ_i	u_i	v_i	u_i'
1·0	1·03	0·22	0·38
1·5	1·59	0·20	0·55
2·0	2·40	0·18	0·85
2·5	3·45	0·16	1·34
3·0	4·68	0·15	2·14
3·5	6·01	0·14	3·46
4·0	7·38	0·13	5·63
4·5	8·76	0·12	9·22
5·0	10·12	0·12	15·14
5·5	11·47	0·11	24·89
6·0	12·81	0·11	40·98

It is reasonable to approximate $\min(F)$ by zero. This assumption yields postulates for f:

$$\langle f_i \rangle = 1 \quad \text{and} \quad \min(f_i) = 0$$
$$\text{and } \|f_i\| \text{ is maximum.}$$

Examples of imitative functions and the comparison with functions used in traditional direct methods are given in Appendix 2. The results presented there illustrate that the idea of imitative functions is well applicable to the phase problem. Now we can try to construct a new function as a 'better imitation'.

Suppose we have imitative functions in the form

$$F(\varphi) = \sum_l w_l \operatorname{rsd}^2 \left(\sum_j^m a_{lj}\varphi_j - c_l \right).$$

Such a function for triple-phase relationships in the form

$$F(\varphi) = \sum_i^n \kappa_i Y_i^2(\varphi)$$

is used in the program *YZARC* (Wright, 1983). A method for the minimization of such functions for a very sparse matrix $A = (a_{ij})$ is given by Kříž (1982). Some results of this work are given in Appendix 3.

For the construction of a new imitative function we can consider

$$f_i[Y_i(\varphi)] = u_i\{Y_i^2(\varphi) + v_i \operatorname{rsd}^2[Y_i(\varphi) + s_i]\} - u_i v_i s_i^2/(1+v_i).$$

This formula satisfies the requirement $\min(f_i) = 0$. For the next two requirements, $\langle f_i \rangle = 1$ and $\|f_i\|$ maximal, there is an analytical solution from which the following conclusions result: If Y_i contains only special phases then v_i must be zero. For general Y_i, $s_i = \pi$ is obtained. Table 1 shows some values of u_i and v_i for general Y_i and values of u_i' for special Y_i if Y_i are triple-phase relationship.

We can interpret the non-zero values of v_i and s_i as a useful and important prevention against the so-called trivial or large-peak solution. But non-zero values of v_i retard the iteration process for the calculation of local minima. As a compromise we can use only a part (*e.g.* 20%) of v_i non-zero and for the remaining indexes select $v_i = 0$ and use u_i according to Table 3 in Appendix 2.

Improvement of local minima

The algorithm described in Appendix 3 produces stable minima of the function F. Stable minima are 'better local minimum points', but there is a problem in searching for the '*best* local minimum points'. For real cases (large values of m, n) the number of stable minima is practically infinite and further improvement is necessary.

A method for the improvement of local minima consists of two steps:

(*a*) The unknown phases are suboptimally decomposed into three subsets with approximately equal number of elements, so that the (weighted) number of subfunctions containing the phases from one subset and the phases from the remaining ones is as small as possible. The decomposition is made by an algorithm based on a graph representation of a sparse matrix K. The complete description of this algorithm is given by Kříž (1982). For a formal definition of the phase-set decomposition see Appendix 4.

(*b*) Good local minima of F are chosen as starting points for improvement. These sets are stored in the table T. From table T the best set t^* with minimum value $G(t^*)$ is chosen. The values of all phases from one subset given by the decomposition (about $m/3$ phases) are fixed. The minimization procedure described in Appendix 3 is applied only to the rest of the phases (the unfixed $2m/3$ phases) and a new local minimum t' is calculated. If t' and t^* differ considerably ($\pi/5$ per phase, for example) then t' is put into table T, otherwise if $G(t') < G(t^*)$ then t' replaces t^*. From three to ten trials for each subset may be processed and as a result there is an improvement of starting vector t^* (the output for the Fourier procedure) and an improvement of sets in table T (for the next generation).

Some local minima of F (*e.g.* 50–500) are needed as initial values for the table T. These local minima are calculated by iterations (described in Appendix 3) from starting points which are assigned randomly or better by the solution of the 'regular choice' from the set of functions Y_i. The phase set φ' is the solution of the regular choice from Y_i, if $Y_i(\varphi') = 0$ for the strongest functions Y_i (Appendix 5).

Remark

The operations concerning the table T are the essential step from the good local minima of the imitative function F to the global (or 'very good') minimum of the chi-square test G.

One may save on computing time by the following procedure: choose a subset of 50–70% unknown phases and at first consider only functions Y_i depending on this subset; solve the problem for reduced function G (and F) and generate 20–50 sets (good minima of the reduced system); extend these sets by setting the remaining phases randomly; calculate

local minima from starting points given by these extended sets and use these minima as initial values for a new table T; and apply the improvement for the final solution of the primary system.

Trial phases

A small subset of phases (from one to six) can be chosen as trial phases, as in the multiple-tangent-formula method (Woolfson, 1976), and then the best minima for all combinations of the possible values of these phases (or six values $\pi/6, 3\pi/6, \ldots, 11\pi/6$ for general phase) can be searched for. There are two reasons for this procedure: the minimum close to the 'physical solution' may be more dominant among other minima of the functions G and F if the trial phases are replaced by the correct values; and the simplification of function F by fixing the small subset of phases may be significant and useful.

On the other hand the number of trial phases must be small, because of the exponential growth of computing time.

Evaluation procedure of numerical experiments

For numerical experiments only the program system *MULTAN*80 (Main *et al.*, 1980) was available as a tool for the production of functions Y_i. This fact reduces testing possibilities to $\sum_2$ relationships only.

If at least one phase in the relationship were general, the distribution function was supposed to be of the form

$$\exp[\kappa \cos(Y)]/2\pi I_0(\kappa),$$

where I_0 is a modified Bessel function of the second kind.

The probability $[1+\exp(-\kappa)]^{-1}$ was supposed for the special phase relationships (triplets) with zero values.

All the normalized structure amplitudes generated by *NORMAL*80 were used and $\sum_1$ relationships were suppressed in the *MULTAN FIRST* program.

Three approaches were used for structure solution. In class 1 50% of unknown phases were taken into account and 20–40 phase sets were produced. All these sets were extended and used for the next improvement. There were maximally ten final sets generated and the three with the best chi-square values were interpreted using programs *EXFFT*80 and *SEARCH*80 from the *MULTAN*80 package.

Class 2 differs from class 1 only in the fact that 70% of the unknown phases were taken into account.

Class 3 differs significantly. 100% of the unknown phases were used and also four to six trial phases. Five to eight sets were generated for different combinations of trial phase values consecutively.

Only the approaches of class 1 and 2 may be useful in practical structure solutions. Class 3 is too time consuming. The typical computing time for a computer like the IBM 4341-1 (*ca* 800 000 operations s^{-1}) is

class	minutes
1	90
2	150
3	900–2000.

Table 2. *Test structures*

No.	Name, formula, space group, Z	NA/NF	C	CHIQ
1	TURIO, $C_{15}H_{24}O_2$, $P6_322$, $Z=12$	17/17	1	35
2	EX4, $C_{12}H_{20}N_2O_2$, $P2_12_12_1$, $Z=4$	16/16	2	140
3	QUINOL, $C_6H_6O_2$, $R\bar{3}$, $Z=54$	24/24	1	340
4	DIAM, $C_{14}H_{20}O$, $P4_2/n$, $Z=8$	15/15	2	480
5	INOS, $C_6H_{12}O_6.H_2O$, $P2_1/n$, $Z=8$	26/25	2	227
6	EX1, $C_{17}H_{13}NS$, $P2_1/c$, $Z=4$	19/19	1	167
7	ALKA, $C_{31}H_{39}N_3O_5$, $P2_12_12_1$, $Z=4$	39/38	2	121
8	JINDRA, $C_{12}H_{15}N_3O_3$, $P2_1$, $Z=2$	18/18	2	19
9	EX2, $C_9H_{14}N_2O_2$, $P2_12_12_1$, $Z=4$	14/14	1	6
10	EX5, $C_{10}H_{16}N_2O_2$, $P2_12_12_1$, $Z=4$	14/14	1	11
11	EX3, $C_{12}H_{20}N_2O_2$, $P2_12_12_1$, $Z=4$	16/16	1	63
12	LOGANIN, $C_{17}H_{26}O_{10}$, $P2_12_12_1$, $Z=4$	27/27	1	62
13	BOBBY, $NaCaN(CH_2CO_2)_3$, $P2_13$, $Z=4$	5/5	2	17
14	MUNICH1, $C_{20}H_{16}$, $C2$, $Z=8$	40/40	3	12
15	BED, $C_{26}H_{26}N_4O_4$, $I4$, $Z=8$	34/22	3	149
16	TPH, $C_{24}N_2H_{20}$, $C222_1$, $Z=12$	39/39	3	9
17	AZET, $C_{21}H_{16}ClNO$, $Pca2_1$, $Z=8$	48/5	2	356
18	SCHWZ2, $C_{46}H_{70}O_{27}$, $P1$, $Z=1$	73/0		30
19	MGHEX, $C_{48}H_{68}N_{12}O_{12}Mg.2ClO_4.4CH_3CN$, $P3_1$, $Z=3$	95/0		2362
20	SELENID, $C_{22}H_{28}O_2Se$, $P2_1$, $Z=2$	25/4	2	1329
21	ApApA, $C_{30}H_{37}N_{15}O_{16}P_2.6H_2O$, $P4_12_12$, $Z=8$	69/0		433
22	ERGO, $C_{28}H_{44}O$, $P2_12_12_1$, $Z=8$	58/0		42
23	GOLDMAN2, $C_{28}H_{16}$, Cc, $Z=8$	56/0		59

No. is sequence number.
C is class necessary for successful solution.
NA is number of non-H atoms in the asymmetric unit.
NF is number of non-H atoms found by *TRYMIN*.
CHIQ is a minimum chi-square test value, which was calculated for published and correct sets and for degree of freedom $k=14$.
References: 1, 3, 4, 5, 12–23 (Sheldrick, 1982); 2 (Symerský, Huml & Petříček, 1987); 6 (Podlaha, Podlahová & Symerský, 1987); 7 unpublished; 8 (Symerský, Bláha & Ječný, 1988); 9 (Symerský, Bláha & Langer, 1987*a*); 10 (Symerský, Huml & Petříček, 1987); 11 (Symerský, Bláha & Langer, 1987*b*).

Testing structures

The efficiency of the program system *TRYMIN* has been tested for 23 structures. 17 of them were taken from the testing-structures set of Sheldrick (1982), consisting of difficult and interesting examples. The correct phase values were known as well as the positions of atoms for all tested structures. Examples 3, 4, 5 and 6 are centrosymmetric, the other are non-centrosymmetric.

In Table 2 some characteristics of the structures are given: sequence number, working name, chemical formula, space group, number of formulas in the unit cell, number of non-H atoms in the asymmetric unit, the class and the best chi-square value corresponding to the correct set.

The structures 1–13 are easily solved. Approximate positions of the non-H atoms in the asymmetric unit

were found among the first three phase sets with the lowest chi-square values. One atom was missing in structures 5 and 7.

These structures possess relatively small numbers of atoms and, excluding 13, they do not contain heavy atoms.

Structures 14–23 are notoriously difficult structures for direct methods (Sheldrick, 1982). However, with greater expense of computational effort, all atoms of MUNICH1 and TPH were found, and also the essential fragment of BED (22 atoms). It must be noted that these three structures also do not contain either a great number of atoms nor heavy atoms.

No successful solution was found for structures 17–23. Only a small number of atoms, if any, were found by the Fourier transform of several most promising phase sets with the lowest chi-square values. These structures contain a greater number of atoms and some of them also contain heavy atoms.

To decide if the application of the present method for triple-phase relationships is useful in practice we can compare the results of a *MULTAN*87 (Debaerdemaeker, Germain, Main, Tate & Woolfson, 1987) test on an identical set of examples (Symerský & Kříž, 1989). The default run of *MULTAN*87 gave a solution for the seven easiest structures (4, 5, 6, 9, 10, 11 and 13). The use of the statistically weighted tangent formula (*SWTR*) and the generation of more phase sets (*RANTAN MAXSET* 300) gave similar results to the use of *TRYMIN*. *MULTAN*87 was more successful in examples 18 and 23 and it was also less time consuming than *TRYMIN*. It has failed to solve example 16.

As no implementation of the fitting of distributions for quartets was made, comparison with the results of the Sayre tangent formula was not possible.

Concluding remarks

These examples confirm that the system *TRYMIN* is capable of solving the phase problem. There are no problems with trivial solutions. The sets limited to a trivial solution have enormously great chi-square values and are automatically excluded from the minimization process.

The presented formulation of the phase-problem solution as a distribution-fitting task reduces the demands for the number of sets necessary to find a solution. Of course, good consistency of expression is necessary between the predicted distributions and those calculated from semi-invariants of the physically correct set of phases.

If the consistency were not good, then it would be impossible to reach results useful in practice by means of the method described here. This is the case with the unsuccessful determination of structures MGHEX, SELENID, ApApA and AZET. The chi-square value of the sets generated by *TRYMIN* is significantly better than that generated for a correct set.

The consistency between physically correct solutions and theoretically correct solutions for the remaining examples, SCHWZ2, GOLDMAN2 and ERGO, may be characterized as acceptable, but not expressive. *TRYMIN* has generated here a great number of quite uninterpretable sets with chi-square values close to the value for a correct set. Similarly, it is possible to evaluate the results for examples 14, 15 and 16. The only difference is that here the correct set was successfully generated.

For both types of unsuccessful structures a very different method may be useful. It need not be so close to the theory, but it must generate a great number of diverse sets for Fourier transform (Yao, 1981).

On the other hand, we can hope that better consistency between the theory and the physics may be obtained for more exact triplet distributions or for distributions of more complicated semi-invariants (such as quartets). Then the present method could bring an important extension of direct-methods possibilities.

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APPENDIX 1
Distribution-fitting algorithm

Let X be a random variable with a continuous probability density function $p(x)$. The transformed random variable Z

$$Z = \int_{-\infty}^{X} p(x)\,\mathrm{d}x$$

has uniform probability distribution function on the interval (0, 1).

Let X be a discrete random variable (X may be only 0 or 1). Let *RANDOM* be independent random variables with a uniform distribution on interval (0, 1). Let Z be a random variable constructed by the rule:

if $X = 0$ then $Z = \text{prob}\,(X = 0) \times RANDOM$

else $Z = \text{prob}\,(X = 0) + \text{prob}\,(X = 1)$

$\times RANDOM$;

Table 3. *Comparison of traditional functions and imitative functions*

$$-\sum \kappa_i \cos[Y_i(\varphi)] \text{ with } -\sum v_i \cos[Y_i(\varphi)],$$

$$\sum \kappa_i Y_i^2(\varphi) \text{ with } \sum w_i Y_i^2(\varphi),$$

$$\sum \{\cos[Y_i(\varphi)] - \langle \cos(Y_i^*)\rangle\}/\mathrm{var}_i \text{ with } \sum u_i \{\cos[Y_i(\varphi)] - c_i\}^2,$$

where Y_i are general three-phase relationships; $\langle\cos\rangle$ is an abbreviation for $\langle \cos(Y_i^*)\rangle$.

κ_i	v_i	w_i	$\langle\cos\rangle$	c_i	$1/\mathrm{var}_i$	u_i
1·0	0·98	0·73	0·45	0·77	2·82	2·18
1·5	1·34	1·08	0·60	0·80	4·05	3·47
2·0	1·79	1·53	0·70	0·82	6·09	5·55
2·5	2·31	2·08	0·77	0·85	9·19	8·68
3·0	2·85	2·69	0·81	0·86	13·53	13·03
3·5	3·41	3·31	0·84	0·88	19·15	18·66
4·0	3·97	3·93	0·86	0·89	26·01	25·51
4·5	4·53	4·55	0·88	0·90	34·03	33·54
5·0	5·08	5·16	0·89	0·91	43·12	42·67
5·5	5·63	5·77	0·90	0·92	53·24	52·75
6·0	6·18	6·37	0·91	0·92	64·35	63·88

then Z has a uniform probability distribution on the interval (0, 1).

These two transformation rules may be used for calculated values $\bar{Y}_i = Y_i(\bar{\varphi})$. Then the test of compatibility of calculated and expected frequencies may be simply realized by the chi-square test.

Remark

The result of this test must be interpreted only relatively, because the values $\bar{Y}_i$ are not a sample of independent observations.

APPENDIX 2
Examples of imitative functions

The well known tangent formula can be derived from an application of the cyclic coordinate descent method to the minimization of the function

$$-\sum_i^n \kappa_i \cos[Y_i(\varphi)]$$

for three-phase invariants.

For $f_i(\varphi)$ in the form $d_i - u_i \cos[Y_i(\varphi) - y_i]$ we can (after application of the postulates for imitative functions) obtain the task:

$$\text{minimization of } c_0 - c\sum_i^n v_i \cos[Y_i(\varphi)],$$

where c_0, c are constants and the weights v_i (for three-phase relations with general phases) depend on κ_i as shown in Table 3. The differences between v_i and κ_i are negligible. This means that the function minimized in the program *MULTAN* can be derived as an imitative function.

Analogously for $f_i(\varphi) = u_i \,\mathrm{rsd}^2[Y_i(\varphi) - y_i]$ we can obtain the task:

$$\text{minimization of } c'\sum_i^n w_i Y_i^2(\varphi),$$

where c' is a constant and the dependence of w_i on κ_i is as shown in Table 3. We can see that this imitative function is practically identical with the function minimized by the program *YZARC* (Baggio, Woolfson & Germain, 1978; Wright, 1983).

Hauptman, Fisher, Hancock & Norton (1969) proposed the minimization of

$$\sum_i^n \{\cos[Y_i(\varphi)] - \langle\cos(Y_i^*)\rangle\}^2/\mathrm{var}_i.$$

For $f_i(\varphi) = u_i\{\cos[Y_i(\varphi)] - c_i\}^2$ we obtain an imitative function that is again nearly identical.

APPENDIX 3
Local minima of the weighted sum of the squares of residuals of the phase relationships

Definitions

In this Appendix we shall work with the phases expressed in cycles, *i.e.* after transformation of the interval $\langle -\pi, \pi\rangle$ into $\langle -1/2, 1/2\rangle$. In order to simplify the following theorems we shall consider (in these theorems) only general phases.

Let m be the number of unknown phases $x_1, \ldots, x_m$ and let n be greater than m. Let $A = (a_{ij})$ be an $m \times n$ sparse matrix with non-zero elements equal to 1 or -1. Suppose that A^TA is a non-singular matrix. Let c be a real vector of length n. Let the phase relationships be expressed in the form

$$\sum_j a_{ij}x_j - c_i = 0 \text{ modulo } 1, \quad \text{where } i = 1, \ldots, n.$$

The residual r_i is defined by

$$r_i = c_i - \sum_l a_{il}x_l - j_i,$$

where j_i is the integer for which the inequalities $-0{\cdot}5 \le r_i < 0{\cdot}5$ are valid.

Let w_i be positive real numbers. Denote $f(x) = \sum_i^n w_i r_i^2$, where $f(x)$ is the function to be minimized. Let W be an $n \times n$ diagonal matrix, where the diagonal elements are w_i. Let $j(x)$ be a vector of integers of length n which satisfies $-0{\cdot}5 \le r(x) < 0{\cdot}5$, where $r(x) = Ax - c + j(x)$ is a vector of residua. The function $f(x)$ may be expressed in the form

$$f(x) = r(x)^T W r(x).$$

Mathematical properties of $f(x)$

Theorem 1. Function $f(x)$ is continuous for all x. If k is an integer vector of length m, then $f(x+k) = f(x)$ for all x. The gradient and Hessian of f exists in point x if and only if absolute values of all components of vector $r(x)$ are not equal to 0·5. This is specified by

$$\nabla f(x) = 2A^TWr(x), \quad \nabla^2 f(x) = 2A^TWA.$$

Theorem 2. Point x is a local minimum point if and only if a continuous gradient exists at the point and the gradient is zero.

Theorem 3. The problem of finding the global minimum point of $f(x)$ is a quadratic integer programming problem.

Stable minima

Theorem 3 shows that our problem is the problem of quadratic integer programming. However, integer programming methods are inconvenient here, because the size of the problem is too large. Steepest descents or other gradient methods do not apply well here too, because $f(x)$ does not have continuous partial derivatives. Also, the regions with a continuous gradient are very small (practically infinitely small). A cyclic coordinate descent method (Luenberger, 1973) seems to be attractive here. This method is based on the idea that a better approximation of the minimum (new iterative point x) is calculated from $x^A = (x_1^A, \ldots, x_m^A)$ by solving

$$f(x^B) = \underset{x_i}{\text{minimize}}\, f(x_1^A, \ldots, x_i, \ldots, x_m^A)$$

where i is cyclically $1, 2, \ldots, m, 1, 2, \ldots, m, 1, \ldots$ *etc.* Minimization in one coordinate is simple for special phases (by comparison of two function values). In the case of the general phase there is a special fast algorithm.

Convergence properties are discussed by Kříž (1982): the cyclic coordinate descent algorithm for minimization of function $f(x)$ converges to the local minimum point for each starting point; the speed of convergence is comparable with Gauss-Seidel iterations for a positive definite matrix $A^T WA$; and the iterative process converges to one from local minimum points x^* with properties

$$f(x^*) < f(x^* + ze_i), \quad i = 1, \ldots, m$$

where e_i is the ith unit vector, and z is an arbitrary real value. We shall call these points x 'stable minima'.

APPENDIX 4
Decomposition of phases into three subsets

Let all the phases φ be decomposed into three subsets φ_A, φ_B and φ_C. As each function f_i in the expression

$$F(\varphi) = \sum_i^m f_i[\, Y_i(\varphi)]$$

depends only on a few phases we can rearrange the summation so that F can be expressed as

$$\begin{aligned} F(\varphi) &= F_1^A(\varphi_A) + F_0^A(\varphi_A, \varphi_B, \varphi_C) + F_2^A(\varphi_B, \varphi_C) \\ &= F_1^B(\varphi_B) + F_0^B(\varphi_A, \varphi_B, \varphi_C) + F_2^B(\varphi_A, \varphi_C) \\ &= F_1^C(\varphi_C) + F_0^C(\varphi_A, \varphi_B, \varphi_C) + F_2^C(\varphi_A, \varphi_B). \end{aligned}$$

We define the weight of the decomposition $\varphi = \{\varphi_A, \varphi_B, \varphi_C\}$ as

$$w(\varphi_A, \varphi_B, \varphi_C) = \max(\|F_0^A\|, \|F_0^B\|, \|F_0^C\|).$$

Let nmb (X) denotes the number of elements of vector X. We define an equable decomposition as a decomposition for which

$$|\text{nmb}(\varphi_X) - \text{nmb}(\varphi)/3| < \text{nmb}(\varphi)/50$$

for $X = A$, B and C.

The decomposition which is equable and has the minimum weight is called the optimal decomposition.

In real cases the weight of the optimal decomposition is about $\|F\|/2$.

APPENDIX 5
Regular choice and its solution

Let M be the set of all non-singular $m \times m$ submatrices from matrix K. For each matrix K' of M the weight $w(K')$ is defined as a sum of $\|f_j\|$ of the chosen Y_j. We define the regular choice as the choice given by matrix $K' \in M$ with maximal value $w(K')$.

Now for chosen functions Y_j we presume zero to be the most probable value. This means that we must solve a regular system

$$Y_j(\varphi) = 0,$$

where the indexes j are defined by the regular choice. A number of its solutions is given by the absolute value of the determinant of matrix K'. This fact can be illustrated, for example, by the system

$$\text{rsd}(\varphi_1 + \varphi_2) = 0$$

$$\text{rsd}(\varphi_1 - \varphi_2 + \pi) = 0;$$

there are two solutions:

$$(\varphi_1, \varphi_2) = (\pi/2, 3\pi/2)$$

$$(\varphi_1, \varphi_2) = (3\pi/2, \pi/2).$$

Let r be the absolute value of the determinant of K' and let $\varphi^{(1)}, \ldots, \varphi^{(r)}$ be a complete solution of regular choice. As initial values for table T we shall use stable minima $t^{(1)}, \ldots, t^{(r)}$. They will be calculated from starting points $\varphi^{(1)}, \ldots, \varphi^{(r)}$ by the iterative process described in Appendix 3.

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New Methods for Deriving Joint Probability Distributions of Structure Factors. II. Strengthening the Triplet Relationship in *P*1

BY J. BROSIUS

Université du Burundi, Département de Mathématiques, BP 2700 Bujumbura, Burundi

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Abstract

Two methods are discussed in detail. In the first method the triplet relationship is treated using the first neighborhood, and the quartet relationship using its second neighborhood. For the triplet relationship it is found that the reliability

$$\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}-\varphi_{\mathbf{h}+\mathbf{k}}\simeq 0$$

is enhanced when

$$R_{\mathbf{h}}\simeq R_{\mathbf{k}}\simeq R_{\mathbf{h}+\mathbf{k}}$$

and large. This conclusion is drawn from formula (16) giving the conditional probability of $\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}-\varphi_{\mathbf{h}+\mathbf{k}}$ using an asymptotic development up to and including terms of order $N^{-1/2}$. For the quartet relationship it is found that the reliability that

$$\varphi_{\mathbf{h}}+\varphi_{\mathbf{k}}+\varphi_{\mathbf{l}}-\varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}}\simeq \pi$$

given $R_{\mathbf{h}+\mathbf{k}}\simeq R_{\mathbf{h}+\mathbf{l}}\simeq R_{\mathbf{k}+\mathbf{l}}\simeq 0$ is diminished when

$$R_{\mathbf{h}}\simeq R_{\mathbf{k}}\simeq R_{\mathbf{l}}\simeq R_{\mathbf{h}+\mathbf{k}+\mathbf{l}}$$

and large. This conclusion is drawn from formula (19) using similar calculations for the triplet relationship. A heuristic theoretical discussion of this last result trying to explain this difference with the usual theories is given. In the second method the triplet relationship is treated using its *first* neighborhood. These calculations have been done using a 'normal' asymptotic development up to and including terms of order $N^{-1/2}$. As a result a formula (28) is obtained that is (at least theoretically) able to predict negative cosine values. A third method that is proposed where one uses the ideas of Patterson superposition will be discussed in detail in a forthcoming paper.

Introduction

Let us consider an equal-atom structure with space group *P*1. For N atoms with respective position vectors $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N$ the normalized structure factor $E_{\mathbf{h}}$ for the reciprocal-lattice vector $\mathbf{h}$ becomes

$$E_{\mathbf{h}}=N^{-1/2}\sum_{j=1}^{N}\exp(2\pi i\mathbf{h}\,.\,\mathbf{r}_j).$$

For deriving joint probability distributions of structure factors we shall consider the atomic vectors $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N$ as random vectors and this leads us to consider the random variable

$$\hat{E}_{\mathbf{h}}=N^{-1/2}\sum_{j=1}^{N}\exp(2\pi i\mathbf{h}\,.\,\mathbf{x}_j) \qquad (1)$$

where the $\mathbf{x}_j$ are random variables that range over the possible positions of the atomic position vectors $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N$. Usually one considers the $\mathbf{x}_j$ to be mutually independent and one imposes each $\mathbf{x}_j$ to range uniformly over the unit cell. Another approach (Brosius, 1985) is to observe that all $\mathbf{x}_i-\mathbf{x}_j$ only have to range over the set of all Patterson vectors. In order to impose this latter condition one can use two methods: (1)

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