Crystal, off-Bragg:

$$\int P(\theta)dAd\theta$$

$$= (1/N_3)[\Delta q_3 a_3/2\sin^2(\pi\, q_3 a_3)](\sin 2\theta_B/\sin 2\theta)R_B.$$

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A Tangent Formula Derived from Patterson-Function Arguments. II. Practical Tests with Single-Crystal Intensity Data

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Abstract

A series of test calculations of the tangent formula derived from Patterson-function arguments [Rius (1993). Acta Cryst. A49, 406–409] using single-crystal intensity data is presented. This new tangent formula has been compared with the results reported [Sheldrick (1990). Acta Cryst. A46, 467–473] for (a) the tangent formula incorporating the most reliable negative quartets and (b) its extension to the phase-annealing method. The success rate of the new tangent formula is an order of magnitude higher than that of (a), is better than that of (b) when the origin can float in at least one direction, and is similar to that of (b) for other space groups.

1. Introduction

Nowadays, the applicability of direct methods to larger crystal structures constitutes an active research field. Since the number of correct solutions produced by direct methods tends to decrease with increasing size of the structure, it is interesting to know which tangent formulas are most effective. Eventually, these tangent formulas or the functions that they maximize or minimize could be selected for further development. Logically, to determine their relative efficiencies, the different tangent formulas have to be tested on the same structures. Unfortunately, this has not been common practice; to date, each new tangent formula has been tested using an arbitrary selection of structures. In order to modify this situation, the test structures given by Sheldrick (1990) have been selected as 'reference' structures in this work. In this way, besides testing the tangent formula derived from Patterson-function arguments, it has also been possible to compare it with the tangent formula that incorporates the most reliable negative quartets. A brief introduction to both tangent formulas follows.

1.1. The tangent formula incorporating the most reliable negative quartets

Most multisolution direct-methods procedures (Germain & Woolfson, 1968) are based on the maximization of a certain function expressed in terms of the collectivity Φ of phases of the reflections with large E's (the basis set). The simplest function of Φ

$$Z(\Phi) = \sum_{\mathbf{h}}\sum_{\mathbf{h}'} E_{-\mathbf{h}}E_{\mathbf{h}'}E_{\mathbf{h}-\mathbf{h}'}\cos\Phi_3(\mathbf{h}, \mathbf{h}') \qquad (1)$$

follows from the product of all the conditional probability distributions of triplets that only involve

reflections of the basis set,

$$\prod_{\mathbf{h},\mathbf{h}'}\mathcal{P}(\varPhi_3|K) \propto \exp[2N^{-1/2}Z(\varPhi)]. \qquad (2)$$

$\varPhi_3(\mathbf{h},\mathbf{h}')$ denotes the phase of the triple phase invariant $-\mathbf{h}+\mathbf{h}'+(\mathbf{h}-\mathbf{h}')$, $K = 2N^{-1/2}|E_{-\mathbf{h}}E_{\mathbf{h}'}E_{\mathbf{h}-\mathbf{h}'}|$ represents the concentration parameter of the associated probability distribution and N is the number of atoms in the unit cell. For smaller structures, (2) and consequently $Z(\varPhi)$ will be close to a maximum with correct phases. As shown by Debaerdemaeker, Tate & Woolfson (1985), $Z(\varPhi)$ can be maximized by means of the conventional tangent formula of Karle & Hauptman (1956),

$$\varphi_{\mathbf{h}} = \text{phase of} \left\{ \sum_{\mathbf{h}'} E_{\mathbf{h}'} E_{\mathbf{h}-\mathbf{h}'} \exp[i(\varphi_{\mathbf{h}'} + \varphi_{\mathbf{h}-\mathbf{h}'})] \right\}. \qquad (3)$$

Nevertheless, the correct phases may be far from a global maximum of $Z(\varPhi)$ for certain space groups (e.g. for space group $P1$). The function $Z(\varPhi)$ can be improved by including the conditional probability distributions $\mathcal{P}(\varPhi_4)$ of the most reliable negative quartets $-\mathbf{h} + \mathbf{k} + \mathbf{l} + \mathbf{m} = 0$ (Schenk, 1974; Hauptman, 1974; Giacovazzo, 1976). The improved function results from multiplication of the left-hand side of (2) by

$$\prod_{\mathbf{h},\mathbf{k},\mathbf{l}} \mathcal{P}(\varPhi_4|K'), \qquad (4)$$

where $K' = 2N^{-1}|E_{-\mathbf{h}}E_{\mathbf{k}}E_{\mathbf{l}}E_{\mathbf{m}}|$ denotes the concentration parameter of $\mathcal{P}(\varPhi_4)$. In general, the addition of (4) to the left-hand side of (2) requires a weighting factor, q, to compensate for the smaller number of reliable negative quartets. This modified function can be maximized by means of the extended tangent formula,

$$\varphi_{\mathbf{h}} = \text{phase of} \left\{ \sum_{\mathbf{h}'} E_{\mathbf{h}'} E_{\mathbf{h}-\mathbf{h}'} - qN^{-1/2} \sum_{\mathbf{k}} \sum_{\mathbf{l}} E_{\mathbf{k}} E_{\mathbf{l}} E_{\mathbf{m}} \right\}, \qquad (5)$$

a complete test of which is given by Sheldrick (1990).

1.2. The tangent formula derived from Patterson-function arguments

$Z(\varPhi)$ can also be improved once its physical meaning is understood. As pointed out by Cochran (1952), $Z(\varPhi)$ may be regarded as the reciprocal-space equivalent of the integral

$$V \int_V \rho^3(\mathbf{r})d\mathbf{r}. \qquad (6)$$

As he argued, it will be large and positive because of the peaked nature of the electron-density function ρ. It is difficult, however, to extract more conclusions from this physical interpretation. As shown by Rius (1993), $Z(\varPhi)$ can be reinterpreted in the form of the integral

$$V \int_V P_o(\mathbf{u})P(\mathbf{u}, \varPhi)d\mathbf{u} = \sum_{\mathbf{H}} E_{\mathbf{H}} G_{\mathbf{H}}(\varPhi). \qquad (7)$$

This integral measures the coincidence between the two Patterson-type syntheses P_o and $P(\varPhi)$. The corresponding Fourier coefficients are the amplitudes of the structure factors of the true structure $(E_{\mathbf{H}})$ and of the squared structure $[G_{\mathbf{H}}(\varPhi)]$, respectively. The analysis of integral (7) indicates that $Z(\varPhi)$ will be dominated by the origin peaks of the Patterson-type syntheses. To avoid this, i.e. to give more influence to the nonorigin peaks, the origin peak of the observed function P_o is subtracted so that the modified $Z(\varPhi)$ becomes

$$\sum_{\mathbf{H}}(E_{\mathbf{H}} - \langle E_{\mathbf{H}} \rangle)G_{\mathbf{H}}(\varPhi). \qquad (8)$$

This expression can be maximized by means of the following tangent formula (Rius, 1993)

$$\varphi_{\mathbf{h}} = \text{phase of} \left\{ \sum_{\mathbf{h}'} X_{\mathbf{h},\mathbf{h}'} E_{\mathbf{h}'} E_{\mathbf{h}-\mathbf{h}'} \right. \\ \left. + \sum_{\mathbf{l}}(E_{\mathbf{l}} - \langle E_{\mathbf{H}} \rangle)E_{\mathbf{h}-\mathbf{l}} \exp i\phi_{\mathbf{l}} \right\} \qquad (9)$$

with $\mathbf{l}$ denoting those reflections not belonging to the basis set, $\phi_{\mathbf{l}}$ being the phase of $G_{\mathbf{l}}$ and $X_{\mathbf{h},\mathbf{h}'}$ being defined as

$$X_{\mathbf{h},\mathbf{h}'} = \left\{ [(1 - \langle E_{\mathbf{H}} \rangle)/E_{\mathbf{h}}] + [(1 - \langle E_{\mathbf{H}} \rangle)/E_{\mathbf{h}'}] \right. \\ \left. + [(1 - \langle E_{\mathbf{H}} \rangle)/E_{\mathbf{h}-\mathbf{h}'}] \right\}/3. \qquad (10)$$

It is interesting to note that (9) uses approximately as many large as small E's, without requiring any weighting scheme.

2. Description of the test conditions

The efficiency test of the tangent formula (9) derived from Patterson-function arguments has been performed on the test structures used by Sheldrick (1990) to determine the effectiveness of the tangent formula incorporating the most reliable negative quartets. These structures were selected by Sheldrick because the correct solutions can be identified from the conventional figures of merit and because they cover a variety of situations: (i) low- and high-symmetry space groups; (ii) space groups with fixed and nonfixed unit-cell origins; and (iii) equal-atom structures with the same symmetry but different numbers of atoms in the unit cell.

The test calculations of the tangent formula (9) were done with the program XLENS94 in default mode (Rius, 1994), using the NES largest and the NWEAK $[= \text{NES} - (\text{NES})^{1/2}]$ weakest reflections with $2(\sin\theta)/\lambda \le 1 \text{ Å}^{-1}$. For large NES, $(\text{NES})^{1/2}$ will be much less than NES, so that NES $\simeq$ NWEAK. In the calculation of $\langle E_{\mathbf{H}} \rangle$, only the large-$E$ and small-E sets were used. The values of $\langle E_{\mathbf{H}} \rangle$ lie in the interval 1.02–1.17. No convergence mapping was done. All trials

Table 1. *Summary of test calculations performed with the tangent formula derived from Patterson-function arguments [(9)]*

(*a*) Code name of the test structure; (*b*) space group; (*c*) number of atoms in the unit cell; (*d*) number of trials; (*e*) success rate (%) and, in parentheses, the number of refined phases for each test calculation. The references for the test structures are: for LOG, Jones, Sheldrick, Glüsenkamp & Tietze (1980); for SUOA, Oliver & Strickland (1984); for PEP1, Antel, Sheldrick, Bats, Kessler & Müller (1995); for BHAT, Bhat & Ammon (1990); for MBH2, Poyser, Edwards, Anderson, Hursthouse, Walker, Sheldrick & Whalley (1986); for HOPS, Hopf, Lehne & Jones (1995).

(*a*)	LOG	SUOA	PEP1	BHAT	HOPS	MBH2
(*b*)	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	Pc	$R3$(hexagonal)	$P1$
(*c*)	108	188	340	84	243	54
(*d*)	1000	1000	10000	200	1000	300
(*e*)	5.7 (210)	0.40 (190)	0.09 (230)	42.5 (210)	9.6 (190)	39.0 (210)
	6.2 (230)	1.80 (210)	0.18 (250)	53.0 (230)	13.3 (210)	47.6 (230)
	5.3 (250)	1.10 (230)	0.08 (270)	71.5 (250)	13.7 (230)	67.6 (250)

started with random phases and no weighting function was employed.

The criteria for considering a solution to be 'correct' were the same as those used by Sheldrick (1990): (*a*) the solution must be clearly identified from the corresponding 'combined figure of merit'; and (*b*) the usual Fourier recycling gives a peak list in which most atoms are higher than any spurious peak.

3. Results and concluding remarks

The most relevant results of the test calculations using the tangent formula (9) are listed in Table 1. It may be concluded that:

(*a*) the tangent formula (9) can solve all test structures;

(*b*) the percentage of correct solutions for structures with fixed origins (LOG, SUOA and PEP1) tends to be lower than for structures having nonfixed origins (BHAT, HOPS and MBH2); and

(*c*) the success rate decreases with increasing number of atoms in the unit cell (LOG > SUOA > PEP1).

Table 2 summarizes the results obtained with both tangent formulas. It is evident from comparison of columns (*a*) and (*b*) that the tangent formula derived from Patterson-function arguments is, at least, one order of magnitude more effective than the one incorporating the most reliable negative quartets. In addition, comparison of columns (*a*) and (*c*) indicates that, for structures with fixed origins, the tangent formula (9) is approximately as effective as the combination of the phase-annealing procedure and tangent formula with negative quartets. For the remaining structures, *i.e.* those with nonfixed unit-cell origins, comparison of columns (*a*) and (*c*) indicates that the tangent formula (9) is clearly superior.

Table 2. *Comparison of success rates (%) for the different tangent formulas*

(*a*) Tangent formula derived from Patterson-function arguments (9); (*b*) tangent formula incorporating the most reliable negative quartets; (*c*) the same as (*b*) but combined with the phase-annealing refinement procedure (only the best result has been selected; B = corresponding initial Boltzmann factor). Values given in columns (*b*) and (*c*) have been taken from Sheldrick (1990).

Code	(*a*)	(*b*)	(*c*)	B
LOG	5.30–6.20	2.1	7.2	0.4
SUOA	0.4–1.8	0.06	0.5	0.3
PEP1	0.08–0.18	0.01	0.25	0.3
BHAT	42.5–71.5	0.26	0.97	0.3
HOPS	9.6–13.7	0.56	2.1	0.2
MBH2	39.0–67.6	4.7	10.2	0.1

In view of these results and considering the ease of implementation, it can be concluded that the tangent formula (9) is the more effective of these two tangent formulas. One possible source of progress, especially for medium-sized structures with fixed unit-cell origins, could be its combination with the phase-annealing procedure (Sheldrick, 1990).

Finally, it should be mentioned that, to get a more complete picture, similar test calculations should be carried out with the Sayre-equation tangent formula (Debaerdemaeker *et al.*, 1985).

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