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On the Application of Phase Relationships to Complex Structures.
XXIV. The Sayre Tangent Formula

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Abstract

The application of the condition that a true set of phases for a substantial subset of normalized structure factors should satisfy Sayre's equation leads to a phase-refining equation called the Sayre tangent formula. Phases refined by this formula tend to satisfy Sayre's equation for a subset of E's containing some of large magnitude and some of small (ideally zero) magnitude. Trials indicate that the new formula, incorporated into a computer program *SAYTAN*, is more effective than *MULTAN*80, especially for symmorphic structures.

Introduction

The tangent formula (Karle & Hauptman, 1956) has played a central role in the development of direct methods. It allows phases to be refined, in an iterative fashion, such that they are increasingly consistent with the three-phase relationships

$$\varphi_{\mathbf{h}} - \varphi_{\mathbf{h}'} - \varphi_{\mathbf{h}-\mathbf{h}'} \simeq 0 \text{ modulo } 2\pi \qquad (1)$$

first given by Cochran (1955).

A way of deriving the tangent formula is to assume that the true phase angles, $\varphi_{\mathbf{h}}$, of the normalized structure factors, $E_{\mathbf{h}}$, correspond to a maximum of the function

$$Z = \sum_{\mathbf{h}} \sum_{\mathbf{k}} E^*_{\mathbf{h}} E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}}. \qquad (2a)$$

Since, in the summation, for every term $E^*_{\mathbf{h}} E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}}$ there is another of the form $E_{\mathbf{h}} E^*_{\mathbf{k}} E^*_{\mathbf{h}-\mathbf{k}}$ then Z is real and (2a) may be written as

$$Z = \sum_{\mathbf{h}} \sum_{\mathbf{k}} |E_{\mathbf{h}} E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}}| \cos(\varphi_{\mathbf{h}} - \varphi_{\mathbf{k}} - \varphi_{\mathbf{h}-\mathbf{k}}). \qquad (2b)$$

The condition for an extremum is

$$\partial Z / \partial \varphi_{\mathbf{h}} = 0$$

for every $\mathbf{h}$ and application of this to (2b) gives

$$\partial Z/\partial \varphi_{\mathbf{h}} = -|E_{\mathbf{h}}| \sum_{\mathbf{k}} |E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}}| \sin(\varphi_{\mathbf{h}} - \varphi_{\mathbf{k}} - \varphi_{\mathbf{h}-\mathbf{k}}) = 0. \qquad (3)$$

This may be rearranged to give

$$\tan \varphi_{\mathbf{h}} = \frac{\sum_{\mathbf{k}} |E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}}| \sin(\varphi_{\mathbf{k}} + \varphi_{\mathbf{h}-\mathbf{k}})}{\sum_{\mathbf{k}} |E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}}| \cos(\varphi_{\mathbf{k}} + \varphi_{\mathbf{h}-\mathbf{k}})}, \qquad (4)$$

which is the normal form of the tangent formula. Thus, if phases are driven to be self consistent with (4) they are taken to a maximum of Z and the expectation is that the true phases will be near, if not quite at, a local maximum.

The tangent formula tends, particularly for symmorphic space groups, to produce pseudo-solutions characterized by statistically too small values for the triple-phase invariants given by the left-hand sides of (1). Frequently all the values are exactly zero; while the true phases may be near a local maximum of Z the pseudo-solutions will be at or close to the global maximum. Various ways of trying to avoid this behaviour have been suggested - for example the statistically weighted tangent formula of Hull & Irwin (1978) - but, by and large, this is still a current difficulty in the application of direct methods.

The basic Sayre tangent formula

Sayre's equation (Sayre, 1952) may be written in the form

$$F_{\mathbf{h}} = \frac{f_{\mathbf{h}}}{g_{\mathbf{h}} V} \sum_{\mathbf{k}} F_{\mathbf{k}} F_{\mathbf{h}-\mathbf{k}}, \qquad (5)$$

where V is the volume of the unit cell and $f_{\mathbf{h}}$ and $g_{\mathbf{h}}$ are the scattering factors for the true equal atoms of the structure and for the 'squared' atoms respectively.

An equation of the same form will be approximately true even if the conditions required for Sayre's

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equation, equal resolved atoms, do not hold. Thus, if we use $E_{\mathbf{h}}$ instead of $F_{\mathbf{h}}$ if the atoms are unequal and if only a subset of E's is used we may write as an approximation

$$E_{\mathbf{h}} = KG_{\mathbf{h}}, \tag{6}$$

where K is an overall scale factor and

$$G_{\mathbf{h}} = (1/g_{\mathbf{h}}) \sum_{\mathbf{k}} E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}}. \tag{7}$$

The $g_{\mathbf{h}}$ are proportional to the scattering factors for the squared structure and may be estimated from the volume in reciprocal space available for the convolution in (7). It should be noted that the subset of E's may contain both those of large magnitude and ones that are very small or even of zero magnitude.

The total least-squares residual for the Sayre equations corresponding to the set $\{\mathbf{h}\}$ is defined as

$$R = \sum_{\mathbf{h}} |E_{\mathbf{h}} - KG_{\mathbf{h}}|^2 / \sum_{\mathbf{h}} |E_{\mathbf{h}}|^2. \tag{8}$$

The best K is found by considering R as a quadratic function of K with a minimum at

$$K = \sum_{\mathbf{h}} E^*_{\mathbf{h}} G_{\mathbf{h}} / \sum_{\mathbf{h}} |G_{\mathbf{h}}|^2.$$

With this expression for K put into (8),

$$R = 1 - S,$$

where

$$S = \Big(\sum_{\mathbf{h}} E^*_{\mathbf{h}} G_{\mathbf{h}}\Big)^2 \Big/ \Big(\sum_{\mathbf{h}} |E_{\mathbf{h}}|^2\Big)\Big(\sum_{\mathbf{h}} |G_{\mathbf{h}}|^2\Big). \tag{9}$$

S has been used as a figure of merit for the phase set $\{\varphi_{\mathbf{h}}\}$. We have

$$0 \le S \le 1 \tag{10}$$

and $S = 1$ is obtained only if all the Sayre equations are exactly satisfied.

It is worth pointing out an important difference between (9) and (2). Z in (2) is simply the sum of the triplets while in (9) Z^2 is divided by $\sum_{\mathbf{h}} |G_{\mathbf{h}}|^2$, which is a sum of quartets. Z is related to $\int [\rho(\mathbf{x})]^3 \, \mathrm{d}\mathbf{x}$, while S is related to

$$\Big\{\int [\rho(\mathbf{x})]^3 \, \mathrm{d}\mathbf{x}\Big\}^2 \Big/ \int [\rho(\mathbf{x})]^4 \, \mathrm{d}\mathbf{x}.$$

As a figure of merit (FOM) S combines features of two separate FOMs used in *MULTAN*. The numerator is similar to ABSFOM while that part of $\sum_{\mathbf{h}} |G_{\mathbf{h}}|^2$ for the $G_{\mathbf{h}}$ corresponding to small $E_{\mathbf{h}}$ is similar to the PSIZERO FOM in *MULTAN*; it is to be expected that any phase-determining process that seeks a maximum of S should produce phases for the large E's that automatically are consistent, according to the PSIZERO FOM, with the magnitudes of the small E's.

Following our previous method for deriving the standard tangent formula we now say that for an extremum of S we require, for all $\mathbf{l}$,

$$\partial S / \partial \varphi_{\mathbf{l}} = 0.$$

Applying this condition to expression (9) and rearranging the result we find

$$\tan \varphi_{\mathbf{l}} = \frac{\operatorname{Im}(t_{\mathbf{l}}) - (2T/3Q) \operatorname{Im}(q_{\mathbf{l}})}{\operatorname{Re}(t_{\mathbf{l}}) - (2T/3Q) \operatorname{Re}(q_{\mathbf{l}})}, \tag{11}$$

where

$$t_{\mathbf{l}} = \sum_{\mathbf{h}} (1/g_{\mathbf{l}} + 1/g_{\mathbf{h}} + 1/g_{\mathbf{l}-\mathbf{h}}) E_{\mathbf{h}} E_{\mathbf{l}-\mathbf{h}}, \tag{12}$$

$$q_{\mathbf{l}} = \sum_{\mathbf{h}} E_{\mathbf{l}-\mathbf{h}} (1/g^2_{\mathbf{h}}) \sum_{\mathbf{k}} E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}}, \tag{13}$$

$$T = \sum_{\mathbf{l}} E^*_{\mathbf{l}} t_{\mathbf{l}} \tag{14}$$

and

$$Q = \sum_{\mathbf{l}} E^*_{\mathbf{l}} q_{\mathbf{l}} = \sum_{\mathbf{h}} |G_{\mathbf{h}}|^2. \tag{15}$$

If $q_{\mathbf{l}}$ is excluded then (11) reduces to the normal tangent formula except for the factor $(1/g_{\mathbf{l}} + 1/g_{\mathbf{h}} + 1/g_{\mathbf{l}-\mathbf{h}})$.

The terms in $q_{\mathbf{l}}$ are derived from a special selection of quartet invariants - those with $E_{\mathbf{l}}$, $E_{\mathbf{l}-\mathbf{h}}$, $E_{\mathbf{k}}$ and $E_{\mathbf{h}-\mathbf{k}}$ belonging to the set of large E's and with the cross terms $E_{\mathbf{h}}$ belonging either to this same set of large E's or to the set of small E's. Because the quartets are selected in this special way $q_{\mathbf{l}}$ factorizes, as is shown in (13), and the computational cost of including the $q_{\mathbf{l}}$ in (11), the Sayre tangent formula, is only about twice that for the normal tangent formula, which contains only the terms $t_{\mathbf{l}}$.

A weighting scheme

The Sayre-equation residual, R, given by (8) can be made more discriminating by associating the two subsets of $\{\mathbf{h}\}$ corresponding to large and small E's with different weights. Thus we write

$$R_w = \sum_{\mathbf{h}} m_{\mathbf{h}} |E_{\mathbf{h}} - \mathrm{K}G_{\mathbf{h}}|^2 / \sum_{\mathbf{h}} |E_{\mathbf{h}}|^2, \tag{16}$$

where $m_{\mathbf{h}} = 1$ if $E_{\mathbf{h}}$ is one of the large E's and $m_{\mathbf{h}} = \mu$, a constant, if it is one of the small (assumed zero) E's. The modified figure of merit, corresponding to (9), then becomes

$$S_w = \Big(\sum_{\mathbf{h}} E^*_{\mathbf{h}} G_{\mathbf{h}}\Big)^2 \Big/ \Big(\sum_{\mathbf{h}} |E_{\mathbf{h}}|^2\Big)\Big(\sum_{\mathbf{h}} m_{\mathbf{h}} |G_{\mathbf{h}}|^2\Big). \tag{17}$$

The Sayre tangent formula is still given by (11) but the quantities $q_{\mathbf{l}}$ and Q are now given by

$$q_{\mathbf{l}} = \sum_{\mathbf{h}} E_{\mathbf{l}-\mathbf{h}} (m_{\mathbf{h}}/g^2_{\mathbf{h}}) \sum_{\mathbf{k}} E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}} \tag{18}$$

and

$$Q = \sum_{\mathbf{h}} m_{\mathbf{h}} |G_{\mathbf{h}}|^2. \tag{19}$$

This is the form of the Sayre tangent formula that we have used; the best results have been obtained when μ is about 5.

SAYTAN

Equation (11) has been incorporated into a computer program called *SAYTAN*, which, like *RANTAN* (Yao Jia-xing, 1981), starts with random phases. The phases are refined by the repeated use of (11) but, in practice, it has been found necessary to introduce the quartet terms in a gradual way. If q_l is given its full weight immediately then the phases tend to be trapped in randomness; the part of q_l arising from weak quartets does not discriminate between random phases and true phases - as is also true for the PSIZERO FOM.

The first method we used for dealing with this problem, which was quite satisfactory, was to give q_l a weight

$$W_q = (n-1)/(n+c), \tag{20}$$

where n is the cycle number and c is a constant in the range 0 to 4. An alternative method, which gives a similar effect and has the advantage of not needing an arbitrary parameter, is to eliminate W_q but to keep Q fixed throughout the refinement at an estimate of its final true value, easily calculated from the Cochran distribution. We also add to Q a contribution from the small E_h based on a random-walk estimate from the Sayre-equation contributors. Experience of the PSIZERO FOM suggests that this is appropriate for a good set of phases. In the early stages of refinement the estimated Q is much bigger than the value given by (19) so that the factor $(2T/3Q)$ in (11) is small for the first few cycles.

It has also been found to be useful to weight individual phases in the triplet terms, as is usual in *MULTAN*, so that (12) should be written

$$t_l = \sum_{\mathbf{h}} (1/g_l + 1/g_{\mathbf{h}} + 1/g_{\mathbf{l-h}}) w_{\mathbf{h}} w_{\mathbf{l-h}} E_{\mathbf{h}} E_{\mathbf{l-h}}. \tag{21}$$

In *SAYTAN* the way in which phase refinement involves calculated weights is similar to that for *RANTAN*. At the start the $w_{\mathbf{h}}$ are set to some low level (usually 0·25). When a new estimate for φ_l is found from (11) we compute $w'_l = \min(1, |t_l|/5)$ and only update φ_l and w_l if w'_l is above some preset level (usually in the range 0·25 to 0·4). In the original program the appropriate weights $w_{\mathbf{h}}$ were also associated with the quartet-derived terms so that, in place of (18), we used

$$q_l = \sum_{\mathbf{h}} w_{\mathbf{l-h}} E_{\mathbf{l-h}} (m_{\mathbf{h}}/g_{\mathbf{h}}^2) \sum_{\mathbf{k}} w_{\mathbf{k}} w_{\mathbf{h-k}} E_{\mathbf{k}} E_{\mathbf{h-k}}. \tag{22}$$

Actually we now use (18) rather than (22) and the results are not very different. In practice most of the $w_{\mathbf{h}}$ approach unity after a few cycles of refinement and, as indicated above, the quartet terms contribute little in these early stages. However, it should be stressed that it *is* important to use (21) for t_l rather than (12) otherwise the results noticeably deteriorate.

SAYTAN trials

The first trial of *SAYTAN* was on the structure of 11-methyltricyclo[4.4.1.0^{1,6}]undeca-2,4,7,9-tetraene-11-carbonitrile, called MUCCAR (Bianchi, Pilati & Simonetta, 1978), $C_{13}H_{11}N$, space group $P1$, $Z=2$ with $a=8·310$, $b=7·026$, $c=9·508$ Å, $\alpha=100·89$, $\beta=97·82$ and $\gamma=113·48°$. The form of the molecule is shown in Fig. 1. Thirty phase sets were generated with the following result:

15 sets showed the complete structure (28 atoms)
5 sets showed all but one atom
8 sets showed between 19 and 24 atoms

Table 1 shows the conventional *MULTAN* figures of merit and also the values of $S_{w'}$ for the 30 phase sets.

For comparison a default run of *MULTAN*80, which generated 40 sets, showed no significant part of the structure at all. Another run of *MULTAN*80 using the statistically weighted tangent formula contained one complete solution with the next best set showing about one half of the structure (parts of each molecule).

SAYTAN was next tested on Cortisone (Declercq, Germain & Van Meerssche, 1972), $C_{21}H_{28}O_5$, space group $P2_12_12_1$, $Z=4$ with $a=10·040$, $b=23·649$, $c=7·784$ Å. The form of the molecule is shown in Fig. 2. In 30 generated sets of phases there were three perfect solutions; figures of merit for these 30 sets are shown in Table 2. Two runs of *MULTAN*80 were made for CORTISONE, one under default conditions and the other using the statistically weighted tangent formula. Each run comprised 36 phase sets and no solutions were found. It seems that with *MULTAN*80 the structure of CORTISONE tends to be obscured by an extensive 'chicken-wire' pattern of peaks.

In another test of *SAYTAN* the E magnitudes calculated from the atomic coordinates of CORTISONE were used. In this case there were ten perfect solutions in 30 phase sets.

Successful trials have been made on other known structures and unknown structures with 50–100 atoms in the asymmetric unit have also been solved. One

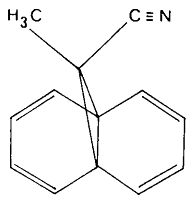

Fig. 1. A molecule of MUCCAR. There are two molecules in the unit cell of space group $P1$.

Table 1. *Figures of merit for the* 30 *phase sets for MUCCAR given by SAYTAN*

In the type-of-solution column the number of atoms in the *E* map is indicated by *A*(28), *B*(27), *C*(19–24), *D*(no solution).

Set	ABSFOM	PSIZERO	RESID	Combined FOM	Sayre FOM	Type of solution
1	1·2134	1·328	17·94	1·7298	0·764	*C*
2	1·1988	1·256	17·33	1·9391	0·779	*A*
3	1·1451	1·392	14·90	2·4860	0·807	*A*
4	1·2140	1·356	18·10	= set 1	0·761	*C*
5	1·2080	1·523	19·05	1·2852	0·725	*C*
6	1·1803	1·113	15·51	2·5305	0·808	*A*
7	1·1845	1·143	15·70	= set 6	0·808	*A*
8	0·7876	3·077	18·66	0·1088	0·727	*C*
9	1·1807	1·345	17·41	1·8469	0·772	*C*
10	1·1407	1·368	14·84	= set 3	0·809	*A*
11	1·1791	1·217	15·54	2·4493	0·796	*A*
12	1·0108	1·795	14·32	2·3003	0·756	*C*
13	1·1796	1·274	18·39	1·6268	0·769	*C*
14	1·0759	1·463	13·98	2·6546	0·785	*B*
15	1·2126	1·349	18·68	1·5118	0·770	*B*
16	1·2050	1·356	17·97	1·6979	0·775	*A*
17	1·1956	1·229	17·19	= set 2	0·789	*A*
18	1·1493	1·383	16·96	1·9306	0·775	*A*
19	1·1130	1·357	14·09	2·7179	0·798	*A*
20	1·1797	1·077	15·73	= set 6	0·811	*A*
21	1·1814	1·456	17·08	1·8617	0·778	*B*
22	1·2035	1·295	17·87	1·7666	0·776	*B*
23	0·8126	2·391	17·30	0·9716	0·728	*C*
24	1·1982	1·189	17·04	2·0660	0·787	*A*
25	1·1792	1·212	16·21	2·2686	0·789	*B*
26	1·1926	1·207	17·31	1·9769	0·784	*A*
27	1·1814	1·264	16·68	2·1069	0·791	*A*
28	1·1896	1·156	16·43	2·2524	0·792	*A*
29	1·0996	1·847	15·74	1·9154	0·753	*D*
30	0·9208	2·644	13·95	1·7659	0·714	*D*

Table 2. *Figures of merit for* 30 *phase sets for CORTISONE given by SAYTAN*

The sets marked with * are complete solutions.

Set	ABSFOM	PSIZERO	RESID	Combined FOM	Sayre FOM
1	1·0296	1·025	19·68	2·8922	0·693*
2	0·6713	1·160	28·98	2·2162	0·518
3	0·2176	1·091	50·78	1·2220	0·247
4	0·7854	1·370	28·71	1·9886	0·562
5	0·6290	1·461	29·95	1·7787	0·539
6	0·5530	1·396	33·15	1·7004	0·569
7	0·9149	1·322	27·12	2·1525	0·574
8	0·7582	1·358	26·17	2·1100	0·551
9	0·5914	1·745	35·14	1·1756	0·547
10	0·6489	1·220	29·39	2·1162	0·529
11	0·9395	1·543	24·74	1·9823	0·564
12	0·5723	1·329	33·71	1·7659	0·541
13	0·4927	0·952	34·62	2·1872	0·568
14	0·9200	1·562	26·19	1·8891	0·572
15	0·5675	1·132	31·97	2·0944	0·577
16	0·9524	1·417	26·19	2·0820	0·531
17	1·0207	1·045	19·34	= set 1	0·703*
18	0·7004	1·290	30·52	1·9892	0·539
19	0·7045	1·067	29·25	2·3314	0·513
20	0·5808	1·221	33·09	1·9341	0·519
21	0·6788	1·376	27·45	2·0110	0·567
22	0·8091	1·455	26·62	1·9796	0·558
23	0·6233	1·114	30·92	2·1772	0·587
24	1·0239	1·039	19·35	= set 1	0·695*
25	0·5668	1·208	30·83	2·0479	0·556
26	0·4393	1·133	38·87	1·7535	0·506
27	0·4270	1·096	38·95	1·7945	0·397
28	0·4408	1·014	38·40	1·9270	0·513
29	0·6597	1·245	29·28	2·0923	0·533
30	0·8545	2·048	30·88	1·0428	0·524

failure with a known structure has been with ergocalciferol (Hull, Leban, White & Woolfson, 1976), a notoriously difficult structure for direct methods. However, when *E* magnitudes were used that were calculated from atomic coordinates one perfect solution was obtained with *SAYTAN*. This, plus the CORTISONE experience, suggests that the quality of data may be of importance in the effectiveness of the Sayre tangent formula.

We wish to record our gratitude to the Science and Engineering Research Council and the Deutsche Forschungsgemeinschaft, which have funded this work. We are also grateful for helpful discussions with Dr P. Main who has pointed out relationships of this work to the least-squares tangent formula developed by himself and S. Fiske (Fiske, 1982).

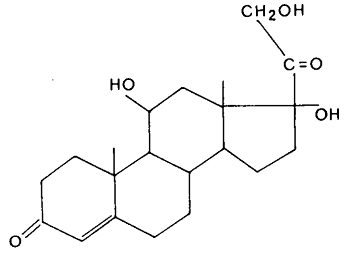

Fig. 2. A molecule of CORTISONE.

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Reflectivity (Rocking) Curves of Imperfect Crystals by an Improved $\Delta\omega$, $\Delta 2\theta$ Technique

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Abstract

A simple experimental modification to the $\Delta\omega$, $\Delta 2\theta$ technique for measuring single-crystal Bragg reflections has been demonstrated [Mathieson & Stevenson (1984). *Aust. J. Phys.* 37, 657-665]. This leads to a significant improvement in this technique in that the source component is reduced to a minor (angular) role, so that the greater resolution-capability/information-content, inherent in the $\Delta\omega$, $\Delta 2\theta$ method relative to the conventional $\Delta\omega$ profile method, is further enhanced. With only two major components in the two-dimensional distribution, the individual distributions of these components can be determined with some accuracy. These components are the reflectivity (often referred to previously as the mosaic spread) and the wavelength distribution. The resolution function, $R(\Delta\omega, \Delta 2\theta)$, can be estimated from the experimental parameters and is sufficiently small that the deconvoluted reflectivity for imperfect crystals is derivable. This procedure is demonstrated, in the present case, for a small single crystal of $CuInSe_2$.

1. Introduction

The basic design of the single-crystal X-ray diffractometer was established by Bragg (1914). In essence, it has not changed a great deal nor has the measurement procedure associated with it. This procedure involves traversing a single reflection by changing the orientation of the specimen crystal, step by step, and recording, at each step, $\Delta\omega$, the diffracted intensity passed through a relatively wide aperture in front of the detector, thereby providing the one-dimensional intensity profile, $I(\Delta\omega)$, of the reflection. The main purpose of the original instrument was the estimation of the integrated intensity, $\int I(\Delta\omega)\, d\Delta\omega$.

For several decades, this instrument was overshadowed by photographic recording, using effectively a very large (or no) aperture. Then, in the 1950's, the X-ray diffractometer was resurrected as an instrument for quantitative measurements on small single crystals (see Arndt & Willis, 1966), and Alexander & Smith (1962) carried out an analysis of the relationship of the profile curve $I(\Delta\omega)$ to what they nominated as the various major components of the experiment. They assumed the probable functional form, in terms of the one variable $\Delta\omega$, of a number of components, the mosaic spread, μ, the source size, σ, the wavelength distribution, λ, and the specimen-crystal size, c. The theoretical intensity curve, $I(\Delta\omega)_{\mu,\sigma,\lambda,c}$, was derived by sequential convolution of the functions. In this analysis, however, there was one component whose parametric relevance was largely ignored, namely the aperture in front of the detector. The variation of signal distribution across the aperture, $I(\Delta 2\theta)$, for a given value of $\Delta\omega$, was not examined or explored, only the outer limits necessary to ensure collection of the total signal within the specimen scan limits were investigated ('minimum receiving aperture'). Hence, what is measured under the circumstances of the conventional procedure is detailed in (1):

$$I(\Delta\omega)_{\mu,\sigma,\lambda,c,A(\Delta 2\theta)} = \int_{\Delta 2\theta_1}^{\Delta 2\theta_2} I(\Delta\omega, \Delta 2\theta)_{\mu,\sigma,\lambda,c}\, d\Delta 2\theta, \tag{1}$$

and it is evident that one is really dealing with a five-component system in which the square-wave function, $A(\Delta 2\theta)$, corresponding to the aperture, is the largest component, in angular terms, by the nature of the determination of its outer limits.

The main aim of the analysis by Alexander & Smith (1962) was directed at measuring relative integrated intensities with high reliability. If, however, one wishes to use the diffractometer to extract, from such one-dimensional intensity measurements, informa-

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