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Comments on the short communication, *Astatistical evaluation of absorption* by C. Katayama, N. Sakabe and K. Sakabe. By G. KOPFMANN, *Max Planck-Institut für Eiweiss- und Lederforschung, München, und Physikalisch-Chemisches Institut der Technischen Universität München, München, Germany*

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In a recent paper by Katayama, Sakabe & Sakabe [*Acta Cryst.* (1972), A**28**, 293] some principles of an empirical absorption correction method are described. These have been published previously [Kopfmann & Huber (1968). *Acta Cryst.* A**24**, 348].

Katayama, Sakabe & Sakabe (1972), in describing their method of absorption correction, referred to the paper of North, Phillips & Mathews (1968). In the same issue of *Acta Crystallographica* we have proposed a general method of empirical absorption correction by X-ray intensity measurements. Our paper stresses the application to crystals with arbitrary shapes and the use of multiple measurements of the same reflexion and equivalent reflexions for the determination of absorption. General formulae as well as special algorithms for the numerical evaluation of the absorption correction were given. The application of the method to proteins has been pointed out and experimental results have been published in another paper (Huber & Kopfmann, 1969).

In a recent short communication (Katayama, Sakabe & Sakabe, 1972) some principles of this method are described again and the general algorithm in our first paper [equation (10), page 351 of Kopfmann & Huber, 1968] is presented as a special case [equation (3) in the short communication]. Furthermore the least-squares evaluation of these authors is restricted to equivalent reflexions, limited in number by the space group, whereas in our method, as many observations of the same reflexion as necessary may be used by a rotation about the reciprocal-lattice vector.

In our opinion no new detail has been given in the short communication of these authors.

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The usefulness of the generalized tangent formula. By H. SCHENK, *Laboratory for Crystallography, University of Amsterdam, Nieuwe Prinsengracht 126, Amsterdam, The Netherlands*

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The generalized form of the tangent formula [Tsai, C-C. & Collins, D. M. (1972). *Acta Cryst.* B**28**, 1601] cannot work except for the trivial case where the generalized form equals the ordinary tangent formula. The T'_{21} formula is in contradiction with the Harker–Kasper inequality for $\bar{1}$.

Recently Tsai & Collins (1972) described a generalized form of the tangent formula:

$$\tan(r\varphi_H) \simeq \frac{\sum_K |E_K|^p |E_{\frac{r}{q}H-\frac{p}{q}K}|^q \sin(p\varphi_K + q\varphi_{\frac{r}{q}H-\frac{p}{q}K})}{\sum_K |E_K|^p |E_{\frac{r}{q}H-\frac{p}{q}K}|^q \cos(p\varphi_K + q\varphi_{\frac{r}{q}H-\frac{q}{q}K})}. \quad (1)$$

They use in the phase-determining procedure the following special cases of (1):

$$\tan(\varphi_H) \simeq T'_{11} = \frac{\sum_K |E_K E_{H-K}| \sin(\varphi_K + \varphi_{H-K})}{\sum_K |E_K E_{H-K}| \cos(\varphi_K + \varphi_{H-K})} \quad (2)$$

the well known tangent formula and

$$\tan(\varphi_H) \simeq T'_{22} = \frac{\sum_K |E_K|^2 |E_{H-2K}| \sin(2\varphi_K + \varphi_{H-2K})}{\sum_K |E_K|^2 |E_{H-2K}| \cos(2\varphi_k + \varphi_{H-2K})}. \quad (3)$$

Whereas the reliability of a single term of (2) is a function of $|E_H E_K E_{H-K}|$, the reliability of a single term of (3) is a function of $|E_H E_K^2 E_{H-2K}|$.

The purpose of this paper is to show that in centrosymmetric structures (3) does not work. In our opinion the only useful form of (1) is that with $p=q=r=1$, the ordinary tangent formula (2).

For centrosymmetric structures (3) reduces to

$$\cos(\varphi_H) = \frac{\sum_K |E_K|^2 |E_{H-2K}| \cos(2\varphi_K + \varphi_{H-2K})}{\sum_K |E_K|^2 |E_{H-2K}|}. \quad (4)$$

Because $\varphi_K = 0$ or π, equation (4) is equal to

$$\cos(\varphi_H) = \frac{\sum_K |E_K|^2 |E_{H-2K}| \cos \varphi_{H-2K}}{\sum_K |E_K|^2 |E_{H-2K}|}. \quad (5)$$

Equation (5) states that the signs $S(H)$ of H and $S(H-2K)$ of $H-2K$ are equal if the normalized structure factors

Table 1. *The number of triplets H, K, $H-2K$ as a function of $E_4=|E_HE_K^2E_{H-2K}|\sigma_3\sigma_2^{-3/2}$ for a structure in space group $P2_1/c$* (*Schenk*, 1972*b*)

For comparison: the 600 triplets $H,K,H-K$ of highest magnitude $|E_HE_KE_{H-K}|$ all give the correct sign relationship $S(H)S(K)S(H-K)=+1$.

E_4 value	Number of triplets $H,K,H-2K$ above the E_{21} value	Number of triplets with $S(H)S(H-2K)=+1$	Number of triplets with $S(H)S(H-2K)=-1$	Relative percentage of correct information
8·0	2	2	0	100
7·0	7	7	0	100
6·0	16	15	1	93·7
5·0	29	25	4	86·2
4·0	67	53	14	79·1
3·0	207	150	57	72·5
2·0	623	396	227	63·6
1·0	1986	1101	885	55·4

E_H, E_K and E_{H-2K} are large. This may be in contradiction with the Harker–Kasper inequality for $\bar{1}$ (Harker & Kasper, 1948). A brief note on this inequality relation will be given here; for a more detailed treatment see, *e.g.*, Woolfson (1961).

If the magnitudes of the reflexions $H-K$, K,H and $H-2K$ (h,h', $h+h'$, $h-h'$ in Woolfson's notation) are all sufficiently large, it can be shown that both

$$S(H-K)S(K)S(H)=+1$$

and

$$S(H-K)S(K)S(H-2K)=+1 \tag{6}$$

hold so that then also

$$S(H)S(H-2K)=+1\,. \tag{7}$$

However the relations (6) are already included in the tangent formula (2) so that in these cases relation (7) in the alternative tangent formula (3) gives no new information.

In the case that E_H, E_{H-2K} and E_K are sufficiently large and $E_{H-K}=0$ it can be proved that

$$S(H)S(H-2K)=-1\,. \tag{8}$$

Thus here, although (8) and (5) correlate the signs of the same reflexions on the basis of the same information, the exact results of (8) are in contradiction with (5). In fact relation (8) was found to be very helpful in the direct determination of structures in space group $P\bar{1}$ (Schenk, 1972*a*).

Apart from these systematic failures it can be easily seen that the triplets H, K, $H-2K$ contain a much smaller amount of phase information than the corresponding triplets H, K, $H-K$. This follows from the fact that both tangent formulae 2 and 3 are special cases of the easily derivable expression:

$$\tan(\varphi_H)=\frac{\sum_K\sum_L|E_KE_LE_{H-K-L}|\sin(\varphi_K+\varphi_L+\varphi_{H-K-L})}{\sum_K\sum_L|E_KE_LE_{H-K-L}|\cos(\varphi_K+\varphi_L+\varphi_{H-K-L})}\,. \tag{9}$$

For tangent formula (2) $E_L=E_{000}$ and for (3) $E_L=E_K$. In the centrosymmetric case the related expression was already given by Simerska (1956):

$$\overline{E_HE_KE_L}^{H+K+L=\text{constant}}=\frac{1}{N^2}E_{H+K+L} \tag{10}$$

from which the sign relationship

$$S(H)S(K)S(L)S(H-K-L)=+1 \tag{11}$$

follows. The reliability of this relationship is a function of the magnitude $\sigma_3\sigma_2^{-3/2}|E_HE_KE_LE_{H-K-L}|=E_4$.

For a recently solved structure the 600 strongest triplets H, K, $H-K$ all give sign relations $S(H)S(K)S(H-K)=+1$. The first relation $S(H)S(K)S(H-K)=-1$ appears for $E_3=\sigma_3\sigma_2^{-3/2}|E_HE_KE_{H-K}|=1·5$, which is equal to an E_4 value of $1·5\,E_{000}=11·2$. From Table 1 it can be seen that the list of triplets H, K, $H-2K$ contains a highest $E_4=\sigma_3\sigma_2^{-3/2}|E_HE_K^2E_{H-2K}|$ of approximately 8. Thus it is clear that the alternative tangent formula (3) cannot be of much value in phase determining processes.

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