A New Figure of Merit for Multisolution Methods of Phase Determination

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For a structure consisting of equal atoms, the point-atom densities of both the normal structure $[\hat{\varrho}(\mathbf{r})]$ and the squared structure $[\hat{\varrho}^2(\mathbf{r})]$ must be identical except for a scale factor. Starting from this consideration, similar to that which led Sayre [*Acta Cryst.* (1952). **5**, 60–65] to his well-known equation, the volume integral of the squared difference between $\hat{\varrho}(\mathbf{r})/I_1$ and $\hat{\varrho}^2(\mathbf{r})/I_2$ must be zero, I_1 and I_2 being appropriate scale factors. Consequently a new figure of merit for a set of phases is derived; the method requires consideration of both triples and quadruples of reflexions with $\sum \mathbf{H}_i = 0$. It proves to be effective in selecting the correct phase sets for four centrosymmetrical compounds whose structures are already known. An improved expression of the tangent formula is also derived from the new figure of merit.

The choice of the correct set of phases from among the several sets having approximately the same degree of consistency in terms of the structure invariants related to the Sayre triples is frequently a time-consuming step. The criterion usually adopted consists essentially of the analysis of the different Fourier maps, searching for the one which gives the most acceptable image of the structure. The analysis may be speeded up by the adoption of suitable criteria. We believe it to be particularly worth mentioning the procedure suggested by Woolfson (1972), consisting of a fully automated search of the distances (and, possibly, of the angles) between the Fourier peaks, thus avoiding tedious manual analysis of the maps.

In the present note we propose an alternative criterion, which consists of considering a single parameter, or figure of merit, for each phase set; as we shall see, its evaluation requires consideration of quadruples, in addition to triples, of reflexions. The underlying logic is as follows.

The Fourier maps obtained with phase sets which, although incorrect, satisfy most of the triple products, are quite often characterized by exceedingly strong peaks. A well known example is offered by the trivial solution consisting of all *plus* signs for a $P\bar{1}$ space group, which leads to positive signs of all the structure invariants $s(\mathbf{H}) \cdot s(\mathbf{K}) \cdot s(\mathbf{H}+\mathbf{K})$ and is characterized by a very heavy peak at the origin. If we assume that all the atoms have the same weight then, as Sayre (1952) first pointed out, the squared structure must closely resemble the real structure. In fact, if we refer to the point-atom density

$$\hat{\varrho}(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{H}} E_{\mathbf{H}} \exp\left(-2\pi i \mathbf{H} \cdot \mathbf{r}\right),$$

the real and the squared structures should be identical except for a scale factor. The simplest overall measure of the difference between the two structures is the in-

tegral of the squared difference between the two Fourier maps which, therefore, must approach zero for the correct phase set. In order for $\hat{\varrho}(\mathbf{r})$ and $\hat{\varrho}^2(\mathbf{r})$ to be put on the same scale, they must be divided by I_1 and I_2 respectively, where

$$I_n = \int_{(\text{cell})} \hat{\varrho}^n(\mathbf{r}) \, dV. \tag{1}$$

The integral which must approach zero for the correct structure is

$$\mathscr{I} = \int_{(\text{cell})} \left(\frac{\hat{\varrho}^2(\mathbf{r})}{I_2} - \frac{\hat{\varrho}(\mathbf{r})}{I_1}\right)^2 dV. \tag{2}$$

We want to point out here that positive contributions to the above integral may arise not only from inequalities of the point maxima of $\hat{\varrho}$ and $\hat{\varrho}^2$, but also from negative values of $\hat{\varrho}$ in any region of the unit cell.

If the argument of the above integral is developed and equation (1) taken into account, equation (2) reduces to

$$\mathscr{I} = \frac{I_4}{I_2^2} + \frac{I_2}{I_1^2} - 2\frac{I_3}{I_1 I_2}. \tag{3}$$

If N is the number of equal atoms in the unit cell, it is easy to show that

$$I_1 = E_0 = \sqrt{N}; \quad I_2 = \frac{1}{V} \sum_{\mathbf{H}} |E_{\mathbf{H}}|^2;$$

$$I_3 = \frac{1}{V^2} \sum_{\mathbf{H}} \sum_{\mathbf{K}} E_{\mathbf{H}} E_{\mathbf{K}} E_{-\mathbf{H}-\mathbf{K}};$$

$$I_4 = \frac{1}{V^3} \sum_{\mathbf{H}} \sum_{\mathbf{K}} \sum_{\mathbf{L}} E_{\mathbf{H}} E_{\mathbf{K}} E_{\mathbf{L}} E_{-\mathbf{H}-\mathbf{K}-\mathbf{L}}. \tag{4}$$

Substituting into equation (3), we get

$$\mathscr{I} = \frac{1}{V(\sum_{\mathbf{H}} |E_{\mathbf{H}}|^2)^2} \left[\sum_{\mathbf{H}} \sum_{\mathbf{K}} \sum_{\mathbf{L}} E_{\mathbf{H}} E_{\mathbf{K}} E_{\mathbf{L}} E_{-\mathbf{H}-\mathbf{K}-\mathbf{L}} \right.$$

$$- 2(\sum_{\mathbf{H}} \sum_{\mathbf{K}} E_{\mathbf{H}} E_{\mathbf{K}} E_{-\mathbf{H}-\mathbf{K}})$$

$$\left. \times (\sum_{\mathbf{H}} |E_{\mathbf{H}}|^2/E_0) + (\sum_{\mathbf{H}} |E_{\mathbf{H}}|^2)^3/E_0^2 \right]. \tag{5}$$

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For the correct set of phases we know that

$$\langle|E_H|^2\rangle=1; \quad \langle E_H E_K E_{-H-K}\rangle=1/\sqrt{N};$$
$$\langle E_H E_K E_L E_{-H-K-L}\rangle=1/N, \quad (6)$$

and consequently from equation (5), $\mathscr{I}$ approaches zero.

In practice, once a set of phases is given for the strongest reflexions, the right-hand side of equation (5) may be computed. Since $\mathscr{I}$ is intrinsically positive [see equation (2)], the resulting value should be a minimum for the correct structure. Alternatively, other figures of merit, linearly related to $\mathscr{I}$, may be derived from equation (5). As an example, if we define

$$\mathscr{F}=(\sum_H |E_H|^2)/E_0 \cdot [\sum_H |E_H|^2 - \mathscr{I} \cdot V \cdot E_0^2], \quad (7)$$

$\mathscr{F}$ is to be a maximum with respect to the phases. It may be convenient at this point to introduce the phase angles in an explicit way, remembering that

$$E_H=|E_H| \exp(i\varphi_H); \quad \varphi_{-H}=-\varphi_H;$$
$$E_H E_K E_{-H-K}+E_{-H}E_{-K}E_{H+K}$$
$$=2|E_H E_K E_{-H-K}| \cos(\varphi_H+\varphi_K+\varphi_{-H-K}), \quad (8)$$

with an analogous expression for the quadruples. From equations (5), (7) and (8) we obtain

$$\mathscr{F}=2\sum_H\sum_K |E_H E_K E_{-H-K}| \cos(\varphi_H+\varphi_K+\varphi_{-H-K})$$
$$-(E_0/\sum_H|E_H|^2)\cdot\sum_H\sum_K\sum_L|E_H E_K E_L E_{-H-K-L}|$$
$$\times\cos(\varphi_H+\varphi_K+\varphi_L+\varphi_{-H-K-L}). \quad (9)$$

Numerical tests of the above criterion for phase selection, based on maximization of expression (9), have been made on the following four centrosymmetric structures (space group $P\bar{1}$): cyclododeca-2,4,8-triene-1,6-dione (*cis–trans–cis* stereoisomer) (I; Kennard, Wampler, Coppola, Motherwell & Watson, 1971);

Table 1. *List of the figures of merit in an arbitrary scale [$\mathscr{F}$ – see equation (9)] for the most probable sets of signs of four different structures (see text)*

Structure I

h	k	l	E(hkl)	Sets	1	2	3	4	5	6	7	8	9	10	11	12	13*	14	15	16
1	$\bar{3}$	5	4·35		+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
$\bar{1}$	2	1	2·56		+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
3	9	0	2·03		+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
4	3.	2	3·55		+	−	−	+	+	−	−	+	+	−	−	+	+	−	−	+
2	$\bar{4}$	4	3·35		+	+	+	+	−	−	−	−	−	−	−	−	+	+	+	+
0	1	2	2·61		+	+	+	+	+	+	+	+	−	−	−	−	−	−	−	−
4	8	0	2·22		+	+	−	−	+	+	−	−	−	−	+	+	−	−	+	+
			$\mathscr{F}=$		245	280	275	302	264	296	293	318	336	317	319	295	350	333	332	311

Structure II

h	k	l	E(hkl)	Sets	1	2	3	4	5*	6	7	8
$\bar{8}$	2	5	6·73		+	+	+	+	+	+	+	+
$\bar{7}$	0	6	6·13		+	+	+	+	+	+	+	+
$\bar{6}$	$\bar{1}$	5	2·51		+	+	+	+	+	+	+	+
$\bar{7}$	0	5	5·69		+	+	+	+	−	−	−	−
$\bar{10}$	$\bar{2}$	7	5·36		+	+	−	−	−	−	+	+
$\bar{7}$	0	1	4·10		+	−	+	−	−	+	−	+
			$\mathscr{F}=$		660	713	698	695	739	678	711	710

Structure III

h	k	l	E(hkl)	Sets	1	2	3	4	5*	6	7	8
3	$\bar{1}$	1	4·85		+	+	+	+	+	+	+	+
$\bar{5}$	6	1	3·63		+	+	+	+	+	+	+	+
5	4	4	2·72		+	+	+	+	+	+	+	+
$\bar{3}$	0	6	5·64		+	−	+	−	−	+	−	+
4	4	4	3·21		+	−	−	+	+	−	−	+
$\bar{2}$	$\bar{4}$	7	3·18		+	−	−	+	−	+	+	−
			$\mathscr{F}=$		119	131	139	134	139	134	119	131

Structure IV

h	k	l	E(hkl)	Sets	1	2	3	4	5	6	7	8	9	10	11	12	13	14*	15	16
$\bar{5}$	$\bar{5}$	4	5·73		+	+	+	+	+	+	+	+	+	+	¬	+	+	+	+	+
$\bar{1}$	4	1	5·71		+	+	+	+	+	+	+	+	+	+	¬	+	+	+	+	+
6	$\bar{5}$	4	5·27		+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
6	$\bar{1}$	6	5·49		+	−	+	−	+	−	+	−	+	−	+	−	+	−	+	−
2	$\bar{19}$	5	5·48		+	+	−	−	+	+	−	−	+	+	−	−	+	+	−	−
3	18	1	5·21		+	+	+	+	−	−	−	−	+	+	+	+	−	−	−	−
7	$\bar{6}$	9	3·52		+	+	+	+	+	+	+	+	−	−	−	−	−	−	−	−
$\bar{1}$	0	3	3·03		+	+	−	−	−	−	+	+	+	+	−	−	−	−	+	+
			$\mathscr{F}=$		723	979	948	852	979	723	852	948	995	788	850	516	788	996	916	850

p-toluic acid (II; Takwale & Pant, 1971); 1,14-bis-(2′,6′,6′-trimethylcyclohex-1′-enyl)-3,12-dimethyl-tetradeca-1,3,5,7,9,11,13-heptaene-6,9-dinitrile (III; Braun, Hornstra & Leenhouts, 1971); $(N,N'$-dibenzyl-4,4′-bipyridylium$)^{2+}$-(7,7,8,8-tetracyanoquinodimethane$)_4^{2-}$ (IV; Sundaresan & Wallwork, 1972), with 12,10, 19 and 45 independent non-hydrogen atoms respectively.

For each of the four structures, Table 1 reports the most probable sets of basic signs from which the complete sets used in the calculations may be generated through Sayre triples, together with the corresponding figures of merit. The correct set of signs is marked with an asterisk. For structure I, Table 1 shows that, out of the 16 sets of signs sharing the same highest figure of merit in terms of the Sayre triples, the correct set is characterized by the highest value of $\mathscr{F}$ calculated from 134 independent reflexions $(d_{\min} = 1·03$ Å). For structure II the correct set is characterized analogously out of eight sets, using 151 independent reflexions $(d_{\min} = 0·96$ Å). For each of structures III and IV, the correct set shares the highest $\mathscr{F}$ value with another set out of eight sets (III), or 16 sets (IV), with the same largest consistency in terms of the Sayre triples; the number of independent reflexions used for the calculations was 166 $(d_{\min} = 0·78$ Å) and 157 $(d_{\min} = 1·09)$ for III and IV respectively. The times required on a UNIVAC-1108 computer were about 3, 4, 5 and 4 min in cases I, II, III and IV. The time is critically dependent on the number of reflexions employed in the evaluation of the figure of merit. As an example, with 200 reflexions the time would be about 20 min. In our experience it is most convenient to select the reflexions within a limiting sphere as small as possible.

Imposing the maximum condition $\partial\mathscr{F}/\partial\varphi_H = 0$, under the assumption that all the phases are independent variables, produces a new tangent formula, i.e.

inasmuch as the requirement leading to equation (10) [i.e. $\mathscr{I} = $ minimum, see equation (2)] should be more stringent than the condition

$$\int_{(cell)} \varrho^3(\mathbf{r}) \, dV = \text{maximum},$$

which leads to the usual tangent formula. We have not carried out any numerical test on equation (10) as yet.

There is an interesting, although qualitative, analogy between maximization of equation (9) and that of a Karle–Hauptman determinant (Karle & Hauptman, 1950). Namely, in both cases the triple products appear with positive signs, whereas the quadruples have negative signs, although the ratio of their coefficients is different in the two cases. However, equation (9) is more easily computed than the corresponding Karle–Hauptman determinant. On the other hand, it has the disadvantage that a reasonably complete set of phases of the reflexions contained within some limiting sphere is needed, which would limit the use of equation (9) to the final stage of phase assignment, at least at the present level of development of this approach.

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$$\text{tg } \varphi_H = \frac{\sum_K |E_K E_{H+K}| \sin(\varphi_{H+K} - \varphi_K) - \frac{1}{2}(E_0/\sum_H |E_H|^2) \sum_K \sum_L |E_K E_L E_{H+K+L}| \sin(\varphi_{H+K+L} - \varphi_K - \varphi_L)}{\sum_K |E_K E_{H+K}| \cos(\varphi_{H+K} - \varphi_K) - \frac{1}{2}(E_0/\sum_H |E_H|^2) \sum_K \sum_L |E_K E_L E_{H+K+L}| \cos(\varphi_{H+K+L} - \varphi_K - \varphi_L)}. \quad (10)$$

The above expression would reduce to the usual tangent formula if the triple contributions were neglected. The new result should provide a better estimate of φ_H

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