Reply to *Comments on From a partial to the complete crystal structure. II. The procedure and its applications*, by M. Camalli, C. Giacovazzo & R. Spagna (1985), by Paul T. Beurskens.

By M. CAMALLI, *Istituto di Strutturistica Chimica 'G. Giacomello', Area della Ricerca del CNR, CP10, 00016 Monterotondo Stazione, Roma, Italy*, C. GIACOVAZZO, *Dipartimento Geomineralogico, Università, 70121 Bari, Italy*, and R. SPAGNA, *Istituto di Strutturistica Chimica 'G. Giacomello', Area della Ricerca del CNR, CP10, 00016 Monterotondo Stazione, Roma, Italy*

Abstract

In a recent paper [Beurskens (1987). *Acta Cryst.* A43, 283–284] comments are made on a new method [Camalli, Giacovazzo & Spagna (1985). *Acta Cryst.* A41, 605–613] for recovering the complete from a partial structure. Comments by Beurskens dealing with similarities and differences between the proposed method and *DIRDIF* are wrong and have to be rejected.

Abbreviations

The reader is referred for the various symbols to Table 1 of Beurskens (1987). Henceforth, B will refer to Beursken's (1987) paper, CGS to Camalli, Giacovazzo & Spagna (1985) and G to the paper by Giacovazzo (1983).

Comparison and comments

When probabilistic methods are used for estimating phases the conclusive formula is always a conditional distribution function of type

$$P(\varphi|\{\Phi\}, \{R\}) \tag{1}$$

where φ is the phase to be estimated, and $\{\Phi\}$ and $\{R\}$ are suitable sets of known phases and diffraction magnitudes respectively. If a partial structure is available, then one may choose

$$\varphi = \varphi_{\mathbf{h}}, \quad \{\Phi\} = \{\varphi_{p,\mathbf{h}}, \varphi_{p,\mathbf{k}}, \varphi_{p,\mathbf{h}-\mathbf{k}}, \varphi_{\mathbf{k}}, \varphi_{\mathbf{h}-\mathbf{k}}\},$$

$$\{R\} = \{|E_{p,\mathbf{h}}|, |E_{p,\mathbf{k}}|, |E_{p,\mathbf{h}-\mathbf{k}}|, |E_{\mathbf{h}}|, |E_{\mathbf{k}}|, |E_{\mathbf{h}-\mathbf{k}}|\}.$$

The calculation of (1) for the above choice of $\{\Phi\}$ and $\{R\}$ has been performed by Giacovazzo (1983) [see equation (G.21), rewritten in a more useful form as equation (CGS.2)]; a practical method based on this has been described by CGS, and has been implemented in the *SIR* program (Cascarano, Giacovazzo, Burla, Nunzi, Polidori, Camalli, Spagna & Viterbo, 1985).

In *DIRDIF* the phase $\varphi_r(\mathbf{h})$ is estimated according to (B.2). This is in practice a truncated Sayre's equation applied to the remainder of the structure, which cannot be interpreted in terms of the conditional probability function (1), because this time $\{\Phi\}$ and $\{R\}$ are empty sets. In order to clarify this point we refer to equation (CGS.A2):

$$P(E'_{\mathbf{h}}| E'_{\mathbf{k}}, E'_{\mathbf{h}-\mathbf{k}}, E'_{p,\mathbf{h}}, E'_{p,\mathbf{k}}, E'_{p,\mathbf{h}-\mathbf{k}})$$

$$\simeq (2\pi)^{-1/2} \exp\left[-\tfrac{1}{2}(E'_{\mathbf{h}} - E'_{p,\mathbf{h}})^2\right.$$

$$\left. + r^{-1/2}(E'_{\mathbf{h}} - E'_{p,\mathbf{h}})(E'_{\mathbf{k}} - E'_{p,\mathbf{k}})(E'_{\mathbf{h}-\mathbf{k}} - E'_{p,\mathbf{h}-\mathbf{k}})\right]. \tag{2}$$

Writing (2) in terms of E_r, we get

$$P[E_r(\mathbf{h})|\ldots] \simeq \exp\left[-|E_r(\mathbf{h})|^2 + r^{-1/2}E_r(\mathbf{h})E_r(\mathbf{k})E_r(\mathbf{h}-\mathbf{k})\right]. \tag{3}$$

The change of variable is not immaterial and requires caution. Indeed from (3) it not possible to obtain the conditional distribution

$$P[\varphi_r(\mathbf{h})\,\big|\,|E_r(\mathbf{h})|, |E_r(\mathbf{k})|, |E_r(\mathbf{h}-\mathbf{k})|, \varphi_r(\mathbf{k})\,\varphi_r(\mathbf{h}-\mathbf{k})]$$

since $\varphi_r(\mathbf{k})$, $\varphi_r(\mathbf{h}-\mathbf{k})$, $|E_r(\mathbf{h})|$, $|E_r(\mathbf{k})|$, $|E_r(\mathbf{h}-\mathbf{k})|$ are all unknown quantities which are not accessible from the $|E|$ and E_p sets. Thus the phase relationship

$$\tan \varphi_r(\mathbf{h}) = \frac{\sum |E_r(\mathbf{k})E_r(\mathbf{h}-\mathbf{k})| \sin\left[\varphi_r(\mathbf{k}) + \varphi_r(\mathbf{h}-\mathbf{k})\right]}{\sum |E_r(\mathbf{k})E_r(\mathbf{h}-\mathbf{k})| \cos\left[\varphi_r(\mathbf{k}) + \varphi_r(\mathbf{h}-\mathbf{k})\right]} \tag{4}$$

used in *DIRDIF* is neither accessible from nor legitimized by Giacovazzo's theory. Consequently Beursken's statement (at the end of his comments) that the '*DIRDIF* method is justified by the probabilistic formula obtained by Giacovazzo (1983)' is a serious misunderstanding of the problem and has to be rejected.

On the other hand, and in contradiction to his own statement, Beurskens is well aware that (4) cannot be applied on the basis of available prior information: indeed *DIRDIF* provides probabilistic (and therefore imperfect) estimates of $|E_r(\mathbf{h})|$, $|E_r(\mathbf{k})|$, $|E_r(\mathbf{h}-\mathbf{k})|$, $\varphi_r(\mathbf{h})$, $\varphi_r(\mathbf{k})$, $\varphi_r(\mathbf{h}-\mathbf{k})$, which are continuously refined during the phasing process. Thus (4) is really used only in the final stage of the refining process, provided that estimates of $|E_r(\mathbf{h})|$, $|E_r(\mathbf{k})|$, $|E_r(\mathbf{h}-\mathbf{k})|$, $\varphi_r(\mathbf{h})$, $\varphi_r(\mathbf{k})$, $\varphi_r(\mathbf{h}-\mathbf{k})$ have converged to the correct values. In conclusion the *DIRDIF* procedure should find Beurskens's theoretical background somewhere, but certainly not in the paper G.

A residual doubt of the reader should be that, even if quite different from the theoretical point of view, *DIRDIF* and *SIR* may be equivalent in practical application. This is not the case. Indeed, equation (CGS.2) imposes the use of E' and this imposed choice involves several consequences:

(1) *DIRDIF* and *SIR* work on completely different sets of reflexions. In particular, all reflexions with estimates $|E_r|$ greater than, say, 0·9 (set $\{\mathbf{h}\}_D$) are subject to tangent refinement and phase extension in *DIRDIF*. All reflexions with $|E'|$ larger than a given threshold (set $\{\mathbf{h}\}_S$) are phased by *SIR*. For example, reflexions with $|E'| \simeq |E'_p| \gg 0$ belong to $\{\mathbf{h}\}_S$ and have a prominent role in *SIR*, while they are of no use in *DIRDIF*;

(2) even in the case in which the same reflexion $\mathbf{h}$ belongs both to $\{\mathbf{h}\}_D$ and $\{\mathbf{h}\}_S$, its roles in *SIR* and *DIRDIF* are completely different, because $\varphi_{\mathbf{h}}$ and $\varphi_r(\mathbf{h})$ are determined with quite different accuracies by (CGS.2) and by (4) respectively. Thus quite different starting sets will be chosen by *DIRDIF* and by *SIR*: in addition, phase expansion will follow different pathways.

(3) The prior information (observed magnitudes $|E'|$ and structure factors E'_p) does not change cycle by cycle in *SIR* and can be considered as a set of fixed pivots of the phasing process. In *DIRDIF* the quantities $E_r(\mathbf{k})$ and $E_r(\mathbf{h}-\mathbf{k})$ (which play in the process the role of prior information) are changed cycle by cycle both in modulus and in phase.

Besides the above points there are further peculiar opportunities offered by *SIR* to the user:

(a) a multisolution technique is always used in accordance with the good grounds described by CGS (*DIRDIF* uses symbolic addition techniques and sometimes single solutions are obtained);

(b) the phase expansion according to CGS is secured *via* a special weighting scheme which is based on functions depending on the fixed (once and for all) prior information;

(c) specialized figures of merit are used for finding the correct solutions taking into account prior information.

It is now unquestionable that *DIRDIF* and the CGS contributions share almost only the final purpose of recovering the complete from a partial structure, but have to be considered quite different from one another because they are based on different probabilistic backgrounds, work on different sets of reflexions, have quite different starting sets, estimate phase reliabilities by different formulae, find different pathways for phase expansion, employ different tangent weighting schemes, find the correct solutions by different figures of merit, and the one uses difference structure factors and the symbolic addition technique while the other works by structure factors and a multisolution technique (we want to say: *vive la différence!*).

The supposition by Beurskens that the CGS contribution, even if important, shows only that the *DIRDIF* method is justified by formula (G.21) of Giacovazzo (1983) reveals a serious misconception of the various theoretical and practical aspects here discussed and has to be resolutely rejected.

References

BEURSKENS, P. T. (1987). *Acta Cryst.* A43, 283–284.
CAMALLI, M., GIACOVAZZO, C. & SPAGNA, R. (1985). *Acta Cryst.* A41, 605–613.
CASCARANO, G., GIACOVAZZO, C., BURLA, M. C., NUNZI, A., POLIDORI, G., CAMALLI, M., SPAGNA, R. & VITERBO, D. (1985). Ninth Eur. Crystallogr. Meet., Torino, Abstract 1-046.
GIACOVAZZO, C. (1983). *Acta Cryst.* A39, 685–692.

Theory and computation of optical rotatory power in inorganic crystals. Erratum.

By V. DEVARAJAN and A. M. GLAZER, *Clarendon Laboratory, University of Oxford, Parks Road, Oxford OX1 3PU, England.*

Abstract

Equation (10) of Devarajan & Glazer [*Acta Cryst.* (1986). A42, 560–569] appearing on p. 561 should read

$$\alpha_s^{-1}\mathbf{p}_s = \sum_{s'} \mathbf{p}_{s'}\left\{\sum_{l'} a(\mathbf{r}_s^l - \mathbf{r}_{s'}^{l'}) \exp\left[-i\mathbf{k}\cdot(\mathbf{r}_s^l - \mathbf{r}_{s'}^{l'})\right]\right\}. \quad (10)$$

All relevant information is given in the *Abstract*.

Isomorphous replacement: effects of errors on the phase probability distribution. Erratum.

By THOMAS C. TERWILLIGER and DAVID EISENBERG, *Molecular Biology Institute and Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024, USA.*

Abstract

In the paper by Terwilliger & Eisenberg [*Acta Cryst.* (1987). A43, 6–13], equation (18) should read

$$\bar{F}_{PH} \equiv \tfrac{1}{2}(|\mathbf{F}_{PH}^+| + |\mathbf{F}_{PH}^-|) \doteq |\mathbf{F}_{PH}|. \quad (18)$$

All relevant information is given in the *Abstract*.