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**Reply to the comment by Hansen (1988) on 'Determining skewness in atomic probability density functions for non-centrosymmetric structures'.** By R. J. NELMES and Z. TUN,\* *Department of Physics, University of Edinburgh, Mayfield Road, Edinburgh EH9 3JZ, Scotland*

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**Abstract**

Hansen [*Acta Cryst.* (1988). **A44**, 1097] questions a recent conclusion that the Gram-Charlier expansion has advantages over the Edgeworth (cumulant) expansion for determining skewness in atomic probability density functions for non-centrosymmetric structures [Nelmes & Tun (1987). *Acta Cryst.* **A43**, 635-638]. His argument applies to the expansions extended to infinite order - which are mathematically equivalent - rather than to the truncated expansions necessarily used in actual structure-refinement procedures.

In a Comment by Hansen (1988) on a recent paper by us (Nelmes & Tun, 1987), the author questions our claim that the Gram-Charlier expansion has advantages over the Edgeworth (or cumulant) expansion for determining skewness in atomic probability density functions (p.d.f.'s) for non-centrosymmetric structures.

Hansen's argument is in terms of the two expansions to infinite order when, as is known, they are mathematically equivalent. In particular, he considers a third-order cumulant  $K^{jkl}$  (in the notation of our paper) of the type that gives rise to the problem at issue, and the effect of adding the arbitrary amount  $d^{rst}$  (his notation) to it. In this case, *only* the phase of the structure factors is altered and hence the absolute magnitude of this third-order cumulant cannot be determined from diffraction data. Hansen refers to this as the 'phase problem'. He then asks what effect the same phase change has on the Gram-Charlier expansion of the structure factor, and shows that the third-, sixth- and higher-order terms (the quasimoments  $C^{jkl\dots}$  in our notation) are altered. Hansen appears to conclude, first, that these quasimoments are thereby shown to be undetermined too, presumably on the grounds of the mathematical equivalence of the two (infinite) series, and, secondly, that our stable refinement of such quasimoments is thus revealed to be an (unreliable?) artefact of our use of a truncated series. We are not convinced that the first conclusion can be reached on the basis of mathematical equivalence alone - a more detailed analysis of the relationship between the two series is needed. In any case, we do not accept that properties of the infinite series affect the use of the truncated series.

For the purposes of this Reply, 'skewness' will be used with the restricted sense of the kind that is indeterminate when modelled by the odd-order cumulants of the Edgeworth expansion - because of the 'phase problem'. The *primary* purpose of our paper was to show that such skewness must, in fact, affect the amplitudes as well as the phases of structure factors - in all but a very few special cases - and, hence, that the absolute magnitude of the

skewness itself is *not* indeterminate. The 'phase problem' is hence a problem of modelling skewness in a way that captures the dependence on amplitude. This conclusion stands quite independently of any argument as to whether the information in the amplitudes can be utilized by available structure-refinement procedures. But, separately, we did go on to show that the truncated Gram-Charlier expansion can access this information - because its odd-order terms depend on the amplitude as well as the phase of the structure factors, unlike the Edgeworth expansion. The effectiveness of this method in practice was tested in two ways. First, we used a split-atom model to represent a two-atom structure with a skewed p.d.f. for one of them; we could then generate exact structure factors - which showed the skewness altering amplitudes as well as phases; and we satisfied ourselves that a free refinement with the truncated Gram-Charlier expansion reasonably reproduced the form of the skewness, on the correct atom. (This test was not mentioned in our paper.) Secondly, we successfully refined the skewness in the polar phase of  $\text{PbTiO}_3$ , as described in our paper. (It is, perhaps, important to emphasize that no additional constraints were applied in these refinements. All non-zero anharmonic terms up to fourth order were allowed to vary freely.)

The determination of skewness by this means is thus simply a matter of fitting the data to an appropriate parametrization of a skewed p.d.f. This is not invalidated by any indeterminacy there may be in the corresponding terms of the infinite series: the truncated series is, as Hansen stresses, a different mathematical entity. Care ought to be taken, though, not to claim that a quasimoment (cumulant) refined with the truncated series is identical to that of the infinite series. Also, truncated series are always unphysical to some extent, giving rise to negative regions in the corresponding p.d.f., and Hansen rightly warns of the need to be careful about assuming the higher-order terms to be negligible. However, these points apply to *all* anharmonic refinements with truncated series and not to skewness in particular.

In summary, whatever the properties of the infinite Gram-Charlier expansion, the truncated expansion clearly has a form capable of modelling skewness, and does so in practice. How *well* it does so may depend on the order at which the series is truncated. Moreover, it may not be capable of making maximal use of the information in the structure amplitudes, and some other series may prove preferable. Such matters do now merit further analysis.

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**References**

- HANSEN, N. K. (1988). *Acta Cryst.* **A44**, 1097.  
NELMES, R. J. & TUN, Z. (1987). *Acta Cryst.* **A43**, 635-638.

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**Increasing the size of search fragments for use in Patterson method calculations – the partial fragment rotation function. Erratum.** By C. C. WILSON, *Neutron Division, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, England*

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**Abstract**

Equations given by Wilson [*Acta Cryst.* (1988) **A44**, 478–481] are corrected. There are misplaced brackets in equations (1) and (3) and an incorrect lower summation limit in equation (3).

Equation (1) should read

$$\sigma(\theta_1, \theta_2, \theta_3) = \sum_{\mathbf{h}} |F_{\mathbf{h}}^s|^2 \left[ \left( \sum_i \cos 2\pi \mathbf{h} \cdot \mathbf{r}_i \right)^2 + \left( \sum_i \sin 2\pi \mathbf{h} \cdot \mathbf{r}_i \right)^2 \right] \quad (1)$$

and equation (3) should read

$$\begin{aligned} \sigma(\theta_1, \theta_2, \theta_3, \theta_p) &= \sum_{\mathbf{h}} |F_{\mathbf{h}}^s|^2 \left[ \left( \sum_{i=1}^{n_1} \cos 2\pi \mathbf{h} \cdot \mathbf{r}_i \right)^2 + \left( \sum_{i=1}^{n_1} \sin 2\pi \mathbf{h} \cdot \mathbf{r}_i \right)^2 \right] \\ &+ \sum_{\mathbf{h}} |F_{\mathbf{h}}^s|^2 \left[ \left( \sum_{j=n_1+1}^{n_2} \cos 2\pi \mathbf{h} \cdot \mathbf{r}_j \right)^2 \right. \\ &\left. + \left( \sum_{j=n_1+1}^{n_2} \sin 2\pi \mathbf{h} \cdot \mathbf{r}_j \right)^2 \right]. \end{aligned} \quad (3)$$

All relevant information is given in the *Abstract*.

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**Synchrotron X-ray diffraction on a CaF<sub>2</sub> microcrystal with 2.2 cubic micrometres volume.** By WOLFGANG RIECK, HARALD EULER and HEINZ SCHULZ, *Institute for Crystallography and Mineralogy, University of Munich, D-8000 Munich, Federal Republic of Germany*, and WILFRIED, SCHILDKAMP, *Cornell High Energy Synchrotron Source, Cornell University, Ithaca, NY 14853, USA*

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**Abstract**

The photon flux generated by the six-pole wiggler at CHESS combined with a focusing mirror and a focusing monochromator allowed diffraction experiments at 1.56 Å wavelength with a 2.2(5) μm<sup>3</sup> CaF<sub>2</sub> single crystal. The crystal was oriented by means of a multiwire proportional area counter. Reflection profiles and Bragg intensities were collected with a scintillation counter. The Bragg intensities were used for a structure refinement. The results demonstrate that crystals composed of light elements with volumes down to only 0.5 μm<sup>3</sup> can be mounted and used for single-crystal X-ray diffraction experiments. Until now such crystals have been considered as powder grains. Besides the possibility of applying single-crystal methods to materials of which larger crystals are not available the essentially extinction-free data from microcrystals allow a high-precision determination of electron densities and vibrational amplitudes.

Synchrotron radiation allows experiments on very small single crystals because of the low divergence and high brilliance of the beam. This feature stimulated experiments with a 200 μm<sup>3</sup> CaF<sub>2</sub> microcrystal (Bachmann *et al.*, 1983) and an 800 μm<sup>3</sup> zeolite microcrystal (Eisenberger, Neusam, Leonowicz & Vaughan, 1984). Rocking curves and reflec-

tion intensities have been recorded for these microcrystals. The Bragg intensities measured from the 200 μm<sup>3</sup> CaF<sub>2</sub> crystal have also been used for structure refinements and analyses of the mosaic spread of the crystal (Bachmann, Kohler, Schulz & Weber, 1985; Höche, Schulz, Weber, Belzner, Wolf & Wulf, 1986). Microcrystals of about 10<sup>4</sup> μm<sup>3</sup> volume have been used recently for diffraction experiments with macromolecular materials (Andrews, Papitz, Blake, Helliwell & Harding, 1988).

From the viewpoint of an X-ray scattering experiment the size of a crystal provides only a very rough estimate of the expected scattering effect, which is a function of the scattering power of a single crystal. The scattering power may be defined for an ideally imperfect crystal as

$$S = (F_0/V_e)^2 V_c \lambda^3 \quad (1)$$

where  $F_0$  is the number of electrons per elementary cell,  $V_e$  and  $V_c$  are the volumes of the elementary cell and of the crystal, and  $\lambda$  is the wavelength. Usually crystals with  $S = 10^{16}$ – $10^{17}$  are used for standard structure investigations. The above-mentioned CaF<sub>2</sub> (Bachmann *et al.*, 1983) and zeolite (Eisenberger *et al.*, 1984) microcrystals had scattering powers of  $1.45 \times 10^{14}$  and  $1.85 \times 10^{15}$ , respectively.

Microcrystals with diameters smaller than the extinction length  $L$  behave as ideally imperfect crystals. The extinction