

SHORT COMMUNICATIONS

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A comment on 'Determining skewness in atomic probability density functions for non-centrosymmetric structures' (Nelmes & Tun, 1987). By NIELS K. HANSEN, *Laboratoire de Minéralogie-Cristallographie, UA CNRS 809, Université de Nancy I, BP 239, F-54506 Vandoeuvre-les-Nancy CEDEX, France*

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Abstract

In a recent publication Nelmes & Tun [*Acta Cryst.* (1987). **A43**, 635–638] give the impression that the atomic probability density function can be determined unambiguously even for non-centrosymmetric crystal structures when using the Gram–Charlier expansion technique. This is only true under a tacit assumption of rapid convergence of the Gram–Charlier series. A similar problem exists in the analysis of electron deformation densities for non-centrosymmetric structures.

In a recent publication, Nelmes & Tun (1987) discuss the merits of the Gram–Charlier expansion over the Edgeworth series for the description of anharmonic vibrations of atoms in crystals. Both of these formalisms are based on Taylor expansions and in the expressions below, the coefficients, d^{rst} (similar to the cumulants) and $c^{klmn\dots}$, are related to the moments of the nuclear probability density function describing the deviation from a Gaussian distribution. Nelmes & Tun (1987) draw the conclusion that not only is the former description preferable because of the easier physical interpretation as shown by Kuhs (1983), but also because it does not lead to singular normal-equation matrices in the least-squares-method analysis of diffraction data as does the Edgeworth (or cumulant) treatment for certain space groups. It seems thus as if the Gram–Charlier expansion solves the phase problem. This is not possible, since it has been pointed out that the two descriptions are mathematically equivalent when the expansions are carried through to infinity.

As an illustration, multiply the structure factor by a phase factor of the form

$$\Phi(\mathbf{h}) = \exp(-ih_x h_y h_z d^{rst}).$$

d^{rst} takes an arbitrary value, and no implicit summation is assumed; the product $h_x h_y h_z$ must be chosen invariant under the crystal class symmetry operations. The Taylor expansion of $\Phi(\mathbf{h})$ (note that it is convergent for all \mathbf{h}) is given by

$$\Phi(\mathbf{h}) = 1 - ih_x h_y h_z d^{rst} - \frac{1}{2} h_x h_y h_z h_x h_y h_z d^{rst} d^{rst} + \dots$$

The expression for the structure factor using the Gram–Charlier expansion for the individual atoms reads

$$F(\mathbf{h}) = \sum_j F_j^{\text{harmonic}} (1 - ih_k h_l h_m c^{klm} + h_k h_l h_m h_n c^{klmn} + \dots).$$

Multiplication of F by Φ corresponds to modifying the coefficients,

$$\begin{aligned} (c^{rst})' &= c^{rst} + d^{rst} \\ (c^{rstrst})' &= c^{rstrst} + c^{rst} d^{rst} + \frac{1}{2} d^{rst} d^{rst}; \end{aligned}$$

all higher orders will also be modified in a similar manner. For a phase factor of the above form, note that the fourth and fifth order remain unchanged.

Contrary to the cumulant expansion where only single terms will be undetermined because of symmetry, in the Gram–Charlier series several terms, including real even-order terms, are undetermined. The phase problem is 'solved', or rather circumvented, by the convenient assumption that, above a certain order, the coefficients of the expansion are identical to zero. This assumption ought to be justified for each compound studied.

The same type of argument may be carried over to the determination of electron densities from X-ray diffraction measurements. The aspherical pseudo-atom model using multipole expansions (e.g. Hansen & Coppens, 1978) succeeds quite well in obtaining electron density maps for non-centrosymmetric structures. Once again the phase problem is solved by limiting the expansion to a finite number of terms (in general the order of the spherical harmonics are kept less than or equal to 4), and by choosing a physically reasonable radial dependence of the multipole functions.

The problem of exactly what parameters can be uniquely determined from structure-factor amplitudes certainly deserves a rigorous treatment.

References

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 KUHS, W. F. (1983). *Acta Cryst.* **A39**, 148–158.
 NELMES, R. J. & TUN, Z. (1987). *Acta Cryst.* **A43**, 635–638.