SHORT COMMUNICATIONS

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible.*

Acta Cryst. (1993). A**49**, 590

Kitajgorodskij's categories. Corrigenda.

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Abstract

Two errors in the paper by Wilson [*Acta Cryst.* (1993), A**49**, 210–212] should be corrected. In the heading of the final column of Table 1, s/mP is a misprint for $2/mP$, and in line 24 of the second column on page 212, *Fdd* is a misprint for *Fddd*.

All relevant information is given in the *Abstract*.

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The maximum-entropy method in charge-density studies: aspects of reliability.

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Abstract

The maximum-entropy method (MEM) was applied to accurate γ-ray diffraction data from MnF_2 and NiF_2 to explore details of the charge-density distribution. For a fair judgement of the results, Si *Pendellösung* data [Saka & Kato (1986). *Acta Cryst.* A**42**, 469–478] were also treated. It is shown that conclusions drawn from MEM maps must be accepted with some reserve, particularly in the regions of interest in charge-density studies.

1. Introduction

In recent years, high expectations have been raised by the application of the maximum-entropy method (MEM) to the crystallographic inversion problem. Here, MEM is considered to be promising for the following reasons: the results are independent from structural models; the reconstructed maps must be positive; and Fourier components may be extrapolated from incomplete data sets. In particular, it has been suggested that MEM would be well suited for an accurate determination of the electron density distribution (Wei, 1985; Gull, Livesey & Sivia, 1987). Up to now, however, there have been only a few demonstrations of its use (Sakata & Sato, 1990). Therefore, the present note will concentrate on some practical aspects of the method and on the reliability of its results.

The conditional entropy of a map $\{p_i\}$ with respect to the map $\{m_i\}$ is given by

$$H(\{p_i\};\{m_i\}) = -\sum p_i \ln (p_i/m_i),$$

where $p_i = \rho_i/\sum \rho_i$ is the proportion of the electron density ρ in pixel i. The m_i represent the initial density and may be based on prior knowledge but are usually all set equal. The constraint function is given by

$$\chi^2 = \sum_{k=1}^{N} (|F_o| - |F_c|)^2/\sigma_k^2,$$

where $|F_c|$ is the structure-factor magnitude calculated from $\{\rho_i\}$, σ_k^2 is the variance of the kth observed structure factor $|F_o|$ and N is the number of observations. $\{\rho_i\}$ is to be determined so as to maximize H subject to the constraints $\chi^2 = N$ and a fixed number of electrons per unit cell. In addition, the signs of the structure factors are assumed to be known. The density obtained from MEM is an exponential.

The method was applied to extended γ-ray diffraction data sets from MnF_2 ($N = 324$; Jauch, Schultz & Schneider, 1988) and NiF_2 ($N = 298$; Palmer & Jauch, 1993). To investigate any potential influence of limited data quality on the results, MEM was also applied to highly accurate *Pendellösung* data from Si ($N = 30$; Saka & Kato, 1986), which was the subject of another study (Sakata & Sato, 1990). In the present work, the program *MEED* (Sakata, Mori, Kumazawa, Takata & Toraya, 1990) was used. Normally, the unit cell was divided into 64^3 pixels and convergence was reached after about 10^3 iterations.

2. Non-random scatter of residuals

In all cases studied, a highly non-random distribution in the contributions of individual reflections to χ^2 was found after convergence. The value of χ^2 is dominated by a small number of reflections, whereas the other observations are reproduced almost perfectly. As a consequence, the R factors are much smaller than their expected values based on the standard deviations of the data.

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