

References

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The maximum-entropy method in charge-density studies. II. General aspects of reliability. By
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Abstract

Several general properties of maximum-entropy maps are reviewed that substantiate previous results from selected applications. In particular, the maximum-entropy method (MEM) is depicted as a smoothing scheme and the intrinsic bias introduced by this procedure is pointed out. It is argued that the MEM is not well suited for accurate charge-density mapping.

1. Introduction

In a previous note (Jauch & Palmer, 1993; hereafter referred to as paper I), several unsatisfactory features of the maximum-entropy method (MEM) have been found empirically. The observed peculiarities can be traced back to general properties of MEM images, which were deduced earlier in the field of astronomy (Nityananda & Narayan, 1982; Narayan & Nityananda, 1986). These results have remained unnoticed in the crystallographic literature. As there is a growing interest in using the MEM in charge-density studies (e.g. Kumazawa, Kubota, Takata & Sakata, 1993), some aspects relevant to this context will be pointed out in the present note.

2. A smoothing scheme

Entropy maximization was originally introduced (Jaynes, 1957) as a plausible scheme for constructing probability distributions: from the set of all distributions compatible with the available information, the one that maximizes Shannon's entropy is chosen. Well known properties and familiar special cases of probability distributions can thus be generated by a unified variational treatment. *Via* an axiomatic approach, Shore & Johnson (1980) have established that the maximum-entropy criterion is the only consistent way to determine an underlying probability distribution.

When applied to nonprobabilistic problems, the conceptual foundations for the choice of entropy maximization become controversial. Here, it has been argued that the MEM is to be preferred solely on grounds of consistency, without the corresponding map being more likely than others (e.g. Livesey & Skilling, 1985). A different view rests on the belief that the MEM map must correspond to the most probable one (e.g. Gull & Daniell, 1978). Electron-density reconstruction from incomplete Fourier data represents an example where the MEM is used as a statistical analogue for the evaluation of a continuous function that happens to be restricted to non-negative values, thus allowing a formal identification with a probability distribution. From a pragmatic point of view, the ME principle can be interpreted as a smoothness criterion. Following Titterton (1985), MEM image reconstruction is then regarded merely as one particular case of a very general scheme aiming at a compromise between smoothness and agreement to the data (χ^2 deviation), the relative weight between the two being adjusted to yield a desired value of χ^2 .

In actual practice of the MEM, the local contribution to the smoothness functional is chosen as $h(\rho_x) = -\rho_x \ln(\rho_x/\tau_x)$, where ρ_x represents the calculated scattering density located at \mathbf{x} and τ_x denotes the prior distribution. For the usual assumption of a uniform prior, the local contribution reduces to $-\rho_x \ln \rho_x$. Nityananda & Narayan (1982) have shown that, in the context of incomplete Fourier image reconstruction, the detailed form of the smoothness functional is not critical but can be chosen rather arbitrarily as long as certain general restrictions are satisfied. Of crucial importance are the signs of the second and third derivatives of $h(\rho_x)$ with respect to ρ_x : $h''(\rho_x) < 0$ (required for the uniqueness of the solution) and $h'''(\rho_x) > 0$ (necessary sign for nonlinearity in order to generate nonzero Fourier coefficients of higher orders). This contrasts with the view according to which MEM maps are 'better' than all other maps. In fact, the above authors have even recommended that the entropy

$-\rho_x \ln \rho_x$ should be replaced by $\rho_x^{1/2}$, which has no information-theoretic justification, thereby avoiding misleading impressions.

As indicated above, the entropy criterion rests on stronger theoretical foundations than the interpretation as a smoothing scheme might suggest. This conceptual background, however, appears to be irrelevant to our subsequent discussion, where we are concerned with practical consequences of the MEM, independent of the underlying probabilistic or logical principles.

3. Intrinsic bias

It is a most desirable property of any estimator that it is free from systematic bias: the expected value of a parameter should be equal to the true value. Provided that certain conditions are fulfilled (purely random uncertainties of finite variance in the observations, no defects in the model, appropriate weights approximating the population variance), least-squares estimates are unbiased. The MEM image represents smoothing of the least-squares solution towards a flat map. The set of calculated structure factors $\{F_k^c\}$ averaged over various realizations of noise, with a given χ^2 constraint, will therefore differ from the true data. Hence, bias is inevitable and the consequent pattern in the residuals cannot be expected to be random. Non-random patterns with a disturbingly large degree of inconsistency were indeed found in I.

Generally, smoothing procedures will tend to a non-random distribution of the residuals and to results statistically inconsistent with the observations. Nonparametric regression by spline functions represents one simple example for the occurrence of 'oversmoothing'. The smoothness of fit is expressed by some global measure of curvature (Reinsch, 1967) and, in situations where the curvature varies appreciably only in small subintervals, closeness of fit will always be sacrificed in favour of smoothness. The residuals from these local data regions are too large and this in turn is compensated by too closely fitting the noisy data from the remaining regime in order to satisfy a prescribed χ^2 constraint. The resulting pattern of residuals has little relation to the uncertainties in the measurements.

Consider the Lagrangian

$$L = \int h(\rho_x) dx - \lambda(\chi^2 - N)$$

with the integration over the unit-cell volume V . From $\partial L / \partial \rho_x = 0$, it follows that $h'(\rho_x) = \lambda(\partial \chi^2 / \partial \rho_x)$. The quantity χ^2 is defined for phase-known structure factors as

$$\chi^2 = \sum_{\{k\}} \sigma_k^{-2} (F_k^c - F_k^o)^2$$

and its partial derivative is given by the Fourier summation

$$\partial \chi^2 / \partial \rho_x = 2 \sum_{\{k\}} \sigma_k^{-2} (F_k^c - F_k^o) \exp(2\pi i \mathbf{k} \cdot \mathbf{x}),$$

where $\{k\}$ comprises the set of reflections used. Since

$$h'(\rho_x) = -1 - \ln(\rho_x / \tau_x),$$

the density has the form

$$\rho_x = \tau_x \exp[-1 - h'(\rho_x)].$$

The MEM density distribution therefore has the notable feature that it may be regarded as a nonlinear transform of the first derivative $h'(\rho_x)$, which in turn is represented by a partial Fourier series based on the finite number of observed hkl harmonics. This operational approach, which was adopted by Narayan & Nityananda (1986), provides an intuitive grasp of the properties of MEM images. Unmeasured harmonics are generated by the nonlinearity. As a consequence of the band limitation of $h'(\rho_x)$, however, it follows that MEM maps are susceptible to exhibiting similar artifacts to those inherent in Fourier inversion (dependence on completeness, error accumulation at special positions), except that positivity is ensured by the underlying exponential model. Omission of strong reflections introduces unpredictable false detail in MEM maps, a phenomenon that has actually been observed in paper I. Fourier interpolation with the MEM is therefore of limited use only.

From the previous considerations, it is obvious that the residuals are proportional to the Fourier coefficients of $h'(\rho_x)$:

$$(1/V) \int h'(\rho_x) \exp(-2\pi i \mathbf{k} \cdot \mathbf{x}) dx = 2\lambda(F_k^c - F_k^o) / \sigma_k^2.$$

As a rule, the position and the shape of the peaks in a Fourier synthesis are determined primarily by the stronger low-order harmonics, which suggests that the residuals are dominated by strong low-order reflections. This conjecture is borne out by the results reported in paper I. The $F(000)$ term remains unbiased since its constancy is usually ensured by a separate equality constraint. Because $h'(\rho_x)$ may depend on τ_x , the residuals will exhibit some dependence on a nonuniform prior density which, however, turned out to be rather weak for the cases dealt with in paper I.

The peaks in a MEM map are often sharper than those in a conventional Fourier synthesis. The corresponding spatial resolving power, however, is nonuniform. It depends on the dynamic range $r \equiv \rho(\text{peak}) / \rho(\text{background})$. The peak width varies approximately as $(\ln r)^{1/2}$: the stronger the peak, the sharper its width (Narayan & Nityananda, 1986). Therefore, the strengths and shapes of the peaks are usually not reliable and may be quite misleading. The integrated density appears to be better defined, however, as was noted in paper I. It should be pointed out that the apparent increase in resolution emerges from the imposition of 'artificial' high Fourier components, whose behaviour is not controlled by a physical criterion.

4. Concluding remarks

Attempts may be made to retrieve charge densities from phased structure factors by applying the MEM. However, one should then be aware of the fact that one is choosing an inconsistent estimator and is relying only on one particular smoothing scheme. Some reluctance concerning the apparent attractiveness of the MEM seems to be appropriate. Fitting the data exactly ($\chi^2 = 0$) would avoid bias at the price of introducing spurious detail into the map arising solely from the noise. If the density reconstruction has a more limited objective, such as locating strong peaks only, then less stringent criteria of reliability can be adopted.

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Book Reviews

Works intended for notice in this column should be sent direct to the Book-Review Editor (R. F. Bryan, Department of Chemistry, University of Virginia, McCormick Road, Charlottesville, Virginia 22901, USA). As far as practicable, books will be reviewed in a country different from that of publication.

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Cristallographie. By D. SCHWARZENBACH. Pp. x + 274. Lausanne: Presses polytechniques et universitaires romandes, 1993. Price SF 77 (soft cover). ISBN 2-88074-246-3.

Ce volume est surtout destiné aux étudiants de physique, de génie ou des sciences des matériaux. Le présent volume vise l'enseignement des notions fondamentales plutôt que les applications de la cristallographie. Ainsi, il ne traite pas des méthodes de détermination des structures. L'auteur, grâce à son expérience d'enseignant, prend un soin particulier à bien définir et à clarifier les termes utilisés.

Dans le premier chapitre sur la *Cristallographie géométrique* (25 pp.), l'auteur traite de la géométrie analytique des repères obliques, des formes polyédriques des cristaux, des pavages périodiques et conclut par une définition de ce que l'on entend par cristal. La plus grande partie du volume concerne la *Symétrie* (70 pp.) au second chapitre et la *Diffraction par les cristaux* (78 pp.) au chapitre trois. Dans le chapitre *Symétrie*, l'auteur passe en revue les opérations de symétrie, les éléments de symétrie, les classes et systèmes cristallins, les réseaux, les symétries des systèmes périodiques pour aboutir aux groupes spatiaux. La diffraction des rayons X par la matière est décrite au chapitre suivant où l'on mentionne aussi les méthodes expérimentales de diffraction et où est abordé le problème des phases.

Ce qui fait l'originalité de ce livre est le chapitre quatre où sont décrites les *Propriétés tensorielles des cristaux*. Dans ce chapitre d'une soixantaine de pages l'auteur commence par faire la distinction entre des matériaux isotropes et anisotropes. Il en tire des conclusions sur les propriétés particulières qui en dépendent. La notion de tenseur est introduite et les contraintes et déformations dans un solide cristallin sont examinées. Un certain nombre de propriétés tensorielles sont décrites (polarisation électrique, élasticité, pyroélectricité, piezoélectricité). Le chapitre se termine par des notions d'optiques cristalline (biréfringence et microscope polarisant).

Une vingtaine de pages sont consacrées à des exercices (avec les solutions) sur chacun des chapitres. Les illustrations de ce volume ont été réalisées à l'aide du programme

MacDrawII, de *SHAPE* et d'*ATOMS*. Je trouve que les traits sont souvent trop épais et il en résulte pour certain illustrations un manque de clarté. Les adaptations d'illustrations tirées de volumes ou de publications antérieures ne sont pas toujours très heureuses. J'ai bien apprécié la citation, tirée de Voigt (1910), où cet auteur compare l'ordre cristallin à l'activité d'un orchestre dirigé par un directeur renommé. 'La musique des lois physiques se manifeste dans la physique des cristaux par les accords les plus beaux et les plus riches.'

Le volume est écrit en français, ce qui est assez rare de nos jours mais très utile. Ainsi les étudiants francophones pourront acquérir le vocabulaire assez spécialisé de la cristallographie dans leur langue.

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Handbook of crystal growth. Vol. 1: Fundamentals. a: thermodynamics and kinetics; b: transport and stability. Edited by D. T. J. HURLE. Pp. xiv + 1218. Amsterdam: North Holland Elsevier Science Publishers, 1993. Price \$388.50. ISBN 0-444-88908-6.

These are the two parts of the first volume of a three-volume series planned for the growth of bulk crystals and thin films. One might expect from the title a 'how-to-do-it' handbook, but the stated objective of the series is to expose the underlying scientific basis of crystal growth to help keep theory and practice in touch with each other. The two parts of this volume deal principally with the theory of crystal growth and include some results from experiments and computer simulations. Subsequent volumes are scheduled to cover growth techniques.