4. Finding averaged coordinates

A frequent problem in computer-assisted molecular modelling is that of obtaining a weighted average structure for a substructural fragment contained in a number of different molecular structures determined by X-ray diffraction techniques.

There are several ways to obtain such averaged fragment structures. A particularly convenient one is to average atomic positions in a set of appropriately superimposed fragment structures. This section demonstrates that our superposition procedure provides a basis for obtaining weighted average structures.

We require that a weighted average structure (x_l^0) obtained from M molecules (x_l^m) be an average taken after suitable reorientation of the molecules. The reoriented molecules have the coordinates

$$y_l^m = O^m x_l^m. \tag{14}$$

The weighted average structure is given by

$$x_l^0 = \sum_m u^m y_l^m, \quad \sum_m u^m = 1. \tag{15}$$

The requirement that the average structure be optimal can be formulated as

$$\sum_l w_l \sum_m u^m (y_l^m - x_l^0)^2 = \sum_l w_l \sum_m u^m (y_l^{m2} - x_l^{02})$$

$$= \text{minimum}, \tag{16}$$

where the parameters to be varied are the orientation matrices O^m. Again, y_l^{m2} is unchanged if the rotation matrix O^m is varied; hence (16) is equivalent to

$$\sum_l w_l x_l^{02} = \text{maximum}. \tag{17}$$

Inserting the definition (15) of x_l^0, we get

$$\sum_{m,n} u^m u^n \sum_l w_l y_l^m y_l^n = \text{maximum}. \tag{18}$$

The term with $m = n$ is again invariant. Thus, after inserting (14), we may equivalently write

$$\sum_{m \neq n}^{M} u^m u^n \, \text{Tr} \, (O^m S^{mn} \hat{O}^n) = \text{maximum}. \tag{19}$$

This condition is exactly equivalent to (6) if we take instead of constant pairing weights v^{mn} [see (2)] the values

$$v^{mn} = u^m u^n. \tag{20}$$

Therefore, in order to obtain an optimized structure as a weighted average of M given stuctures, one has to perform the superposition of the M molecules as described in § 2, taking as pairing weights the values (20). The average coordinates (x_l^0) are then obtained through (15) from the matched coordinates.

This procedure can also be applied to symmetrize a structure which is expected to show a certain symmetry, but for which the actual coordinates deviate slightly from the required symmetry. The symmetrized structure is easily obtained as the average structure of all possible symmetry-related orientations superimposed with equal weight factors $(v^{mn} = \text{constant})$.

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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.

Sayre's equation is a Chernov bound to maximum entropy.

By ROBERT W. HARRISON, *Center for Chemical Physics, National Bureau of Standards, Gaithersburg, MD 20899, USA*

Abstract

Sayre's equation is fundamental to a large part of classical direct methods. In this paper, it is shown that this equation can be derived *via* an integral bound to the entropy integral. While positivity is implicit in this derivation, atomicity is not used.

Introduction

Sayre's equation and similar triplet-based forms have formed the basis for the highly successful direct methods used in small-molecule crystallography (Sayre, 1952; Karle & Hauptmann, 1950). The maximum-entropy method has the potential to extend these methods to larger and more

difficult systems and, for this reason, is the subject of much current research (Bricogne, 1984; Britten & Collins, 1982; Steenstrup & Wilkins, 1984; Narayan & Nityananda, 1982; Livesey & Skilling, 1985). Maximum-entropy methods can ·be shown to be related to regular direct methods in a number of ways. The relationship between maximum-entropy and maximum-determinant methods can be shown with the use of a theorem about the logarithm of the Karle-Hauptman determinant (Britten & Collins, 1982; Narayan & Nityananda, 1982; Steenstrup, 1984). Sayre's equation has been found by the repeated use of the central limit theorem of statistics (Livesey & Skilling, 1985). In this paper an integral bound is used to show the relationship between direct methods and maximum entropy in a straightforward manner.

The Chernov bound will be used. This bound consists of replacing $\ln \rho$ with the line $\rho - 1$. More formally $\rho - 1$ is always greater than or equal to $\ln \rho$. This is just a Taylor-series expansion of $\ln \rho$ about 1. The expansion can be about any point, but for unitary E's 1 is most appropriate. (Unitary E's are, for the purposes of this paper, structure factors scaled in such a way that the average value of the square of the electron density and the average value of the electron density are both equal to one so that no scale factor need be propagated in the equations.) the quality of the Chernov bound is shown in Fig. 1, which is a graph of $\rho \ln \rho$ and $\rho(1-\rho)$. The discrepancy is quite small in the region around 1, which is where the expansion of $\ln \rho$ was centered. As this bound tends to give analytically tractable results, it is used extensively in communications theory.

Definition of entropy

Entropy was introduced as a measure of the quality of a probability distribution by Jaynes (1957). When the entropy of a probability distribution is at a maximum, and the probability distribution agrees with any observed data, the distribution is optimal in the sense that the fewest assumptions about the unobserved data are used. As such it allows the use of simple physical models of electron density, such
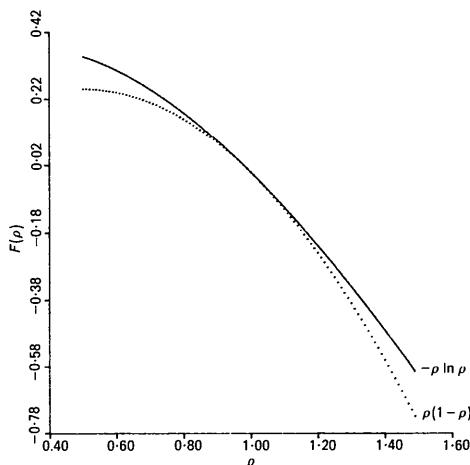
as positivity, to determine unobserved parameters, namely the phases.

The entropy is best defined in terms of the expected value of the information, which is defined as the negative logarithm of the probability. The concepts of probability density and information are only defined for always-positive functions. A maximum-entropy map is one in which the functional

$$H = \int (-\rho \ln \rho)\, dV, \qquad (1)$$

where ρ is a probability density, such as the electron density, and dV is a differential volume element, is maximized as a function of some set of variables such as the phases (where, for example, ρ is constrained to be a Fourier sum). For crystallographic applications ρ is the electron density; the integration is over the unit cell, and the measure $-\rho \ln \rho$ is maximized as a function of the phases and amplitudes of the structure factors. The global maximum of this functional occurs when ρ is constant, but because the Fourier coefficients of a constant are in general non-zero, the maximum for a system with non-zero structure factors is not a constant.

Finding a lower bound to the entropy functional

Starting from (1), the substitution $-\ln \rho \geq 1 - \rho$ is used. This results in the following integral inequality:

$$\int (-\rho \ln \rho)\, dV \geq \int \rho(1-\rho)\, dV. \qquad (2)$$

This states that the entropy functional is always greater than the modified functional. This bound is valid because $\rho(1-\rho)$ is always less than $-\rho \ln \rho$ and both functions have finite maxima and minima for finite positive arguments. Furthermore, since this is an inequality between variational equations the addition of an arbitrary constant to both sides of the inequality does not change the location of the maxima or the validity of the bound. Methods for using the right-hand side of (2) directly in real space have been summarized recently (Lunin, 1985). However, it is of interest to work in reciprocal space, and when ρ is a Fourier series this bound replaces the analytically intractable logarithm of a Fourier series with the square of a Fourier series.

Making the substitution that $\rho = \sum_h U_h \exp(2\pi i \mathbf{h} . \mathbf{x})$, where U_h are the unitary E values, gathering terms of constant index, taking the absolute value and using the triangle inequality one finds that (2) is maximized when

$$\left| U_h - \sum_k (U_{h-k} U_k) \right| \qquad (3)$$

is minimized, which occurs when it is equal to zero. This condition yields

$$U_h = \sum_k (U_{h-k} U_k). \qquad (4)$$

which, when the domains of the sums over k and h are the same, is just Sayre's equation for unitary E's. Implicit in (4) is the assumption that for every pair of U_h and U_k the reflection U_{h-k} can also be found. With real observations this condition is often not true so that a modified form of (4) is used in practice.

Concluding remarks

From this point much of classical direct methods can be developed, which makes it clear that the maximum-entropy

Fig. 1. A graph showing the values of $-\rho \ln \rho$ and $\rho - \rho^2$. Notice that the values are very close in the vicinity of 1 and do not diverge by much over the range from 0·5 to 1·5.

method is a true member of the set of direct methods. It is interesting to note that the conditions under which Sayre's equation is most valid, that is when p is nearly constant except at atomic positions, are also the conditions under which the bound given in (2) is tight.

The bound used in this paper can be improved by going to a higher-order expansion of ln p. This would correspond to the use of higher-order invariants. However, a word of caution is needed, since the next uniform bound occurs with a cubic expansion of ln p (it is important that a uniform, i.e. a single-function, bound be used, because it is not trivial to perform the Fourier substitution with a non-uniform bound). This would correspond to the use of at least a quintet expansion.

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Are (TSeT)₂I crystals homochiral or microtwinned?

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Abstract

A simple experimental test is described for deciding whether a crystal with a chiral space group is built from homochiral or heterochiral domains; this test is applied to $(TSeT)_2I$ {TSeT = tetraselenotetracene (naphthaceno[5,6-*cd*, 11,12-*c'd'*]bis[1,2]diselenole)}.

Introduction

Crystals in chiral space groups are sometimes obtained under achiral conditions by spontaneous resolution. It may then be important to know whether a given crystal specimen is homochiral or built from domains of opposite chirality [*e.g.* hexahelicene. Green & Knossow (1981)]. In principle, chiroptical measurements may provide an answer but they may not always be feasible, especially for very small or highly absorbent crystals. We describe here a simple non-destructive test which may provide an answer.

Example

Although the tetraselenotetracene (TSeT) molecule (Fig. 1) has potential D_{2h} symmetry, $(TSeT)_2I$, prepared by co-sublimation of TSeT and iodine, crystallizes in the chiral space group $P2_12_12$, $a = 18\cdot336$, $b = 17\cdot450$, $c = 5\cdot077$ Å (Hilti, Mayer & Rihs, 1978). In connection with our interest in chiral conductors (Wallis, Karrer & Dunitz, 1986), we wanted to know whether the crystals were actually
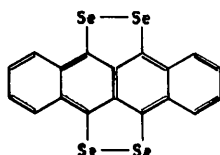

Fig. 1. Structural formula of tetraselenotetracene (TSeT).

homochiral or multiple twins consisting of left- and right-handed domains.

Method

The intensity ratio $\alpha = I(hkl)/I(\bar{h}\bar{k}\bar{l})$ of a Bijvoet pair of reflections is measured on a diffractometer with as fine a collimator as possible. The primary-beam cross section must be considerably smaller than the crystal under investigation. The measurement is repeated over the whole length of the (preferably needle-shaped) crystal.

Several results are conceivable:

$\alpha \simeq 1$. Crystal is microtwinned (consists of heterochiral domains that are smaller than the primary-beam cross section), or else anomalous dispersion is too weak to be detectable.

α *changes to* $1/\alpha$. Crystal is macrotwinned (consists of heterochiral fragments comparable in size with the primary beam).

α *does not change.* Crystal is homochiral.

Note that refinement of the absolute-structure (twin) parameter, as proposed by Flack (1983) and Bernardinelli & Flack (1985), would not distinguish between the first two cases if only one intensity measurement per reflection were available.

Experimental

Weissenberg photographs of five sample crystals showed that all were macroscopically twinned across the (110) planes, so that the *hhl* reflections of both reciprocal lattices coincided. Most of the other reflections were easily resolvable. The ratio between the two macrotwins varied widely from crystal to crystal. The crystal structure of $(TSeT)_2I$ had been established without considering anomalous scattering (Hilti, Mayer & Rihs, 1978). The cell dimensions and

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