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Two Methods of Presentation of Electron-Density Maps Using a Small-Store Computer

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A method is described for plotting electron-density maps on a cathode ray tube plotter attached to a small computer. The map may be presented either as contours or, by using a distribution of points, as a direct representation of density. Using a single pass of magnetic tape, only two thousand words of core store are needed.

Introduction

The automatic generation of contour maps of electron density by means of an X–Y plotter controlled by a computer is now fairly widespread, and a number of papers have been published concerning the methods used (Anzenhofer, 1964; Cherin, Madigen & Martin, 1965). For the most part, these have assumed the use of a pen-type plotter, in which it is desirable that each contour should be plotted continuously.

The basic information is usually in the form of a matrix of spot values of density, typically 100 points square, *i.e.* a total of some ten thousand points. For a reasonably fast generation of the path of one contour, all these values should be held in the core store of the computer; if the store is not large enough for this, and the information is held on magnetic tape, then many passes will be necessary.

By using a cathode ray tube (C.R.T.) plotter, however, it is possible to plot contours discontinuously, and this removes these difficulties. A method will be described for producing contour maps which uses less than two thousand words of core store in a single pass of magnetic tape.

On the C.R.T. plotter it is also possible to produce a simulation of actual density, without modulation of spot intensity.

Plotter system

The methods described below have been implemented on a Ferranti Argus 304 computer, which is used for a number of on-line applications in this laboratory.

The principal mode of input for plotting purposes is industries-compatible magnetic tape, although paper tape is sometimes used as an alternative. The data, in the form of spot densities on a regular grid, held by rows, are generated separately on an IBM 7090 computer as a by-product of a Fourier synthesis program. One reel of magnetic tape can hold between fifty and a hundred sections – enough for a complete protein molecule.

The plots are produced on a high resolution C.R.T. without modulation of brightness. A 35 mm camera is fitted, having computer-controlled winding mechanism, so that a complete sequence of sections can be plotted automatically. The user has a number of optional facilities available, for the production of titles and grid lines, and for the choice of contour level.

Method

The problem falls into two distinct parts. The first is to derive a satisfactory method of interpolation between the spot values, and the second to produce the contours of the interpolated function. The axes of the grid on which the function is defined are not necessarily orthogonal, but the transformation required is trivial.

Mathematically, we have a function $f(x,y)$ defined at points $x=i\Delta x$, $y=j\Delta y$, where Δx and Δy are constant. Any point (x,y) may be redefined as:

$$x=(i+\alpha)\Delta x$$
$$y=(j+\beta)\Delta y\,,$$

where α and β lie in the range [0,1). The range of x and y covered by this definition for given i and j forms the 'plotting unit' of the program.

Within each plotting unit, a simple bilinear interpolation is used, of the form:

$$f(x,y)=(1-\alpha)(1-\beta)f_{i,j}+(1-\alpha)\beta f_{i,j+1}+\alpha(1-\beta)f_{i+1,j}+\alpha\beta f_{i+1,j+1}$$

where $f_{i,j}=f(i\Delta x, j\Delta y)$.

Contours within each plotting unit are sets of hyperbolae on common asymptotes parallel to the axes. The function $f(x,y)$ is continuous over the whole plotting area, but its derivatives are not, being discontinuous at the boundaries between units. The contours have the same properties; they are liable to sharp changes in direction in the neighbourhood of peaks and areas of fine detail, but they are always continuous, and fully determinate. (The reasons for this are given below.)

The program operates on a television-scan principle, evaluating the points at which contours cross a line of constant y, for successive lines separated by $\varepsilon=1/2048$ of the plotting area. Within each plotting unit, the separation between contours at equal intervals Δf on one line is constant, since $\partial f/\partial x$ is constant along that line.

Since contours are then plotted at constant intervals of y, they tend to break up into a sequence of separated points if the contour becomes nearly parallel to the x axis. In order to overcome this, it is necessary to consider each plotting 'element', ε^2, separately, and to compare the values of f at the four corners. If the integral parts of $f/\Delta f$ are different, then a contour passes through the element, and the point is plotted. With this modification, the contours are continuous in any direction.

It may be of interest to describe the contours produced in certain special cases. The first is when the same contour level occurs once on each of the four edges of the plotting unit; the contour is then represented by both branches of the same hyperbola, whose asymptotes pass through the unit, as in Fig. 1 (left). A further degeneration is shown in Fig. 1 (right), where the hyperbola is reduced to the asymptotes themselves. If a contour level occurs at two adjacent grid points, and thus by implication along the edge of a plotting unit, then the edge may or may not be plotted, depending on conditions in the units on either side. This applies even in the exceptionally rare case when all four vertices of a unit lie on a contour.

In all these cases, the results are consistent with the topological properties of contours. This arises naturally from the fact that the computer considers zero to be a positive number, so that the value of f is always considered to be either above or below a contour level, as is implicit in the use of the integral part of $f/\Delta f$.

Negative contours are plotted 'half-weight'. Since the computer does not work along contours, dotted or broken lines are not easily produced. Instead, a chequerboard sieve is used, which effectively ensures that only half the normal number of points on a contour is plotted. This is achieved by comparing the least significant bit (2^{-10}) of x and y on any contour point, and plotting only if they are equal.

An example of a complete contour plot is shown in Fig. 2.

Storage requirements

The amount of storage required is largely determined by the number, $i_{max}+1$, of values of density in each

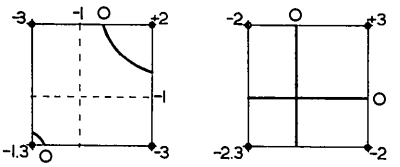

Fig. 1. Contours produced in certain special cases. Left: case in which the same contour level occurs once on each of the four edges of the plotting unit. Right: further degeneration where the hyperbola is reduced to the asymptotes themselves.

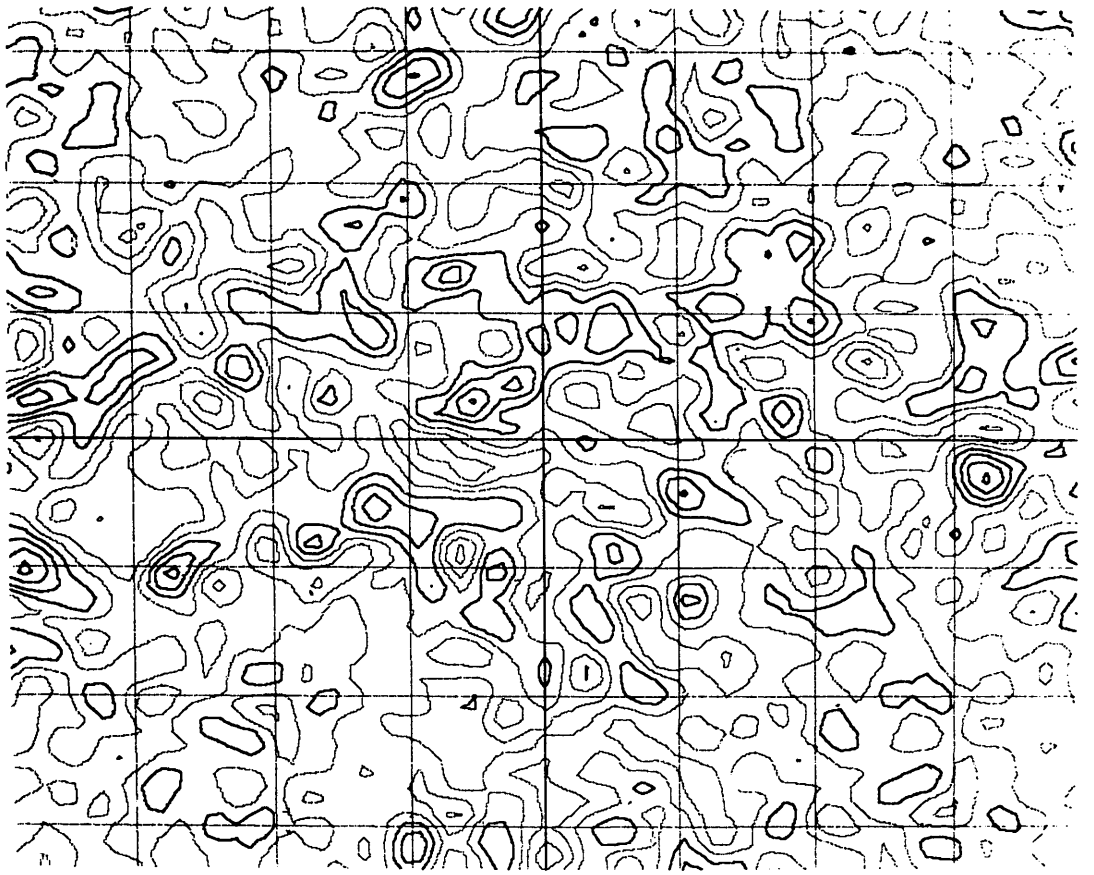

Fig. 2. Contour map of a section of α-chymotrypsin (courtesy of D. M. Blow, B. W. Matthews and P. B. Sigler, unpublished work).

row. At any one time it is necessary to hold one row of densities and the values of $\partial f/\partial y$ for $x=i\Delta x$, together with the densities at $x=i\Delta x$ for the current value of y and at $y+\varepsilon$. Assembly space is also needed when a new row is being assembled from tape, so that the total storage becomes $5(i_{\max}+1)$. For normal purposes, $i_{\max}$ is under 200, so that a thousand words of store are sufficient.

The program is coded in the internal language of the computer, for efficiency. In this form it occupies some 700 store locations, including the additions necessary for including grid lines and titles.

Density plotting

The information of Fig. 2 is also presented in Fig. 3, in the form of a direct representation of density. Modulation of beam intensity is not provided in the hardware, and would in any case be difficult to preserve through a number of photographic processes. The standard-intensity spots of the plotter are therefore distributed with a frequency proportional to the density to be plotted.

The more obvious ways of achieving this distribution have a tendency to introduce apparent additional structure to the plot. To avoid this, the shading method is based on random numbers. The probability of brightening the point (x,y) is made equal to:

$$p(x,y)=\begin{cases}\dfrac{f(x,y)-f_{\min}}{f_{\max}-f_{\min}}, & f_{\min}\le f(x,y)<f_{\max}\\ 0, & f(x,y)<f_{\min}\\ 1, & f(x,y)\ge f_{\max},\end{cases}$$

where $f_{\min}$ and $f_{\max}$ are two constants which can be set by the user. Values of f below $f_{\min}$ are thus not plotted at all, while those above $f_{\max}$ are plotted as uniform solid areas.

The decision whether or not to brighten the point (x,y) is made by considering the quantity:

$$f(x,y)-f_{\min}-r(x,y)(f_{\max}-f_{\min})$$

where $r(x,y)$ is a (pseudo-)random variable with uniform probability distribution over the range [0,1). If this quantity is positive (or zero), the point is plotted.

The choice of a pseudo-random generator for $r(x,y)$ requires some care if apparent structure is to be avoided completely. After some experiment, it was found that the multiplicative-congruence method gave best results, using:

$$R_{n+1}=5R_n+1 \pmod{2^{23}}$$
$$r_n=2^{-23}R_n\,.$$

Using a television-scan principle, as in contour plotting, it is sufficient to take successive values of r_n for $r(x,y)$ as each successive plotting element is considered.

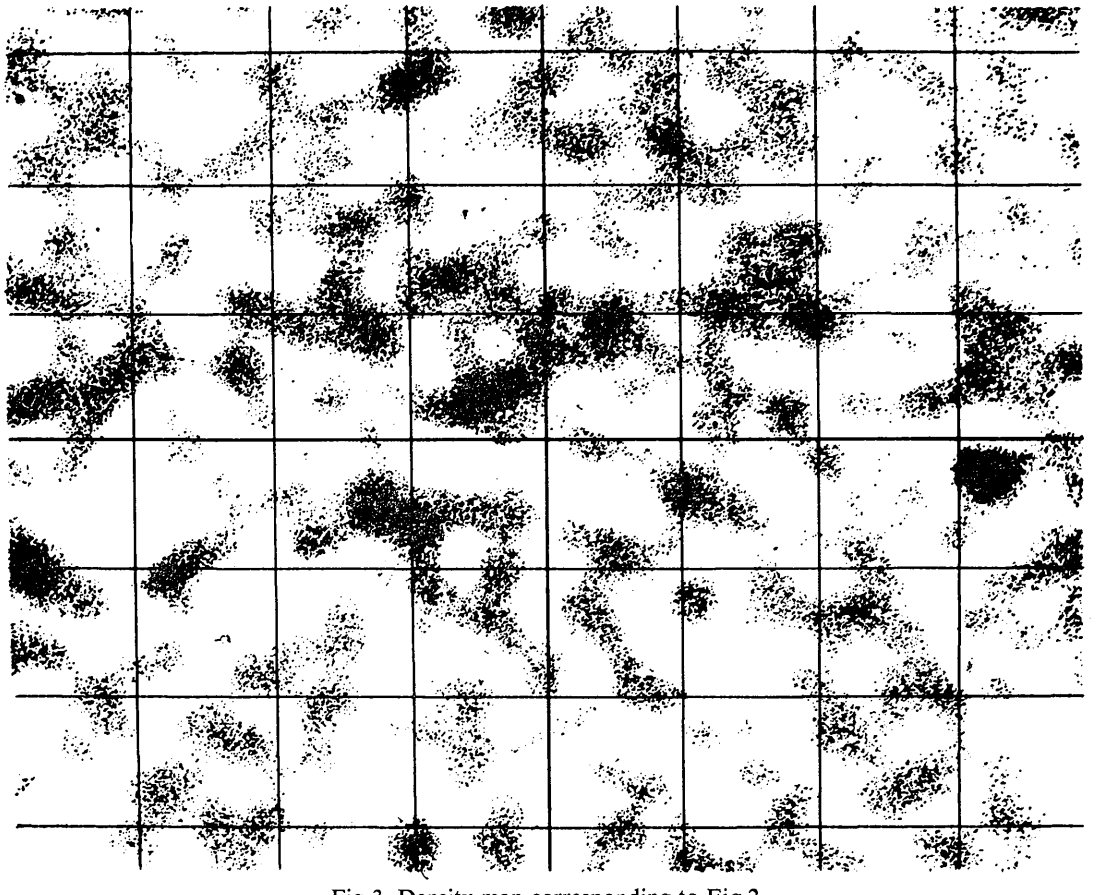

Fig. 3. Density map corresponding to Fig. 2.

The density plotting program is slightly simpler than that for contours, and only requires storage of four rows at any one time. The value of f at one corner of a plotting element is taken as applying to the whole of that element. Density plots do not, in general, show the fine detail of contour plots, and the angularity of contours is no longer apparent. Their use is more for giving an immediate impression than for quantitative measurement.

Conclusion

The methods described could well be adapted to other small computers equipped with a similar display device. Experience has shown that the quality of the contours is quite adequate for resolving details of the order of one plotting unit – the examples shown were both from the same data, on a grid of 64×64 points. The time taken to plot one section is dependent on the plotting hardware and, in the case of density plotting, on the density required. The examples were each plotted in about four minutes, which compares well with other methods.

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The Crystal and Molecular Structure of Nickel-Glyoxime

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Nickel-glyoxime, $(H_2C_2N_2OOH)_2Ni$, crystallizes in the monoclinic system, prismatic class, with two molecules per unit cell and belongs to space group $P2_1/c$. Unit-cell parameters are: $a_0 = 4{\cdot}1961 \pm 0{\cdot}0009$, $b_0 = 7{\cdot}2005 \pm 0{\cdot}0014$, $c_0 = 12{\cdot}4039 \pm 0{\cdot}0021$ Å; $\beta = 91°4' \pm 1'$. The structural analysis of this complex, based on all the reflexions accessible with Cu $K\alpha$ radiation (final R value for 524 'observed' reflexions 3·9 %), shows that the Ni atom coordinates four N atoms in a plane, while the remainder of the molecule is planar only in first approximation. Only symmetry C_2 can be assigned to the Ni-glyoxime molecule; the existence of several intermolecular contacts between C and O atoms explains the departure from strict planarity. By a three-dimensional difference synthesis and from stereochemical considerations, it has also been possible to locate the hydrogen atoms satisfactorily. The intermolecular distance between two oxygen atoms bound by a hydrogen bond is $2{\cdot}453 \pm 0{\cdot}006$ Å, and the bond is likely to be of the symmetrical type. There is no appreciable contact between Ni and other atoms.

Continuing a program of studies on the crystal and molecular structure of glyoxime (Calleri, Ferraris & Viterbo, 1966) and its derivatives, the authors have carried out a structural study of the nickel-glyoxime complex and are now also investigating the structure of palladium-glyoxime.

Experimental

Preparation; optical and crystallographic data

The crystals of nickel-glyoxime, $Ni(H_2C_2N_2OOH)_2$, were obtained by recrystallization from nitrobenzene at 50 °C of the compound prepared by reaction between nickel(II) chloride and glyoxime in aqueous alcoholic solution, made slightly ammoniacal. The crystals so obtained are brick-red, of small dimensions and usually somewhat squat though always elongated in a preferential direction.

From Weissenberg photographs we deduced that nickel-glyoxime (NiG) crystallizes in the monoclinic system and, choosing the elongation direction as [100], we noticed that the systematically absent reflexions were: $h0l$ with l odd and $0k0$ with k odd, which unambiguously indicates that the compound belongs to the space group $P2_1/c$. The reciprocal unit-cell parameters, a^*, b^*, c^*, and β^* were refined by a least-squares procedure using 30 θ_{hkl} values, between 60° and 80°, measured with a single crystal on the diffractometer with Cu $K\alpha$ filtered radiation ($\lambda\alpha_1 = 1{\cdot}54050$ Å, $\lambda\alpha_2 = 1{\cdot}54434$ Å). The minimized function was:

$$d^*_{\text{meas}} - d^*_{\text{calc}} = \delta d^* = \sum_{i=1}^{4} \left(\frac{\partial d^*}{\partial x_i^*} dx_i^* \right), \qquad (1)$$

where x_i^* are the reciprocal-cell parameters. The following values, for the direct-cell parameters were obtained: