

– Gaussian or Fresnellian distribution

$$\frac{\partial \psi_G}{\partial Q} = (\psi_G/Q)^3$$

$$\frac{\partial \psi_G}{\partial g} = (\psi_G/g)^3 \sin^2 2\theta \quad (A13)$$

– Lorentzian distribution:

$$\frac{\partial \psi_L}{\partial Q} = (\psi_L/Q)^2$$

$$\frac{\partial \psi_L}{\partial g} = (\psi_L/g)^2 \sin 2\theta. \quad (A14)$$

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## Tchebycheff Extraction of the Periodic Vector Set from the Patterson Function

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The image-seeking method of Buerger and the procedure of Tokonami and Hosoya appear to be capable of dealing with complex crystal structures *via* the Patterson function, provided that the periodic vector set is accurately determined. Unfortunately, a general and powerful method for the location of peaks in the Patterson function has not yet been developed, and it is the lack of such a method which now prevents the formulation of a general Patterson method of structure analysis. This paper presents further results in the author's attempts to formulate a general method of vector-set extraction by representing the Patterson function as a linear generalized polynomial in a system of independent interatomic functions. This approach has the advantage in that the essentially non-linear problem of vector-set extraction is reduced to an apparently simple linear problem, namely that of determining the coefficients of the approximating polynomial. In the present paper, the Tchebycheff approximation norm is employed with coefficient determination by linear-programming procedures. Since linear-programming methods are flexible and extremely powerful, this Tchebycheff vector-set-extraction procedure is much more promising than the author's earlier published methods, which were based on interpolatory approximations.

### Introduction

In order to formulate a general method of structure analysis, one would naturally think of working in terms of the Patterson function, since this function is not restricted to centrosymmetric structures. It is well known that the Patterson function may be regarded as a badly resolved representation of the weighted periodic vector set (Buerger, 1959). For a crystal containing  $N$  atoms per unit cell, the weighted periodic vector set consists of  $N$  periodic images of the crystal structure, and the phase problem is essentially the problem of separating the various points of the periodic vector set into these images. This separation can be accomplished by the image-seeking method of Buerger (1950) or the procedure of Tokomami & Hosoya (1965). Since

neither of these methods has been widely used in practice, it might well be that their power is restricted in some ways which are not now apparent. At present, however, it appears that they could be successfully applied to extremely complex crystals, provided the weighted periodic vector set could be accurately determined.

In the past, the determination of the periodic vector set from the Patterson function has been attempted *via* various sharpening procedures (Patterson, 1934; Wunderlich, 1965). These sharpening methods depend to a large extent on the initial resolution of the Patterson function, and therefore they do not appear to be capable of dealing with complex structures which produce badly resolved Patterson functions. Certain other methods, which in effect locate individual peaks

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in the Patterson function, have also been proposed. These methods, like the symmetry-minimum function (Simpson, Dobrott & Lipscomb, 1965), can only be applied to crystals of sufficiently high symmetry, and are therefore non-general.

These considerations indicate that, at the present time, the major difficulty in crystal-structure analysis *via* the Patterson function is the problem of extracting the periodic vector set. What is needed is a vastly improved sharpening procedure or a method which can, in some way, 'see through' the overlapping peaks of the Patterson function regardless of any lack of resolution. This paper presents an attempt to formulate a practical method of that kind.

The method is based on the idea of approximating the Patterson function by a generalized polynomial, in a set of interatomic functions, on a discrete set of points. The formulation of the approximating polynomial has been presented in an earlier paper (Goldak, 1971). The determination of the coefficients of this polynomial *via* the solution of a system of linear equations which results from an interpolatory approximation has also been published (Goldak, 1969). It was noted that the power of this particular variant of the method was restricted by certain numerical difficulties associated with ill-conditioning of the system of linear equations. The present paper presents a much more powerful and flexible method of coefficient determination based on a Tchebycheff or minimax approximation with coefficient evaluation by linear-programming procedures.

### The Tchebycheff approximation problem

In this work, it is most convenient to deal with a partial Patterson function of order  $M$ , projected onto some crystal axis. For example, if the  $a$  crystal axis is used, the partial Patterson function of order  $M$  would be defined as

$$P_M(x) = \sum_{h=-M}^{+M} K_h |F_h|^2 \exp [2\pi i h x] \quad (1)$$

where the summation is carried out up to terms of Miller index  $M$ . In (1)  $C = bc/v$  where  $b$  and  $c$  are unit cell parameters and  $v$  is the unit-cell volume. The series (1) may be summed directly, or by Cesaro or Lanczos summation, and  $K_h$  is a summation factor which depends on the summation method employed (Goldak, 1971).

The partial Patterson function can be written in the form (Goldak, 1971)

$$P_M(x) = C \sum_{q=1}^K \sum_{p=1}^{N_q} I_{Mq}^H(x - x_p^q). \quad (2)$$

In (2)  $I_{Mq}^H(x - x_p^q)$  represents the  $p$ th half-cell interatomic function or Patterson peak of the  $q$ th kind, with interatomic function parameter  $x_p^q$ .  $K$  represents the number of kinds of interatomic function associated with the Patterson function, and  $N_q$  denotes the

number of interatomic functions of the  $q$ th kind per unit cell. Each of the interatomic functions is represented by a Fourier series of order  $M$  which may, like the partial Patterson function, be summed directly, or by Lanczos or Cesaro summation. In the case of sharpened Patterson functions, Lanczos or Cesaro summation offers real advantages (Goldak, 1971).

For the practical computation of approximations on an interval, it is usually desirable to replace that interval by a finite set of points and to seek an approximation which is optimum on that set. In this way the problem is discretized (Cheney, 1966). In the present case, we choose any desired crystal axis (say the  $a$  axis) for the analysis of the Patterson function. We then divide that axis into a net of  $Z = KD$  divisional points, where  $K$  is the number of kinds of interatomic function associated with the Patterson function, and  $D$  is the number of divisional points allowed for the location of each kind of interatomic function. Then  $x_j^r$  represents the  $x$  coordinate of the  $j$ th divisional point for interatomic functions of the  $r$ th kind. There is a total of  $(KD - 1)$  equal intervals in  $(0, \frac{1}{2})$ , each interval being of fractional length  $1/(2KD - 2)$ . The fractional coordinate associated with a given  $x_j^r$  is

$$x_j^r = \frac{(r-1) + K(j-1)}{2(KD-1)}. \quad (3)$$

The sequence of divisional points is  $x_1^1, x_2^1, x_3^1, \dots, x_1^K, x_2^K, x_3^K, \dots, x_D^K$  with  $x_1^1 = 0$  and  $x_D^K = \frac{1}{2}$ .

We then consider the generalized polynomial in the half-cell interatomic functions

$$G(x) = \sum_{p=1}^D \sum_{q=1}^K N_p^q I_{Mq}^H(x - x_p^q). \quad (4)$$

The coefficients  $N_p^q$  in (4) are now to be determined in some way so that  $G(x)$  will in some useful sense be a 'good' approximation to  $P_M(x)$ .

The determination of the  $N_p^q$  so that  $G(x)$  interpolates to  $P_M(x)$  on the set of  $KD$  divisional points is done by setting (Goldak, 1969, 1971)

$$G(x_j^r) = P_M(x_j^r) \quad r = 1, 2, \dots, K; \quad j = 1, 2, \dots, D. \quad (5)$$

This represents a linear system of  $KD$  equations, which can be solved for the  $KD$  unknowns  $N_p^q$ . In order to increase resolution, it would be desirable to use a very large number of closely spaced divisional points. Unfortunately, when this is done, the system (5) becomes ill-conditioned or mathematically unstable, and the resulting  $N_p^q$  values tend to alternate successively between positive and negative values of large absolute magnitude. In the present paper, a Tchebycheff approximation norm is employed to overcome these difficulties.

According to the Tchebycheff norm,  $G(x)$  is determined so that it is a minimax (Rice, 1964) approximation to  $P_M(x)$ . The  $KD$  divisional points  $x_j^r$  are employed for the location of interatomic functions, but another set  $\{\bar{x}_1, \bar{x}_2, \dots, \bar{x}_Q\}$  of  $Q$  points is used for the evaluation of the accuracy of the approximation. We

then choose the  $N_p^q$  so that, on the set of points  $\{\bar{x}_1, \bar{x}_2, \dots, \bar{x}_Q\}$  the maximum error of the approximation

$$E_{\max} = \max_{1 \leq i \leq Q} \{P_M(\bar{x}_i) - G(\bar{x}_i)\} \quad (6)$$

is a minimum. Thus we consider the  $Q$  equalities

$$E_i = P_M(\bar{x}_i) - \sum_{p=1}^D \sum_{q=1}^K N_p^q I_{Mq}^H(\bar{x}_i - x_p^q) \quad i=1, 2, \dots, Q \quad (7)$$

and try to find that set of  $N_p^q$  values which will make  $\max_{1 \leq i \leq Q} |E_i|$  as small as possible.

This problem can be directly formulated as a linear-programming problem; an extra variable  $S$  is introduced and the inequalities

$$|E_i| \leq S \quad i=1, 2, \dots, Q \quad (8)$$

are considered. These can be written as

$$\left. \begin{array}{l} E_i + S \geq 0 \\ -E_i + S \geq 0 \end{array} \right\} \quad i=1, 2, \dots, Q. \quad (9)$$

Now the approximation problem can be stated in the form of a linear-programming problem as follows: minimize the linear form

$$Z = S \quad (10)$$

subject to the  $2Q$  constraints

$$\left. \begin{array}{l} E_i + S \geq 0 \\ -E_i + S \geq 0 \end{array} \right\} \quad i=1, 2, \dots, Q \quad (11)$$

and subject to the non-negativity restrictions

$$N_p^q \geq 0 \quad p=1, 2, \dots, D; \quad q=1, 2, \dots, K. \quad (12)$$

Written out in full, the linear-programming problem is: minimize the linear form

$$Z = S \quad (13)$$

subject to the  $2Q$  constraints:

$$\left. \begin{array}{l} \sum_{p=1}^D \sum_{q=1}^K N_p^q I_{Mq}^H(\bar{x}_i - x_p^q) + S \geq P_M(\bar{x}_i) \\ \sum_{p=1}^D \sum_{q=1}^K N_p^q I_{Mq}^H(\bar{x}_i - x_p^q) - S \leq P_M(\bar{x}_i) \end{array} \right\} \quad i=1, 2, \dots, Q \quad (14)$$

and subject also to the non-negativity restrictions

$$N_p^q \geq 0 \quad p=1, 2, \dots, D; \quad q=1, 2, \dots, K. \quad (15)$$

On solving this problem, we obtain a set of positive real numbers  $N_p^q$ , which, when inserted into equation (4) make  $G(x)$  the best possible approximation, out of all possible approximations, to  $P_M(x)$  on the given set of points, in the minimax sense. The value of  $S$  thus obtained is the maximum error of the approximation.

### Construction of the constraint inequalities

In constructing the inequalities (14) for the linear-programming problem, it is first of all necessary to

choose a set of  $KD$  divisional points in  $(0, \frac{1}{2})$ . The number of kinds of interatomic function are known in advance, so only  $D$  must be selected. This selection would be done mostly in terms of the desired size of the linear-programming problem. For example, if  $K=3$  in a given situation, then the selection of twenty interatomic-function location points in  $(0, \frac{1}{2})$  per interatomic-function kind would result in constraints containing 61 terms when the  $S$  term is included. Further, it is necessary to choose the set of points  $\{\bar{x}_1, \bar{x}_2, \dots, \bar{x}_Q\}$  for the error evaluation. In general,  $2Q < KD$ . In the above example,  $Q$  might well be selected as 20. Then the linear-programming problem would contain 40 constraints with 61 terms per constraint, or 60 solution variables  $N_p^q$ . It should be noted that the solution of linear-programming problems with several thousand constraints and several thousand solution variables is common-place at the present time.

In constructing the constraint inequalities the basic relations

$$I_{Mq}(x - x_p^q) = C \sum_{h=-M}^{+M} K_h \{g_q \exp [2\pi i h x_p^q]\}_h \times \exp [2\pi i h x] \quad (16)$$

and

$$I_{Mq}^H(x - x_p^q) = \frac{I_{Mq}(x - x_p^q) + I_{Mq}(x + x_p^q)}{1 + \delta(0, x_p^q) + \delta(\frac{1}{2}, x_p^q)} \quad (17)$$

are employed. The full-cell interatomic functions  $I_{Mq}(x - x_p^q)$  can be calculated from (16) while (17) gives the half-cell functions  $I_{Mq}^H(x - x_p^q)$ . In (16)  $g_q = f_n f_m$  where  $f_n$  and  $f_m$  are the scattering factors for atoms of the  $n$ th and  $m$ th kinds, which correspond to an interatomic function of the  $q$ th kind. To apply (16) it is first necessary to establish an arbitrary correspondence which uniquely defines an interatomic-function-kind index  $q$  in terms of the atom-kind indices  $m$  and  $n$ . For example in a given situation  $q=1$  may denote oxygen-oxygen interatomic functions, while  $q=3$  denotes carbon-oxygen interatomic functions, and so on.

Although the  $I_{Mq}^H(x - x_p^q)$  could be computed straightforwardly from (16) and (17) it is less tedious to proceed in a different way. First the interatomic functions  $I_{Mq}(\bar{x}_i - 0)$  of each kind are computed on the chosen divisional point system in  $(0, 1)$ . That is, the full-cell functions of each kind are initially located at the origin, and computed as a column vector on the points  $\{\bar{x}_i\}$ . Following this, the full-cell interatomic functions of each kind can be shifted to their successive off-origin divisional points by simple index interchanges, after which the additions in (17) can be performed. In general, stationary-atom scattering factors are employed in (16) with Cesaro or Lanczos sigma-summation (Goldak, 1971). The Patterson function  $P_M(\bar{x}_i)$  must then be corrected to correspond as closely as possible to a stationary-atom crystal. When this has been done, the construction of the linear-programming problem is complete.

### Determination of scale and temperature factors

In constructing the constraint inequalities (14) it is necessary that the scattering factors used in computing the  $I_{Mq}^H(x-x_p^q)$  be the same as those which occur in the partial Patterson function. In order to assure this, the observed structure amplitudes should be placed on an absolute scale, and a temperature-factor correction should be applied so that the resulting corrected structure amplitudes correspond as closely as possible to a stationary-atom crystal. If  $P_M(x)$  is not placed on an absolute scale, it is clear that the  $N_p^q$  resulting from the solution of the linear-programming problem will all differ from the correct values by the scale factor which should have been applied to the structure amplitudes. However, an acceptably accurate approximation will be obtained; that is,  $S$  will be small. However, if stationary-atom scattering factors are used in computing the  $I_{Mq}^H(x-x_p^q)$  when  $P_M(x)$  corresponds to a thermally agitated crystal, then the best approximation obtainable will generally be much less accurate than would be the case had stationary-atom scattering factors occurred in both  $I_{Mq}^H(x-x_p^q)$  and  $P_M(x)$ . In employing this method on a real crystal structure, it will never be possible to correct  $P_M(x)$  to correspond exactly to a stationary-atom crystal. However, after the solution to the linear-programming problem, equations (13), (14) and (15), is obtained parametric linear-programming procedures can be employed to systematically vary  $P_M(\bar{x}_i)$  until the lowest possible error  $S$  is obtained. The linear-programming procedures will be considered in more detail in a later section of this paper; here it suffices to state that the parametric-programming procedures are inefficient if large corrections to the initial  $P_M(\bar{x}_i)$  are required to obtain an acceptable approximation error  $S$ . Therefore it is desirable to initially make as accurate a scale and temperature-factor correction as is possible with an acceptable amount of effort.

Wilson's (1942) method could be employed to obtain a scale factor and an average isotropic temperature factor. However, this method is well known to be inaccurate, and scale-factor errors of up to 50% have been reported (Harker, 1953, 1956; Kartha, 1953). The method of Kartha (1953) and the similar but more general method of Krogh-Moe (1956) based on Parseval's theorem applied to the electron-density series require an advance knowledge of an average temperature factor. These inadequacies have led the author to devise a somewhat different method which permits a determination of the scale factor and an average isotropic temperature factor, or individual isotropic temperature factors in terms of the Patterson function zero maximum.

The essential idea behind the present method of scaling structure amplitudes can be stated quite clearly in qualitative terms. The electron-density maxima are decreased in maximum value, and broadened, by the temperature factor. The corresponding Patterson

maxima are therefore affected in the same way. Thus the zero maximum of the Patterson function will be very broad with a relatively low maximum value if  $B$  is high. On the other hand, a low  $B$  factor produces a sharp zero maximum with a relatively high maximum value. Thus the 'shape' of the zero maximum should permit a quantitative evaluation of  $B$ . The scale factor  $K$  does not affect the broadness of the zero maximum but merely multiplies the entire Patterson function by  $K^2$ . Therefore, once  $B$  has been determined from the 'shape' of the zero maximum, it should be possible to calculate  $K$  from the value of the zero maximum at the origin.

In the following work, experimental structure factors are designated  $F_{hkl}$ , while absolute, stationary-atom structure factors are denoted by  $F_{hkl}$ . Then, assuming an average isotropic Debye temperature factor  $B$ ,

$$F_{hkl} = K \exp[-B \sin^2 \theta / \lambda^2] F_{hkl}. \quad (18)$$

It is assumed that all the structure amplitudes involved have been determined on the same relative scale, except for  $F_{000}$ , which is known on an absolute scale. Because of this scale difference the  $F_{000}$  term is treated separately by writing the Patterson function in the form

$$P(x, y, z) = \frac{K^2 F_{000}^2}{V} + 1/V \sum_h \sum_k \sum_l |F_{hkl}|^2 \cos 2\pi(hx + ky + lz). \quad (19)$$

For the later work it is convenient to write this in the abbreviated form

$$P(x, y, z) = \frac{K^2 F_{000}^2}{V} + \bar{P}(x, y, z). \quad (20)$$

It is well known that the Fourier coefficients of the pure, stationary-atom zero maximum can be identified as  $\{\sum_{j=1}^N f_j^2\}_{hkl}$ , where  $f_j$  is the scattering factor of the  $j$ th atom in the unit cell, and  $N$  is the number of atoms per unit cell. It is important to note that, even when a structure factor vanishes owing to a space-group extinction, the corresponding Fourier coefficient of the pure zero maximum remains a positive number. The pure zero maximum,  $\bar{Z}(x, y, z)$ , of the Patterson function (19) is given by

$$\bar{Z}(x, y, z) = \frac{K^2}{V} \sum_h \sum_k \sum_l \exp[-2B \sin^2 \theta / \lambda^2] \times \left\{ \sum_{j=1}^N f_j^2 \right\}_{hkl} \cos 2\pi(hx + ky + lz). \quad (21)$$

Now the series

$$\bar{Z}(x, y, z, B) = \frac{1}{V} \sum_h \sum_k \sum_l \exp[-2B \sin^2 \theta / \lambda^2] \times \left\{ \sum_{j=1}^N f_j^2 \right\}_{hkl} \cos 2\pi(hx + ky + lz) \quad (22)$$

can be computed for any chosen value of  $B$ . If the zero maximum of the three-dimensional Patterson function is well resolved in a certain neighbourhood of the origin, then in that neighbourhood it will be true that

$$P(x, y, z) = K^2 Z(x, y, z, B) \quad (23)$$

provided the  $B$  used in computing  $Z(x, y, z, B)$  is the same as the  $B$  which occurs in  $P(x, y, z)$ . It is therefore natural to consider a function  $K(x, y, z, B)$  defined by

$$K^2(x, y, z, B) = \frac{\bar{P}(x, y, z)}{Z(x, y, z, B) - F_{000}^2/V} \quad (24)$$

If the zero maximum of  $P(x, y, z)$  is fairly well resolved, then equation (7) can be used to determine  $B$  and  $K$ . If, for example, the approximation axis is the  $a$  crystallographic axis, then the expression

$$K^2(x, 0, 0, B) = \frac{P(x, 0, 0)}{Z(x, 0, 0, B) - F_{000}^2/V} \quad (25)$$

is evaluated, for a succession of  $B$  values, on a set of points within 1 Å of the origin. In general, the  $B$  used in  $Z(x, 0, 0, B)$  will not be the same as the  $B$  which occurs in  $\bar{P}(x, 0, 0)$  and then  $K^2(x, 0, 0, B)$  will increase or decrease outwards from the origin. However, when the proper value of  $B$  is used in  $Z(x, 0, 0, B)$ , then  $K^2(x, 0, 0, B)$  will be constant where the zero maximum is resolved. The values of  $B$  and  $K$  obtained in this manner can then be used to correct the observed structure amplitudes.

The method can be extended very easily to the case where different atoms of the crystal have different isotropic  $B$  factors. The Patterson function remains in the form of equation (19). If  $B_j$  is the Debye temperature factor of the  $j$ th atom of the unit cell, then the absolute scale zero maximum is given by

$$\begin{aligned} & Z(x, y, z, B_1, B_2, \dots, B_N) \\ &= \frac{1}{V} \sum_h \sum_k \sum_l \left\{ \sum_{j=1}^N f_j^2 \exp[-2B_j \sin^2 \theta / \lambda^2] \right\}_{hkl} \\ & \times \cos 2\pi(hx + ky + lz). \end{aligned} \quad (26)$$

The value of the scale factor is obtained from a study of

$$\begin{aligned} & K^2(x, 0, 0, B_1, B_2, \dots, B_N) \\ &= \frac{\bar{P}(x', 0, 0)}{Z(x, 0, 0, B_1, B_2, \dots, B_N) - \frac{F_{000}^2}{V}}. \end{aligned} \quad (27)$$

Equation (27) in principle permits a determination of the scale factor for the case where each atom of the unit cell has its own Debye temperature factor. However, for a crystal of even moderate complexity, the calculation of  $K(x, 0, 0, B_1, B_2, \dots, B_N)$  for all the possible combinations of  $B$  factors would require a prohibitive amount of work. There are, however, several cases of practical interest which are accessible to calculation. Crystals which consist of a few rather heavy atoms together with a relatively large number of light atoms

are encountered very frequently in structure analysis. For crystals of this kind, one  $B$  factor could be applied to the heavy atoms and another to the light atoms. For crystals which consist of several kinds of atoms of considerably different atomic numbers, different temperature factors can be assigned to each atomic species. This situation commonly arises in the study of minerals and alloys. Such procedures should provide a reasonably good approximation without involving unduly tedious calculations.

The method has been tested against the copper sulphate pentahydrate structure (Beever & Lipson, 1934; Bacon & Curry, 1962), and the ammonium bifluoride structure (McDonald, 1960), and a few other structures. The results of the copper sulphate pentahydrate calculations, which were done in terms of an isotropic average temperature factor, are given in Table 1. The scale factor was taken to be  $K=0.81$  corresponding to  $B=2.0 \text{ \AA}^2$ .

Table 1. Values of  $K(x, 0, 0, B)$

$x$ (Å)	$B=1.50$	$B=1.75$	$B=2.00$	$B=2.25$	$B=2.50$
0.000	0.73	0.77	0.81	0.85	0.88
0.025	0.73	0.77	0.81	0.85	0.88
0.050	0.73	0.77	0.81	0.85	0.88
0.075	0.73	0.77	0.81	0.85	0.88
0.100	0.73	0.77	0.81	0.85	0.88
0.125	0.74	0.77	0.81	0.84	0.88
0.150	0.74	0.78	0.81	0.84	0.88
0.175	0.74	0.78	0.81	0.84	0.88
0.200	0.75	0.78	0.81	0.84	0.87
0.225	0.75	0.78	0.81	0.84	0.87
0.250	0.76	0.79	0.81	0.84	0.87
0.275	0.76	0.79	0.81	0.84	0.86
0.300	0.77	0.79	0.81	0.84	0.86
0.325	0.78	0.80	0.82	0.84	0.86
0.350	0.79	0.80	0.82	0.84	0.86
0.375	0.79	0.81	0.82	0.84	0.85
0.400	0.80	0.81	0.82	0.83	0.85
0.425	0.81	0.82	0.82	0.83	0.85
0.450	0.82	0.82	0.83	0.84	0.84
0.475	0.83	0.83	0.83	0.84	0.84
0.500	0.84	0.84	0.84	0.84	0.84
0.525	0.86	0.85	0.84	0.84	0.84
0.550	0.87	0.85	0.85	0.84	0.84
0.575	0.88	0.86	0.85	0.85	0.84
0.600	0.89	0.87	0.86	0.85	0.85
0.625	0.90	0.88	0.87	0.86	0.85
0.650	0.90	0.89	0.88	0.87	0.86
0.675	0.91	0.90	0.89	0.88	0.87
0.700	0.93	0.92	0.90	0.89	0.88
0.725	0.94	0.93	0.92	0.91	0.90

The scale factor reported by Beever & Lipson was 0.80. By contrast, a Wilson plot returned  $K=0.68$ , a result which is in error by approximately 15%. A second example calculation was done using the measured ammonium bifluoride structure amplitudes of McDonald (1960). These had been placed on an absolute scale by an experimental procedure which was supposed to be accurate to  $\pm 5\%$ . The structure refined to  $R=0.055$ . Using an average isotropic temperature factor, the  $K$  and  $B$  factors were calculated from the present procedure as  $K=0.99$  and  $B=2.60 \text{ \AA}^2$ . The method therefore appears to provide a convenient

means of determining scale and temperature factors which are sufficiently accurate for the linear-programming procedures.

### Linear-programming procedures

During the past twenty years the methods of linear programming have been rapidly developed, and they now provide an extremely flexible and powerful tool for the applied mathematician. Only a brief summary can be presented here, and the interested reader is referred to the excellent book of Hadley (1962) for a relatively complete exposition.

The general linear-programming problem can be stated as follows: find a set of  $r$  non-negative variables  $x_j$  which maximize (or minimize) the linear objective function

$$z = \sum_{j=1}^r c_j x_j. \quad (28)$$

Subject to the  $m$  linear constraints

$$\sum_{j=1}^r a_{ij} x_j \geq = \leq b_i \quad i=1, \dots, M. \quad (29)$$

In each constraint, only one of the signs  $\geq$ ,  $=$ , or  $\leq$  applies. The elements  $a_{ij}$  of the constraint matrix are known constants, as are the coefficients  $c_j$  of the objective function. Any vector  $X=[x_1, \dots, x_r]$  which satisfies the non-negativity restrictions and the constraints (29) is said to be a feasible solution, and generally there are an infinite number of these. Each inequality constraint requires that an allowable solution be in a closed half space in a Euclidean  $E^r$ ; each equality constraint requires that the solution lie on the constraint hyperplane. Each of the non-negativity restrictions also requires that the solution be in a closed half space. The space region in which all the constraints and non-negativity restrictions are satisfied is a convex polyhedron in  $E^r$ . For a problem with  $m$  constraints and  $r > m$  variables, the corners or extreme points of the solution polyhedron are defined by the intersection of  $m$  of the constraint hyperplanes. The objective function is also a hyperplane which for some values of  $z$  will intersect the polyhedron of feasible solutions. To solve the linear-programming problem, it is in effect necessary to move the objective hyperplane parallel to itself until the maximum value of  $z$  is obtained while it still intersects the solution polyhedron. In general, the maximum or minimum value of  $z$  will be attained when the objective hyperplane intersects a corner of the solution polyhedron. The solutions determined by the polyhedron corners are called basic feasible solutions, and that basic feasible solution which minimizes or maximizes the objective function, as the case may be, is called the optimal solution. Because the optimal solution is a corner point of the polyhedron, an optimal solution to a linear-programming problem of  $m$  constraints never needs to have more than  $m$  variables different from zero.

In order to solve a given problem, it is first of all necessary to transform the inequality constraints into equalities. If a constraint has the form

$$\sum_{j=1}^r a_{hj} x_j \leq b_h, \quad (30)$$

then a slack variable  $x_{r+h} \geq 0$  is introduced so that the constraint becomes

$$\sum_{j=1}^r a_{hj} x_j + x_{r+h} = b_h. \quad (31)$$

Similarly, constraints of the form

$$\sum_{j=1}^r a_{kj} x_j \geq b_k \quad (32)$$

are transformed into

$$\sum_{j=1}^r a_{kj} x_j - x_{r+k} \geq b_k$$

by the introduction of the surplus variable  $x_{r+k} \geq 0$ . The objective function is not modified; that is, the  $c_j$  are set to zero for  $j=r+1, \dots, r+m$ . It can be shown that the solution of the linear-programming problem modified by the introduction of slack and surplus variables is the same as the solution to the original problem.

In principle, a linear-programming problem could be solved by obtaining all basic feasible solutions and subsequently selecting the one which optimizes the objective function. A basic solution can be obtained by setting all but any  $m$  variables to zero in the constraint equations, and solving the resulting  $m \times m$  system of linear equations. The selected  $m$  columns of the constraint matrix then form a set of basis vectors, or simply a basis. Two cases can occur in the solution of the linear system of equations. The solution variables may be all non-negative, in which case the solution is a basic feasible solution, and corresponds to some corner point on the solution polyhedron. Alternatively, some solution variables may be negative, in which case the solution is basic but infeasible. This corresponds to a constraint hyperplane intersection outside the solution polyhedron. To step from one basic solution to another, it is only necessary to remove one column from the basis and replace it by some non-basis column. The resulting new system of linear equations then provides a new basic solution which may be feasible or infeasible.

In the simplex algorithm, an initial basis is constructed in terms of artificial variables introduced expressly to obtain a basis which provides an initial basic feasible solution. By replacing basis column vectors by non-basis vectors at each iteration step, the artificial variables are driven out of the basis and need not be considered subsequently. The essence of the method is the procedure used to determine, at each iteration, which vector should leave the basis and which vector should enter it. This is done in such a way that

only basic feasible solutions are considered, and furthermore the value of the objective function becomes more nearly optimal at each iteration. Finally, an optimal solution is reached when a step from the current basic feasible solution to another which is adjacent on the solution polyhedron cannot further optimize the objective function. Since the solution polyhedron is convex, this optimum is always a global maximum or minimum; problems with local optima never arise, and this constitutes one of the great advantages of the linear-programming method in approximation problems. A further advantage of the method is the ease with which a wide variety of additional conditions may be imposed on the solution. For example, upper and lower bounds on the solution variables can be imposed in an almost trivial way.

Several post-optimality problems can easily be handled. For example, after an optimum solution to a given problem has been obtained, new constraints can be added, or new variables can be added. As long as these new conditions do not drastically change the essential nature of the problem, a revised optimum solution can be found almost instantly. Parametric programming, which permits a systematic variation of the right-side vector or the objective function coefficients, provides further adaptability, particularly for approximation problems.

#### An example solution

A simple example will serve to illustrate the application of the linear-programming problem. A crystal with a 6 Å unit-cell edge and containing three oxygen atoms per unit cell, is considered. The fractional atom coordinates are  $x_1=0/118$ ,  $x_2=20/118$  and  $x_3=30/118$  so that the structure is non-centrosymmetric. Absolute-scale, stationary-atom structure amplitudes were computed (to one decimal place) within the Mo limiting interval.

To extract the vector set, a system of 60 equally spaced interatomic-function divisional points 0.0508 Å apart were constructed on the interval  $[0, \frac{1}{2}]$ , with  $x_{10}^1=0$  and  $x_{50}^1=\frac{1}{2}$ . To evaluate the accuracy of the approximation, a set of 20 equally spaced points, with  $\bar{x}_1=0$  and  $\bar{x}_{20}=60$  was constructed on  $[0, \frac{1}{2}]$ . The linear-programming problem which results thus contains 40 constraints in 61 variables.

The linear-programming problem is:

Minimize

$$Z = S$$

subject to

$$\begin{aligned} 52.3N_1^1 + 103.3N_2^1 + 99.8N_3^1 + \dots + 0.6N_{60}^1 - 1.0S &\leq 227.4 \\ 46.9N_1^1 + 93.3N_2^1 + 91.7N_3^1 + \dots + 0.7N_{60}^1 - 1.0S &\leq 214.0 \\ 0.6N_1^1 + 1.3N_2^1 + 1.3N_3^1 + \dots + 52.3N_{60}^1 - 1.0S &\leq 11.9 \\ 52.3N_1^1 + 103.4N_2^1 + 99.8N_3^1 + \dots + 0.6N_{60}^1 + 1.0S &\geq 227.4 \\ \dots &\dots \\ \dots 6N_1^1 + 1.3N_2^1 + 1.4N_3^1 + \dots + 52.3N_{60}^1 + 1.0S &\geq 11.9 \end{aligned} \quad (34)$$

and also subject to

$$N_j^1 \geq 0 \quad j=1, 2, \dots, 60.$$

The above problem was constructed in suitable form by a program written in the PL1/F language, then passed on to a program written in the IBM MPS (Mathematical Programming System) language for solution of the linear-programming problem. After 91 iterations, which required 2.06 minutes CPU time, the optimal solution was obtained. Rounded to two decimal places, the solution was  $N_1^1=3.00$ ,  $N_{11}^1=1.00$ ,  $N_{21}^1=1.00$  and  $N_{31}^1=1.00$  with all other  $N_j=0$ . This solution provides the correct vector set. The error of the approximation is  $8 \times 10^{-5}$  Patterson units, so that the generalized polynomial provides an extremely accurate representation of the Patterson function. The accuracy of the approximation depends on the number of divisional points used to evaluate its accuracy. If  $Q$  divisional points are employed for this purpose, then the linear-programming problem will contain  $2Q$  constraints and no more than  $2Q$  variables can be non-zero. When the previous problem was formulated with six divisional points for the evaluation of the accuracy of the approximation, the resulting solution bore little resemblance to the correct vector set. The method has been used, with no numerical difficulties, for 'synthetic' crystals with unit-cell edge lengths up to 42 Å and containing 300 atoms of one kind per unit cell (with no heavy atom); the linear-programming problems ranged in size up to 801 solution variables and 400 constraints. The ability to deal with these relatively large problems without difficulty is the principal advantage of the Tchebycheff method over the interpolatory procedure previously published (Goldak, 1969). If the above example were formulated as an interpolatory problem with 60 interatomic function location points, the resulting 60 by 60 system of linear equations would be hopelessly ill-conditioned, and in order to obtain meaningful results, the Patterson function would have to be known to a very large number of decimal places.

The calculation (34) is useful as an example but is unrealistic in that the interatomic functions in the Patterson function were situated exactly on the divisional points, and this will not occur in practical cases. When the interatomic functions are located exactly on the divisional points, the resulting  $N_p^q$  will be very nearly integral, as in the example, and the vector set will be well defined. However, an interatomic function located between two divisional points provides a contribution to the  $N_p^q$  values of both adjacent divisional points. In a specific case, rather than obtaining  $N_{50}^2=0.00$ ,  $N_{51}^2=0.00$ ,  $N_{52}^2=1.00$ ,  $N_{53}^2=0.00$ , we may obtain  $N_{50}^2=0.00$ ,  $N_{51}^2=0.25$ ,  $N_{52}^2=0.75$ ,  $N_{53}^2=0.00$  if an interatomic function of the second kind were located between the 51st and 52nd divisional point of the second kind. Since dense divisional-point systems can be used, the resolution of the present method is far greater than the earlier interpolatory procedure, and

thus interatomic functions located between the divisional points pose a less serious problem. The most appealing solution would be to impose additional constraints on the linear-programming problem, namely that the  $N_p^i$  be integral. Thus the  $N_p^i$  would be the solution of an integer-programming problem. Unfortunately, computational experience with integer-programming algorithms has been disappointing, and no generally time-effective procedure is available. An attractive way of solving this problem involves the use of a large number of interatomic functions with the number of constraints made equal to the number of interatomic functions in the Patterson function. In addition, an upper bound of 1.0 is imposed on each solution variable. As a result a solution will be obtained in which every non-zero solution variable will be nearly equal to 1.0. Then by employing parametric linear-programming methods, each divisional point can be systematically displaced (for example by using the *PARACOL* procedure of the IBM/MPS system) until the most accurate possible approximation has been obtained, still subject to the constraint that each non-zero solution variable must be nearly equal to 1.0. Of course, for complex structures, this procedure would involve a very large number of constraints, and a solution upper bound of 2.0 or more would be required to reduce the size of the problem.

When the method is applied to complex structures, most of the solution variables will turn out to be zero, providing the number of divisional points is large compared to the number of constraints. As a second step, new interatomic-function location points can be introduced in the neighbourhood of the interatomic-function locations, while the divisional points associated with zero solution variables can be removed from the problem. In this way, the divisional points can be made very dense near the interatomic functions. Consequently, the resolution of the problem is greatly improved without increasing the size of the problem.

The above considerations indicate that the method can be applied to the problem of vector-set extraction in a variety of ways, and an optimum procedure has not yet been determined. The results of further tests, against both synthetic and real structures, will be reported in a later paper.

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