A Modified Patterson Function

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If the Fourier coefficients $|F_h|^2$ of a Patterson function are replaced by a power series in $|F_h|^2$, which is approximately proportional to $|F_h|$ over a limited range, the resulting modified Patterson function is sharpened and the smaller vector peaks are emphasized. This facilitates the interpretation of the Patterson function in some cases. As an example, modified and unmodified Patterson projections of basic lead carbonate are compared.

It has been observed that, in two-dimensional Patterson projections calculated from X-ray or electron diffraction intensities, the map is frequently dominated by the few largest terms of the Fourier summation to such an extent that it appears to contain little of the information associated with the smaller intensities. This is noticeable when the range of intensities is large, as in patterns from crystals of relatively high symmetry. It is most striking when the unit cell or its projection is, to a first approximation, made up by the repetition of a sub-cell. The reflexions corresponding to the sub-cell are then much stronger than the rest. The larger number of weaker reflexions contain the information on the deviations from the sub-cell, but this information is largely submerged beneath the large sub-cell vector peaks in the Patterson projection. The interpretation of the detail observed, moreover, is often uncertain because the errors in measurement of the greater intensities are of the same order as the magnitudes of the smaller intensities.
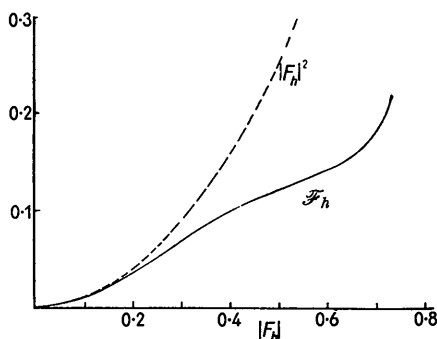

Fig. 1. Plot of $\mathscr{F}_h = |F_h|^2 - 3|F_h|^4 + 4|F_h|^6 - |F_h|^8$ against $|F_h|$.

The question then arises as to whether the Patterson function can be modified in such a way that the information contained in the weaker spot intensities can be more readily appreciated. Intuitively it would seem that the use of $|F_h|$ rather than $|F_h|^2$ as coefficients of the Fourier series would have the desired result, but the theoretical implications of this change are difficult to assess.

It is possible to approximate to $|F_h|$ over a limited range by means of a power series in $|F_h|^2$. For example, as shown in Fig. 1, the function

$$\mathscr{F}_h = |F_h|^2 - 3|F_h|^4 + 4|F_h|^6 - |F_h|^8$$

is approximately linear in the range $0\cdot15 \le |F_h| \le 0\cdot65$. In the range $0 \le |F_h| \le 0\cdot15$ it is very nearly equal to $|F_h|^2$. If this function is used in place of $|F_h|^2$, with a scaling factor included so that the maximum $|F_h|$ is made approximately equal to $0\cdot65$, the smaller coefficients of the Fourier series for the Patterson function will be unchanged while the larger coefficients are considerably reduced.

The Fourier transform of $\mathscr{F}_h$ may be written as

$$P^1 = P - 3(P*P) + 4(P*P*P) - (P*P*P*P),$$

where $P \equiv P(x, y)$, the Patterson projection, and the symbol $*$ denotes a convolution operation of the type associated with the Patterson function, i.e., for X-rays, $P = \varrho(x, y) * \varrho(x, y)$. Since, in general, the zero peak of a Patterson function is considerably higher than any other peak, the principal peaks of the function $P * P$ will be in the same positions as the peaks of P, but will be broader. The function $P * P * P$ will have peaks in the same position as those of $P * P$, but broader again. Similarly for the last term of P^1. Hence in P^1, for each peak in the Patterson function P there will be a peak formed by a superposition of peaks of increasing breadth added and subtracted. There will in addition be a very large number of small positive or negative peaks, all more diffuse than normal Patterson peaks. In general these may be expected to contribute a slightly undulating background. It is possible that at particular positions they may fortuitously add together. However, it may be noted that the most prominent extra peaks will be those arising from the $P * P$ term, and these will be negative. The only positive extra peaks, those from the $P * P * P$ term, will be much more diffuse than Patterson peaks.
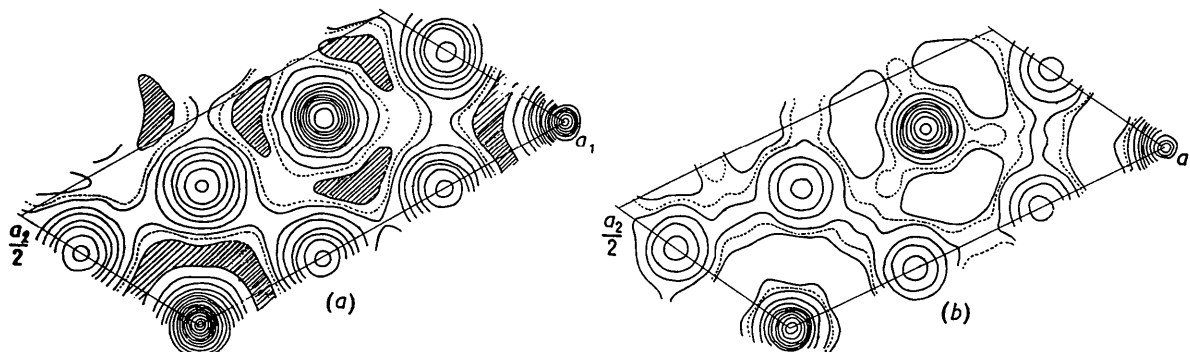
Fig. 2. (a) The c-axis projection of the Patterson function of basic lead carbonate. Negative areas shaded; contours at regular (arbitrary) intervals; broken contour at half-interval. (b) The c-axis projection of the modified Patterson function of basic lead carbonate. Broken contour at half-interval.

The principal peaks of P^1 will be sharper than normal Patterson peaks and may be surrounded by slightly negative regions. This is to be expected from the nature of the function $\mathscr{F}_h$. Since the average intensity of diffraction spots falls off with increasing $(\sin \theta)/\lambda$, part of the effect of using $\mathscr{F}_h$ instead of $|F_h|^2$ is to emphasize the contributions of the larger-angle reflexions. The peak shape is modified, therefore, in the same way as in a 'sharpened' Patterson function. In a one-dimensional trial structure, for which the Patterson function contained only one Gaussian peak, the peak in $P^1(x)$ had a half-width 10% less. The maximum negative excursion was less than 1·5% of the peak height.

The modified Patterson function has been used successfully in the course of the structure analysis of basic lead carbonate (Cowley, 1956a). In the (hk0) spot pattern, which has hexagonal symmetry, the spots with $h = 3n$, $k = 3m$, n and m being integers, are much more intense than others, and have intensities which fall off monotonically with $(\sin \theta)/\lambda$. Consequently the Patterson projection, Fig. 2(a), is dominated by large peaks at the corners of a sub-cell with dimensions one-third of those of the complete unit cell. Of the remaining reflexions, those with $h - k = 3n$ are stronger than the others. This results in a strengthening of the peaks at the $(\frac{1}{3}, \frac{2}{3})$ and $(\frac{2}{3}, \frac{1}{3})$ positions. The only influence of reflexions with $h - k \neq 3n$, comprising two-thirds of the total number of spots, seems to be a suggestion of bridging between the large peaks of the Patterson projection other than the origin. Thus the total contribution of the large number of weak reflexions to the information readily obtained from the Patterson function is very small and does not offer a satisfactory basis for the determination of the deviations from the sub-cell structure.

The modified Patterson function derived by the use of the above power series, $\mathscr{F}_h$, is shown in Fig. 2(b).

In this it can be seen that the large peaks are sharper and of reduced height. The increase in the relative contributions of the reflexions with $h - k \neq 3n$ has led to appearance of definite maxima between the main peaks.

From the subsequently determined structure of the compound it was verified that all of the additional features revealed by the modification of the Patterson function, including even such detail as the shape of the lowest contour of the origin peak, have real significance. No spurious features due to the incorporation of the higher powers of $|F_h|^2$ could be detected.

The modified Patterson function would appear to have advantages for purposes of image-seeking by the use of the minimum function, both because the peaks are sharpened and because the smaller peaks, with which this method of image-seeking is chiefly concerned, are emphasized. In the structure analysis of basic lead carbonate the modified Patterson function was used successfully for image-seeking (Cowley, 1956a) and also in the derivation of a three-dimensional Patterson function by 'stereoscopic' methods (Cowley, 1956b). For both purposes its use appeared to give an increase in resolution, and in the information available.

In conclusion it may be noted that the use of a power series in $|F_h|^2$, similar to that described above, for the coefficients of a Patterson-like function has recently been shown (Bullough & Cruickshank, 1954) to be equivalent to the use of the phase-determining relations derived from the statistical theory of Karle & Hauptman (1954).

References

BULLOUGH, R. K. & CRUICKSHANK, D. W. J. (1954). Acta Cryst. 7, 598.
COWLEY, J. M. (1956a). 9, 391.
COWLEY, J. M. (1956b). 9, 399.
KARLE, J. & HAUPTMAN, H. (1954). Acta Cryst. 7, 375.