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Interpolation Errors in Fourier Projections

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Several different interpolation methods for locating peak positions have been applied to a mock electron-density projection, obtained by superposing three Gaussian peaks of the form $\varrho(r) = 6{\cdot}73 \exp(-4{\cdot}6r^2)$. A study of the resulting interpolation errors shows the danger of an uncritical use of purely analytical methods, and the need for computing the electron density at close intervals when atoms are not very well resolved in projection.

1. Introduction

In the normal Fourier method of structure determination the electron density is computed at the points of a mesh, and the peaks of the distribution are determined by some interpolation process. The present paper is concerned with the errors inherent in the usual interpolation techniques used. In order to determine the errors made in the location of the peaks by several interpolation methods it is necessary to apply them to an electron-density distribution whose peaks are accurately known. The empirically known fact that isolated peaks in projection have approximately a Gaussian form suggested the following procedure:

A two-dimensional distribution resulting from the superposition of three identical Gaussian atoms of the form

$$\varrho(r) = 6{\cdot}73 \exp(-4{\cdot}6r^2) \qquad (1)$$

was computed, and is shown in Fig. 1. Such a distribution is typical of carbon, so that results deduced from a study of it will be especially relevant to organic structures; but they may easily be generalized to apply

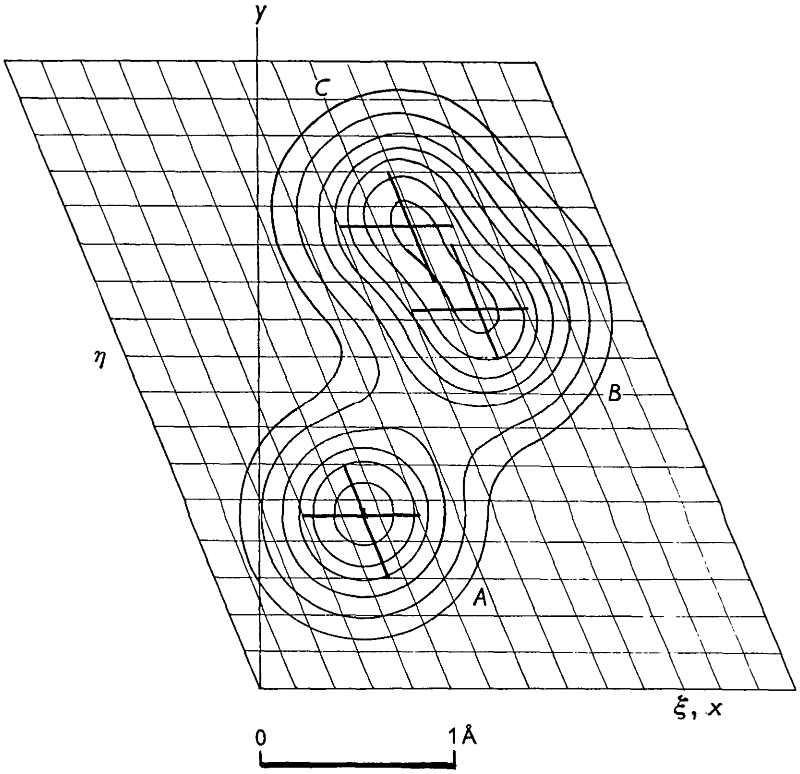

Fig. 1. Degree of resolution of atoms *A*, *B*, *C*, and their true positions relative to the mesh points chosen. Heavy lines indicate the sections referred to in § 2.

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Table 2. *Radial errors $\delta = \Delta/\sqrt{2}$ resulting from different methods of estimating peak positions*

Values of δ in mÅ

Type of electron-density values used	Atom *A*		Atom *B*		Atom *C**		Atom *C*†	
	Best (or only) value	Worst value	Best (or only) value	Worst value	Best (or only) value	Worst value	Best (or only) value	Worst value
§ 2. Natural	1	31	2	52	2	28	—	—
§ 3. Natural	3	—	16	—	11	—	—	—
Logarithmic	0	—	18	—	10	—	—	—
§ 4. Natural (original mesh)	9	—	18	—	23	—	13	—
Natural (alternative mesh)	6	—	18	—	48	—	19	—
§ 5. Natural	4	—	32	—	21	—	—	—
Logarithmic	1	—	38	—	21	—	—	—
§ 6. Natural	—	—	2	14	3	11	—	—
	Exact.	Approx.	Exact	Approx.	Exact	Approx.	Exact	Approx.
§ 7. Natural (original mesh)	10	11	12	19	19	28	11	22
Natural (alternative mesh)	1	19	11	19	28	30	23	22
Logarithmic (original mesh)	7	18	20	18	48	37	9	27
Logarithmic (alternative mesh)	6	34	5	18	215	337	1	37

* Results obtained using the nine points centred on *O*.
† Results obtained using the nine points centred on *O*′ (Fig. 2).

to any structure. The electron-density values were computed, directly from equation (1), at the points of an oblique mesh of spacing 0·2 Å (along ξ), and 0·208 Å (along η), with the angle between the two directions 112° 37′ = arctan (−12/5). These values were chosen to facilitate computation. In order to exclude the effects of any inaccuracies in the electron-density values, these were computed correct to 10^{-4} e.Å^{-2} in the neighbourhood of the peaks. The co-ordinates of the three Gaussian atoms are shown in Table 1.

Table 1. *Co-ordinates of the three Gaussian atoms*

Atom	*x* (Å)	*y* (Å)
A	0·54	0·90
B	1·20	1·90
C	0·72	2·48

The distribution shown in Fig. 1 is a suitably idealized one on which various interpolation techniques may be tested. It shows a degree of resolution frequently met with in practice. Indeed, many published structures have been derived from Fourier projections even less well resolved. Consequently any insufficiency in existing interpolation techniques which the present study may reveal will have great relevance to real structures, which are intrinsically less amenable to interpolation than the present simplified distribution.

The different interpolation techniques tested are described below, and the errors resulting from their application are collected in Table 2. To specify the error, a quantity $\delta = \Delta/\sqrt{2}$ has been chosen, where Δ is the radial error in position. This choice, while simplifying the presentation of results, nevertheless obscures the fact that for atoms *B* and *C* the η (and *y*) co-ordinates are in all cases considerably more in error than the ξ (and *x*) co-ordinates, owing to the orientation of the line of centres of atoms *B* and *C* being nearly along the η direction. This point should be borne in mind throughout. For brevity, the error has been given in milli-Ångström units.

2. The method of sections

In this method, sections of the Fourier map are drawn along both mesh directions in order that intermediate values of the electron density may be obtained. Usually this will be done in any case in order to draw an accurate contour map. Now suppose that the mesh-line $\xi = \xi_1$ passes near the peak position; then the maximum of the section drawn along this mesh-line gives an approximate value $\eta = \eta_1$ for the peak co-ordinate. By graphical interpolation from the curves of section, the section at $\eta = \eta_1$ is drawn, and the maximum of this gives a value $\xi = \xi_2$ for the peak co-ordinate. The process is repeated until no further change occurs in the values. In all cases the sections are drawn carefully on a large scale and the maxima are estimated by eye.

Because of the large subjective element in this method, the help of seven colleagues was enlisted in testing it. To avoid straining their good-will, they were not asked to go through the whole process of successive approximations. Instead sections were computed through the *exact* centres of the three atoms as shown in Fig. 1, and they were presented with the plotted points and asked to draw in the curves, mark the maxima, and estimate the accuracy with which they thought they had done this. They were thus working under much more favourable circumstances than would be the case in practice. The computed values were plotted at intervals of 1 in. for both mesh directions, which corresponds to a scale of 5 in. = 1 Å for the ξ direction, and 4·8 in. = 1 Å for the η direction. The vertical scale was 1 in. = 1 e.Å^{-2} in each case.

In view of the small number of trials no statistical analysis of the results was attempted, and only the best and worst results are shown in Table 2. However, the unreliability of the method may reasonably be inferred. The precision of the best attempts hardly compensates for the large errors in the worst attempts. The superior accuracy in the case of atom C, at first rather surprising, is due to the advantageous location of the peak in C relative to the mesh. In the ξ section it falls very nearly at a mesh point ($\xi = 8{\cdot}963$), and in the η section it falls very nearly half-way between mesh points ($\eta = 12{\cdot}546$). These are specially favourable positions for graphical interpolation of the peaks. For atom B the corresponding values are much less favourable, namely $\xi = 9{\cdot}808$ and $\eta = 10{\cdot}259$.

The estimates of error given by the seven people were interesting. When the plotted points were presented to them and the object of the test explained, they all, without exception, forecast very large errors. But their estimates of error, made *after* they had drawn the curves, were much more optimistic. It would seem that a nicely drawn, smooth curve has a hypnotic effect on the executant. There appeared to be little correlation between the estimates and the actual errors.

3. The method of sections, using Booth's method of peak location

This is an obvious variant of the previous method, in which the peaks of the final sections through the centres of the atoms are located by fitting parabolas to the three electron-density values nearest the peak. The procedure for doing this has been systematized by Booth (1948). In the present study this method was applied to the accurate sections already prepared through the exact centres of the three atoms, using both the actual electron-density values, and the logarithms of these. The use of the logarithms has been suggested at various times, and is natural in view of the Gaussian character of isolated peaks.

The results, shown in Table 2, are satisfactory for atom A, but for atoms B and C the errors are larger than one would like, particularly when it is borne in mind that in practice one does not have accurate sections drawn exactly through the peak positions to deal with. The results for atom C are noticeably better than those for B, for the reason given above. The use of logarithmic electron-density values improves things in the case of atoms A and C, but not in the case of atom B.

4. The analytical method of sections

This is another variant of the method of sections in which the sections near the peak are assumed to be parabolic, and the whole process of arriving at the peak positions by successive approximations is performed analytically, using the equations of these parabolas. This method uses only the electron-density values at nine points around each peak, these points being chosen so that the central point is the point of maximum electron density. This can normally be done unambiguously, but in the present example atom C presents the exceptional case where two different sets of nine points can be chosen. The situation is illustrated in Fig. 2. The electron density at point O is only 0·001 $e.\text{Å}^{-2}$ greater than that at O'. Consequently either the set of nine points centred at O, or the set centred at O', may be used, and the results from both are listed in Table 2. The method was applied using not only the original mesh, but also the alternative mesh formed by ξ and the short diagonal of the original mesh, shown by broken lines in Fig. 2. A valid interpolation technique ought to give the same result for both meshes. Since the method is rather laborious, it was applied only to the natural electron-density values.

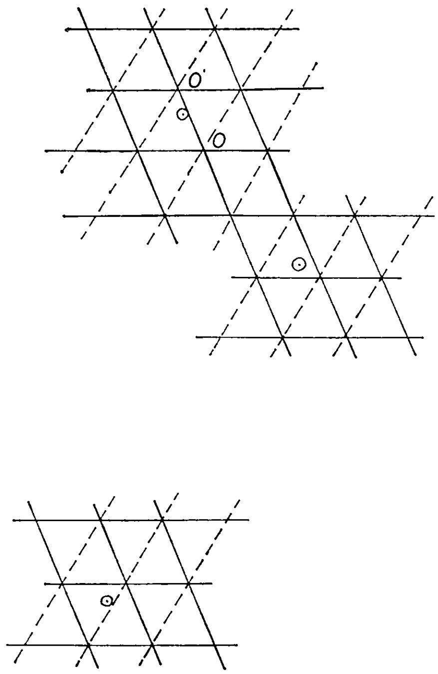

Fig. 2. Solid line: original mesh; broken line: alternative mesh. The mesh points shown are the nine used in each mesh for the methods of § 4 and § 7.

For atom C, two sets of nine points may be chosen, centred on O and O' respectively.

The results for atom A are fairly good, and would presumably be much better if the logarithms of the values were used. For atoms B and C, however, the errors are too large, and it will be noticed that those for C are now worse than those for B if the mesh centred at O is used, and about the same if that centred at O' is used. It may be concluded, particularly in view of the labour involved, that the method is not a satisfactory one.

5. The method of Megaw

This method (Megaw, 1954) is illustrated in Fig. 3. The maxima of the sections along the mesh directions in the vicinity of the peak are located by assuming

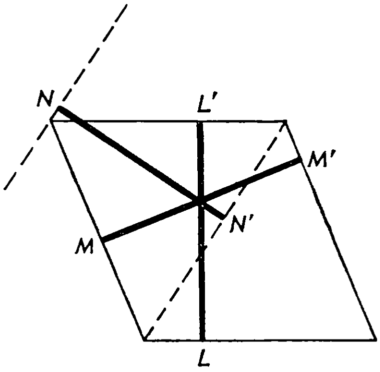

Fig. 3. Illustrating the interpolation method of Megaw. The diagram shows the actual application of the method to atom A.

that the atom is of Gaussian form. This implies that the sections are also of Gaussian form, and so the maxima can be found by fitting parabolas to the logarithms of the electron-density values. Megaw describes a graphical method of doing this, but it is quicker to do it analytically. In this way two pairs of maxima are obtained, L, L' for the sections in the ξ direction, and M, M' for those in the η direction. The intersection of the straight lines LL' and MM' gives the required position of the peak. A check is afforded by repeating the process for sections in the direction of the short diagonal (broken line), a third line, NN', being obtained. For a perfectly resolved peak, the lines LL', MM', and NN' will be perpendicular to the corresponding directions of section, and will meet in an exact point. If for any reason they do not meet in a point, then the size of the triangle formed by their intersection gives an estimate of the uncertainty in the peak position, and the centroid of this triangle may be taken as the best possible result. The method can be applied equally well to the natural electron-density values, and this has been done.

Fig. 3 shows the actual application of the method to atom A, and it will be seen that the three lines meet very nearly in a point. With natural electron-density values the error is a little larger, but is still quite small. For atom B the method runs into serious difficulties because of the proximity of atom C. The second line, MM', cannot be used because the point M lies near atom C and its use would clearly lead to a ludicrous result. Hence the peak is determined from the lines LL' and NN' only, of which the first is very far from being perpendicular to the corresponding mesh lines. The error is very large, but is slightly reduced if natural values are used instead of the logarithms. For atom C, all three lines can be used owing to the more fortunate position of the peak with respect to the mesh, and the error in this case is much less, although still too large. It may be mentioned that the true peak does not lie within the triangle formed by the intersection of the three lines. There is no noticeable difference in this case between using natural or logarithmic values. It may be concluded that the method is insufficiently powerful to deal with cases where masking is appreciable.

6. The method of Burns & Iball

This method (Burns & Iball, 1955) may be regarded as an elaboration of Megaw's method, but was developed independently. A general illustration of the method, not referring to any of the atoms of the present example, is shown in Fig. 4. The same procedure of locating the maxima of the sections near the peak is carried out, but additional points L'', M'', and N'' are used, and the position of the peak determined by the intersection of three *curves*. The method was applied to the natural electron-density values.

For peak A, the intersecting curves were practically straight lines, and the situation was graphically indistinguishable from that obtained by Megaw's method. For peak B, since the point M was not available, the curve $MM'M''$ was not used, and the peak position was obtained as the intersection of curves $LL'L''$ and $NN'N''$ only. Since an infinite number of curves can be drawn through three points there is a large subjective element in this method also. Hence seven colleagues were again asked to help, by drawing in the curves $LL'L''$ and $NN'N''$ and obtaining the point of intersection. The drawing was done using an undistorted reproduction of the portion of the mesh near the peak on a scale of 15 in. = 1 Å. In the case of atom C, the point M'' could not be used because it was too far away from the vicinity of the peak. However, there the peak position lies on the portion MM' of the curve $MM'M''$, and consequently the straight line MM' can be used as a third curve. That this is justifiable may be inferred from the fact that the line MM' is not very far from being perpendicular to the η direction. In testing the method, the seven people were asked to draw in only the curves $LL'L''$ and $NN'N''$, and the straight line was added

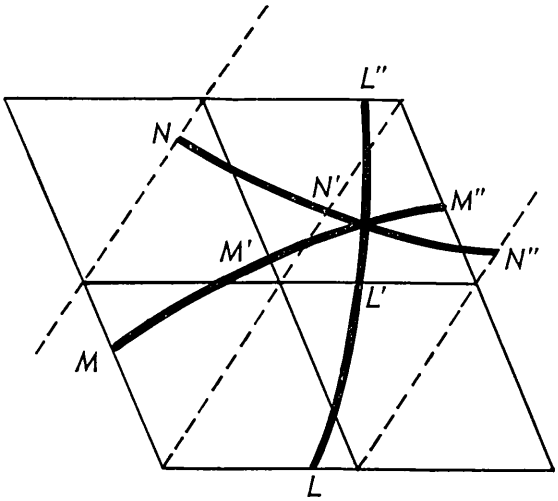

Fig. 4. Illustrating the interpolation method of Burns & Iball.

afterwards. The peak position was taken as the centroid of the triangle formed at the intersection.

In Table 2 only the best and the worst results are shown. The errors are much smaller than those obtained with Megaw's method, and examination shows, in fact, that any curve, no matter how badly drawn, will give better results in badly resolved cases than the straight lines of Megaw's method. The method could, of course, be applied equally well to the logarithms of the electron-density values. This was not done, but it was evident from inspection of the points $L, L', \ldots, N', N''$ obtained using logarithms that, given curves of the same form, they would lead to a slightly worse error for atom B, and about the same error for atom C, in agreement with what was found for Megaw's method.

This method could become much more precise if the form of the curves $LL'L''$, etc. could be obtained. This was investigated in some detail with the hope of being able to produce some sort of master curve, suitable to any situation, but there are too many variables involved and the hope had to be abandoned.

7. The method of Ladell & Katz

In this method (Ladell & Katz, 1954) a surface of the form

$$z(x, y) = Ax^2+By^2+Cxy+Dx+Ey+F \tag{2}$$

is fitted to the electron-density values nearest the peak. Although only six such values are needed to determine the coefficients in (2), the method uses the nine values nearest the peak, and thus effectively averages together four such paraboloids. Here, as in the analytical method of sections, there are two ways of choosing the nine points around atom C, and both sets have been used in testing the method. The method may be used with either the natural electron-density values or their logarithms, and both were tried. In addition, the method was also applied to the alternative mesh formed by ξ and the short diagonal.

It will be seen from Table 2 that for a well resolved atom like A, the method is at best no better than, for example, Megaw's method. For badly resolved atoms it can lead to enormous errors. The trouble is that in using the nine electron-density values near the peak, they are taken into account simultaneously. Since the maximum separation of any two of these nine points is 0·679 Å using the original mesh, and 0·746 Å using the alternative mesh, it is not surprising that the approximation involved in assuming a paraboloidal surface breaks down.

The claim by Ladell & Katz that, if only the peak position is required, one may neglect the obliquity of the mesh and approximate to it by a square was also tested, and the resultant errors are also shown in Table 2. It will be seen that where the method works fairly well, on a well resolved atom like A, the use of the square-mesh approximation introduces considerable additional error. In the other cases where the errors are large in any event, the use of the approximation may either improve or worsen matters. The fact that it can possibly improve the accuracy of the result is a clear enough indication that the basic approximation underlying the Ladell–Katz method has broken down.

It would be possible to modify the method and fit the elliptic paraboloid to the values near the peak by least squares; but it is clear that the additional labour would not be justified, since the breakdown of the method in the case of badly resolved atoms is due to the unsuitability of the interpolation surface, and not to the mathematical method used in fitting it to the observed values.

8. Conclusion

The overall conclusion of the present study is that in Fourier projections, where some degree of overlapping is bound to occur, the determination of peak positions is by no means a simple, routine process, and that, when the electron density has been computed at intervals of about 0·2 Å, very large errors may be introduced by the uncritical use of a purely analytical interpolation method. Interpolation errors, of course, will decrease rapidly as the mesh size is reduced. The mesh size in the present work was purposely chosen large, first because such a mesh size is frequently met with in practice with crystals of large unit cell, and secondly because it was explicitly claimed by Megaw (1954) that her method is reliable for a mesh of this size. It is clear from this study, however, that a much smaller mesh size is needed in those cases where an appreciable degree of overlapping occurs. This implies that for crystals with large unit cells electron-density values must be specially computed in the region of the peaks at intervals closer than those given by conventional strip methods. Alternatively, the differential synthesis method of locating the peaks can be used in such cases.

I am indebted to those colleagues who tried out the two graphical methods for me, and I am particularly grateful to Dr J. Iball for his interest and helpful criticism.

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