

Subtraction of Atom Images from a Fourier Synthesis of a Crystal Lattice

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In the last few years a considerable amount of work has been spent at The University of Oslo on the investigation of the structure of gases and liquids by electron and x-ray diffraction methods. One of the more complicated problems which we had to cope with, was the diffraction error in the Fourier synthesis, and a method which permits a certain control of this error was therefore developed. The principles of this procedure are in fact very simple. The maxima of the experimental distribution curves are removed one by one together with their diffraction maxima and minima. The only difficulty is to find the correct form and magnitude of the diffraction effect relative to a peak representing an interatomic distance in the Fourier synthesis^{1,2}.

A similar method may be applied to the different types of Fourier syntheses of crystal lattices from x-ray data. In the present paper it shall be demonstrated how the images of the different atoms may be removed from the density function determined by a two-dimensional Fourier synthesis of a crystal lattice.

THE REPRESENTATION OF THE ATOMS BY A FOURIER SYNTHESIS

The electron density $\rho(x, y, z)$ of a crystal may be expressed by the following three-dimensional Fourier series:

$$\rho(x, y, z) = \frac{1}{V} \sum_{h, k, l}^{+\infty} \sum_{h, k, l}^{-\infty} F(h, k, l) e^{2\pi i (hx + ky + lz)} \quad (1)$$

where the unities for x , y , and z are the lattice constants a , b and c respectively, V represents the volume of the unit cell, and $F(h, k, l)$ is the crystal structure factor.

However, experimentally it is only possible to determine the numerical value of $F(h, k, l)$ within certain limits, and the expression (1) requires summations from $-\infty$ to $+\infty$. Systematical errors are thus introduced in the density function, $\rho'(x, y, z)$, determined from experimental intensity data:

$$\rho'(x, y, z) = \frac{1}{V} \sum_h \sum_k \sum_l F(h, k, l) e^{2\pi i (hx + ky + lz)} \quad (2)$$

Bragg and West³ who first observed this effect, proved that from a theoretical point of view, this is analogous to the diffraction phenomenon in optics, and therefore they termed it diffraction effect. Accordingly we may regard the result of a Fourier synthesis as an image of the atoms in the lattice produced by optical diffraction. For atoms situated sufficiently close together or especially in one- or two-dimensional projections, the images of the single atoms may overlap. The diffraction waves belonging to one atom may therefore distort the image of another atom considerably. Already Bragg and West³ proposed a method which should make it possible to minimize the influence of the diffraction effect. Their method, which implies the introduction of an artificial temperature factor in the intensity expression, has been thoroughly investigated by Grimm, Brill, Hermann and Peters⁴⁻⁹ and others. The method alters the image of an atom considerably, as it reduces the magnitude of its central peak and at the same time increases its width to a certain extent. This means in fact a reduction of the resolving power of the synthesis.

In a series of publications¹⁰⁻¹⁴ Booth has undertaken a comprehensive investigation of the different errors which are of importance in the application of the Fourier synthesis to structural problems. He has determined expressions which give the approximate magnitude of the shift in the parameter values caused by the different types of errors. Booth also treats the diffraction effect and describes a method for a more correct determination of the parameters. As a practical example Booth applies his method to a two-dimensional projection of oxalic acid dihydrate¹⁴. For our investigation, we also have chosen this substance, Booth's results not being published at the time when our work was started. A comparison between Booth's results and ours are therefore very easy.

SUBTRACTION OF THE IMAGE OF SINGLE ATOMS

Two independent experimental intensity measurements are used as a basis for our computation of a projection in the xz -plane of the oxalic acid dihydrate crystal. The first one is published by Robertson and Woodward¹⁵, and the second one by Brill, Hermann and Peters⁹.

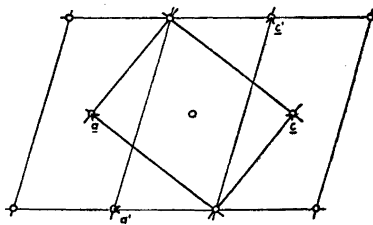


Fig. 1. The xz -plane of the unit cell.

The a and the c -axis used in the computation are derived from the real a' - and c' -axes by the expression (Fig. 1):

$$a = \frac{1}{2} (3 a' + c') \qquad c = \frac{1}{2} (-a' + c') \qquad (3)$$

Fig. 2 represents the AC -plane in the reciprocal lattice, and $F(h, k, l)$ is equal to $F(h, k, l)$ as the crystal has a center of symmetry. The intensities which are measured, are represented by small circles. The part of the diagram above the A -axis corresponds to the results of Brill, Hermann and Peters' measurements, and the part below the A -axis to those of Robertson and Woodward. For reasons which shall be explained later, the intensities which have been measured equal to zero are marked by double circles.

From these experimental intensities three different density functions were now determined. The first one was derived from Robertson and Woodward's

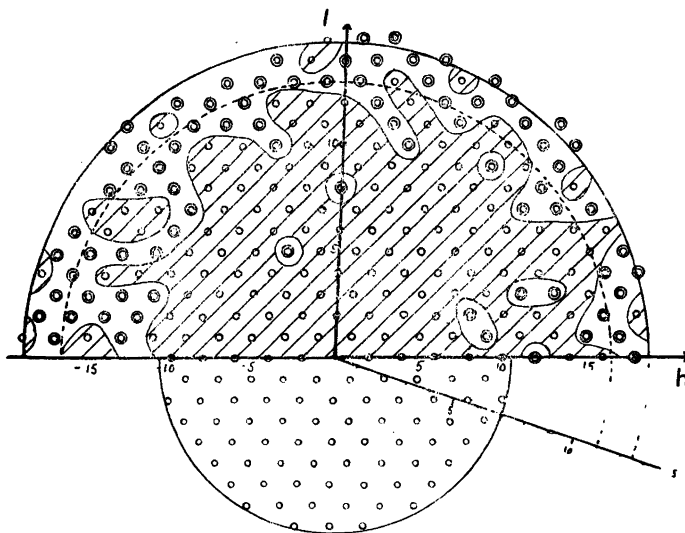


Fig. 2. The AC plane of the reciprocal lattice.

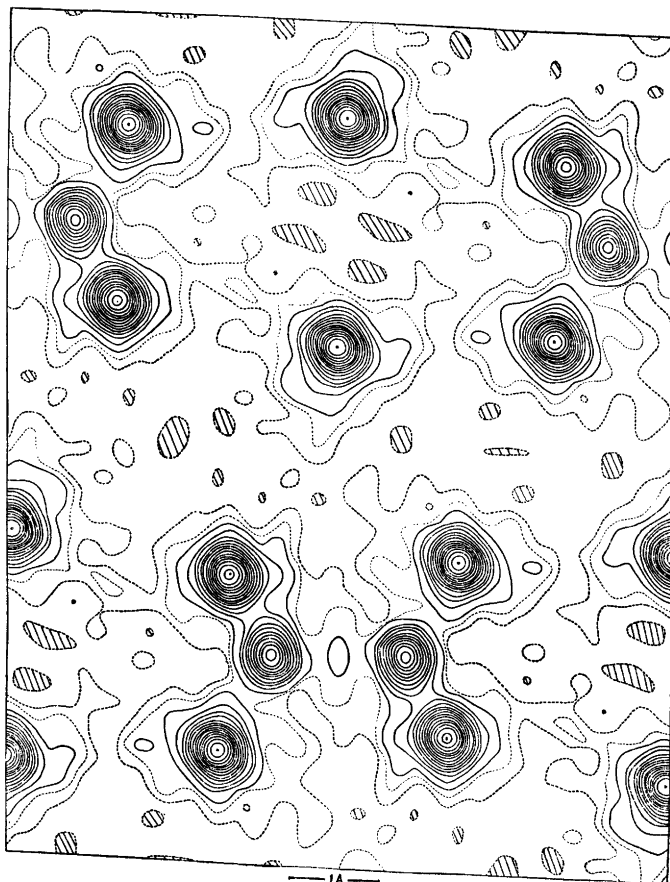


Fig. 3. Electron density map of oxalic acid dihydrate. The equidistance is 1 electron per A^2 . 1 electron per A^2 is given by the heavy broken lines whereas the light broken lines correspond to $1\frac{1}{2}$ electron per A^2 . The shaded areas represent negative density.

data, the second from Brill, Hermann and Peters' intensities taking only those points in the reciprocal lattice into consideration which were also found in Robertson and Woodward's determination, and the third using all the points given by Brill, Hermann and Peters. The oxygen atom in the water molecules and the oxygen atom in the carboxyl group situated farthest away from the carbon atom in the projection, proved to have parameters which were in the very best accordance in the three different diagrams. The parameters of the oxygen atom which is closest to the carbon atom and especially those of the carbon atom itself, showed greater deviations in the three cases. The

magnitude of these deviations proved that they are certainly due to differences in the experimental data. In Fig. 3 the xz -projection based on Brill, Hermann and Peters' intensities is given.

If we want to remove the images of the atoms one by one from the projection, it should be most correct to start with the atoms whose positions are determined with the greatest accuracy. In the case of oxalic acid dihydrate this means the oxygen atoms. On the other hand it is also most important that the image removed is as correct as possible in its form and magnitude. The simplest way in which such an image of the oxygen atom may be obtained, is to choose the best possible model for the electron density in the oxygen atom, to place this model atom in accordance with the determined parameters, and to carry out a Fourier synthesis of the reciprocal lattice corresponding to the single atom. The problem is thus simplified to finding the correct model for the electron distribution in the atom, which again may be reduced to a determination of the correct atomic form factor, $f(s)$, of the atom in question. This determination may, however, be accomplished by means of the observed $F(h, k, l)$ values, if the parameters of the atoms are known with a sufficient degree of accuracy. The structure factor, $F(h, k, l)$, can always be written as a linear function of the atomic form factors. In our special case the structure factor may be expressed by:

$$F(h, k, l) = 4 [f_{0_I} \cos 2\pi (hx_{0_I} + ky_{0_I} + lz_{0_I}) + f_{0_{II}} \cos 2\pi (hx_{0_{II}} + ky_{0_{II}} + lz_{0_{II}}) + f_{0_{H_2O}} \cos 2\pi (hx_{0_{H_2O}} + ky_{0_{H_2O}} + lz_{0_{H_2O}}) + f_C \cos 2\pi (hx_C + ky_C + lz_C)] \quad (4)$$

leaving out the scattering from the hydrogen atoms. This omission of the influence of the lighter atoms represents in this case a satisfactory approximation, and as the atomic form factor of the hydrogen is decreasing very rapidly

with increasing $s = \frac{4\pi \sin \frac{\theta}{2}}{\lambda}$, this approximation is especially good for greater

values of s . If now the parameters x , y and z of the atoms are determined with sufficient accuracy, a system of equations may be derived from expression (4), and from these equations the unknown atomic form factors may be determined. If now the atomic form factor, $f(s)$, is a function of s alone, it should be possible to determine the different atomic form factors for greater values of s . In our special example, we may assume that:

$$f_{0_I} = f_{0_{II}} = f_{0_{H_2O}} \quad (5)$$

Points on the atomic form factor curve for oxygen from Brill, Hermann and Peters' experimental values for $F(h, k, l)$ are shown in Fig. 4. In Fig. 5 the

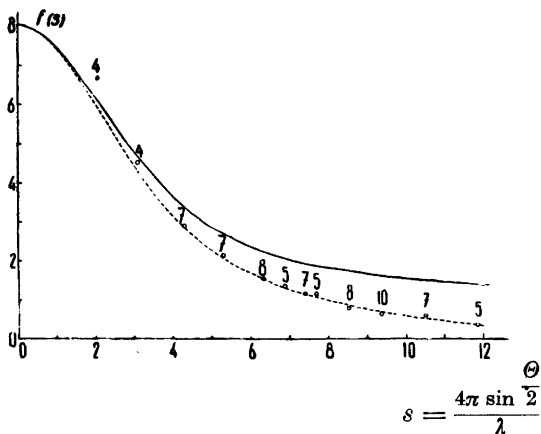


Fig. 4. Atomic form factor for oxygen. \circ Calculated points. The figures indicate the number of points in the reciprocal lattice applied by each computation. — $f(s)$ determined from Hartree's atom model, --- $f(s) e^{-0.01s^2}$.

observed values used in the determination of the different points of Fig. 4 are marked by small circles. These points on the atomic form factor curve may be utilized for different purposes. We have chosen to multiply an atomic form factor, $f(s)$, obtained from Hartree's atom model by a function e^{-Bs^2} . The constant B is given a value which brings the function $f(s) e^{-Bs^2}$ to fit as closely as possible for greater values of s to the atomic form factor values as derived from the experimental $F(h, k, l)$.

In general it is the outer part of the atom image which is the most important and the most difficult to determine correctly. At greater distances from the center of the atom, the image depends in the first place on the value of

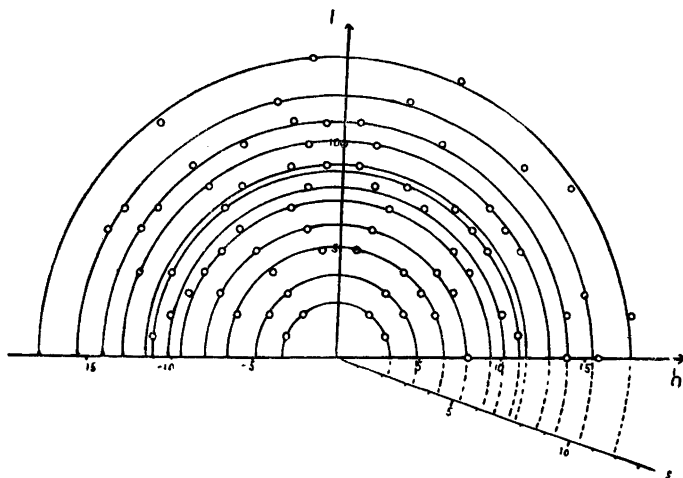


Fig. 5. Points in the reciprocal lattice used for the determination of Fig. 4.

$f(s_0)$ and in the second place on $\frac{df(s)}{ds}$ for $s = s_0$, where s_0 is the greatest value of s for which any intensity is observed.

A more comprehensive theoretical investigation proves that the image corresponding to a spherical atom in a two dimensional Fourier synthesis may be expressed by the converging series:

$$\rho(r) = \frac{1}{4\pi} \sum_{k=0}^{\infty} (-1)^k f_s^{(k)}(s_0) \frac{s_0^{2k+2}}{(k+l)!} J_{k+l}(rs_0) \quad (6)$$

r is given in Ångström units, s_0 in reciprocal Ångström units, $f_s^{(k)}(s)$ represents the k^{th} derivate of $f(s)$ with regard to s^2 , and J_k are functions closely related to the Bessel functions¹⁶. In general the significance of the terms is decreasing rapidly as k is increasing, and for greater values of rs_0 , the series is dominated by the first few terms. It is therefore of the greatest importance that the atomic form factor, used, has a correct form in the neighbourhood of s_0 , and one of the greater advantages of this method is that it leads to an atomic form factor curve which is more reliable for greater values of s .

When a Fourier synthesis based on the corrected atomic form factor curve is carried through for the determination of an atom image, the influence of the limits of summation in the reciprocal lattice should also be taken into consideration. In order to illustate this special problem, $F(h, 0, l)$ values have been computed using the corrected atomic form factor curve, $f(s) e^{-0.01 s^2}$, shown in Fig. 4 for the oxygen atoms, and a correspondingly corrected atomic form factor curve, $f(s) e^{-0.008 s^2}$ for the carbon atom. The result is given in Table 1. The influence of the hydrogen atoms is also in this case left out. For comparison the corresponding experimental values for $F(h, 0, l)$ are given below the theoretical ones in the table. The theoretical and experimental values are, as it is seen, in the very best agreement, and this is, as should be expected, especially the case for greater values of s . It is of special interest to notice that the table seems to indicate the existence of a certain threshold value for the observed intensities at approximately 1.0 in the units used in the table. The most correct way of fixing the limit of summation in the reciprocal lattice, when the image of an atom is determined, should therefore be to leave out all the $F(h, 0, l)$ values which experimentally are found equal to zero.

The procedure by subtraction of atom images from a Fourier synthesis of a crystal lattice should therefore be: First the correct atomic form factors are determined for the atoms whose parameters are best known. Then these atoms are placed in the lattice according to their parameters, and their images are

determined by a Fourier synthesis. In this synthesis it is of the greatest importance to use the same limits of summation as in the Fourier synthesis of the crystal lattice from the experimental data. The images of the atoms in question are then subtracted from the synthesis based on the experimental intensities. In general it should now be possible to determine the parameters more correctly for the atoms whose images are not yet subtracted. The atom images which are not subtracted in the first step, may now be removed in their turn and so on. This procedure should in general lead to a more correct determination of the parameters, especially for the lighter atoms in the lattice.

It may occur, however, that the images of two or more similar or nearly similar atoms are overlapping more or less in the synthesis based on experimental intensities. In one- or two-dimensional projections this is very often the case. These circumstances make the determination of the parameters of the single atoms very difficult. The problem may, however, be overcome in the following manner. First one of the atoms is placed in an approximately correct position and its image subtracted. Then the next atom is placed as correctly as possible in the lattice and its image subtracted. In general it is now possible to determine more accurate parameters for the atom first subtracted, and the procedure is repeated, if necessary several times. In this way it is always possible to improve the parameter values considerably provided the atom images have the correct form.

In the next part of the present paper, the application of the method shall be elucidated by a practical example.

THE APPLICATION OF THE METHOD

The upper part of Fig. 6 represents the remainder of a Fourier synthesis based on the experimental structure factors, $F(h, 0, l)$ given in Table 1, when the images corresponding to all the oxygen atoms in the oxalic acid dihydrate have been removed. The atomic form factor used for the oxygen atoms is represented by the broken line in Fig. 4, and all the $F(h, 0, l)$'s which, according to the experimental intensity data are equal to zero, have also been left out in the Fourier synthesis of the atom images. The parameters of the carbon atom before and after the subtraction of the oxygen atoms, were determined to be respectively: $x = 0.0025$, $z = 0.1011$ and $x = 0.0033$, $z = 0.1006$. This corresponds to a shift in the xz -projection of the carbon atom equal to 0.0085 \AA .

In Fig. 7 the images of both the carbon and the oxygen atoms are removed from the experimental synthesis. The atomic form factor for the carbon atom is determined from Hartrees atom model and multiplied by the function

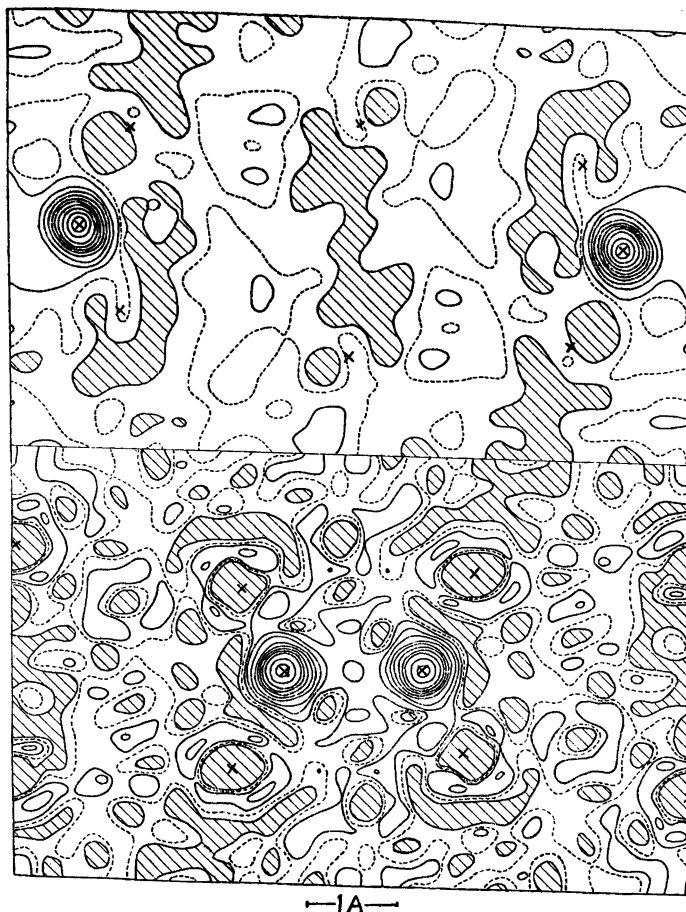


Fig. 6. Electron density map of oxalic acid dihydrate from which the oxygen peaks are removed. The equidistance is 1 electron per Å^2 . The broken lines correspond to $\frac{1}{2}$ electron per Å^2 . Negative density is given as shaded areas.

$e^{-0.008 s^2}$. The figure also illustrates the importance of using the correct limit of summation for the determination of the atom images. In the upper half of the figure, all the $F(h, 0, l)$ values which are found equal to zero in the experimental intensities also are left out in the Fourier synthesis of the atom images. In the lower half all the theoretically determined $F(h, 0, l)$ values for the different atoms are used in the summation, provided they are found within the part of the reciprocal lattice for which observations of intensities are available.

It will be seen that this method indicates some rather interesting possibilities. If the intensity measurements are sufficiently accurate, then Fig. 7

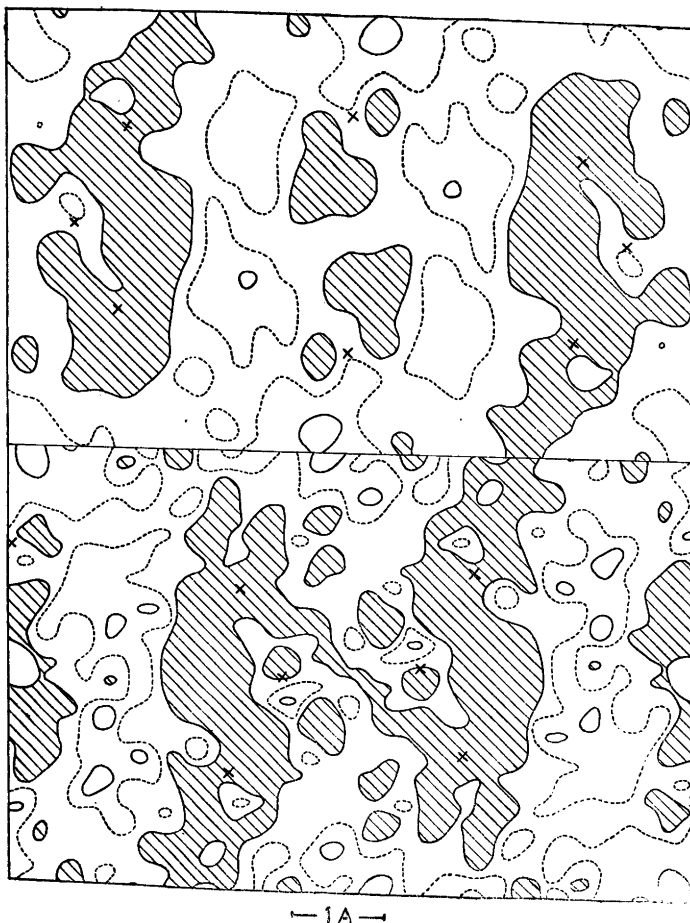
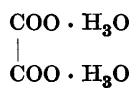


Fig. 7. Electron density map of oxalic acid dihydrate the oxygen and carbon peaks being removed. The equidistance is 1 electron per Å^2 . The broken lines correspond to $\frac{1}{2}$ electron per Å^2 . Negative density is marked out by shading.

should represent a projection in the xz -plane of the hydrogen atoms and an eventual distortion of the carbon and oxygen atoms. The position of the maxima in Fig. 7 are in the very best accordance with the hydrogen bonds predicted by Brill, Hermann and Peters⁹ from the observed interatomic distances between the oxygen atoms. The crystalline oxalic acid dihydrate should therefore rather be described as the oxonium salt of oxalic acid:



As mentioned above, this results depend completely on the reliability of Brill, Hermann and Peters' intensity measurements. If we therefore should want to give a better proof of the existence of the hydrogen bonds by this method, it should be necessary to verify experimentally the results of Brill, Hermann and Peters.

Finally, the lower part of Fig. 6 shows the result of a subtraction in which the atom images are obtained by using atomic form factor curves determined directly from Hartrees atom model. Again the image of the oxygen atoms contains diffraction rings, the maxima and minima of which are found at the same distance from the center of the image as in the Fourier synthesis from the experimental $F(h, 0, l)$ values. The magnitude of the diffraction maxima and minima in the image are, however, about four times as great as in the experimental synthesis. The subtraction of such images accordingly must introduce an enlarged negative diffraction effect into the results.

Already the results illustrated in Fig. 4 proves that the correct atomic form factor curve approaches the s -axis more rapidly with increasing s value than the atomic form factor determined from Hartrees atom model, and Fig. 6 demonstrates quite plainly that an uncritical application of Hartrees atom model in the subtraction may lead to an increased negative diffraction effect, which again may distort the experimental image considerably more than the original diffraction effect. A correction of the parameter values by the subtraction method may therefore easily lead to a deterioration of the results if a proper choice of atom images is not secured.

OTHER METHODS FOR THE DETERMINATION OF ATOM IMAGES

The atomic form factors used in our subtraction method were derived from a theoretical expression for the structure factor $F(h, k, l)$ (4). Other methods for the determination of the proper atom images were, however, also tried.

If we only want to remove the outer part of the atom image, *i. e.* the diffraction maxima and minima, and are not interested in a total removal of its central peak, then the following method may be applied.

The whole atom image obtained from an atomic form factor corresponding to Hartrees atom model may be reduced in such a proportion that the magnitude of the diffraction waves is in accordance with the magnitude of the diffraction waves of the corresponding atom in the experimental synthesis. The procedure can, however, never lead to a complete removal of the total atom image.

From Fig. 4 we may conclude that the observed structure factor values and consequently the correct atomic form factors are falling more rapidly with

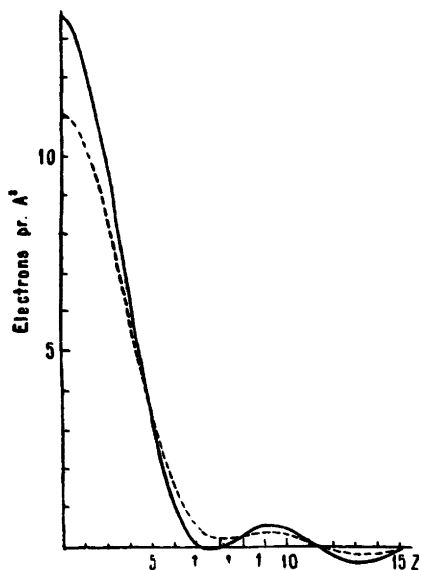


Fig. 8. $s_0 = 7$, — $f(s)$ derived from Hartrees atom model, --- $f(s) e^{-0.011 s^2}$.

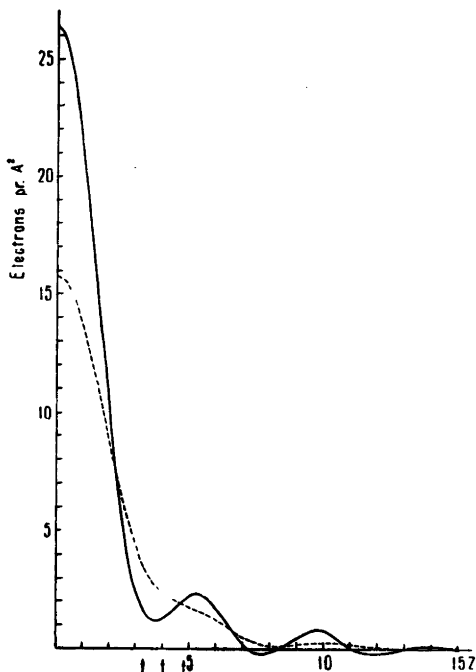


Fig. 9. $s_0 = 12.5$, — $f(s)$ from Hartrees atom model, --- $f(s) e^{-0.011 s^2}$.

increasing s value than the atomic form factors derived from Hartrees atom model. In our subtraction method we attained the correct atomic form factors by introducing the function e^{-Bs^2} , where the constant B is given an appropriate value.

A determination of the constant B may also be attained by a fitting of the image of each atom to the corresponding atom in the experimental synthesis. The Figs. 8 and 9 represent a section through the center of a two-dimensional projection of an oxygen atom, corresponding to a maximum value of $s = s_0$ equal to 7 \AA^{-1} and 12.5 \AA^{-1} respectively. The full drawn curves correspond to a Hartree atom model, and the broken curve represents an image obtained by introducing the function e^{-Bs^2} where the constant B is equal to 0.011 . In the two figures the position of the first minimum of the functions Λ_1 , Λ_2 and Λ_3 ¹⁶ are marked by small arrows. A multiplication of the atomic form factor by the function e^{-Bs^2} increases the width and decreases the magnitude of the central peak in the atom image, and both these effects might perhaps be used for the determination of the constant B . A variation in B has, however, a

small influence on the width but a comparatively great influence on the magnitude of the peak. A more detailed investigation of the connection between the constant B and the elevation of the peak, E , expressed in electrons pr. A^2 , leads to the formula:

$$E \approx \frac{1}{2\pi} \int_0^{s_0} e^{-Bs^2} f(s) s ds \quad (7)$$

where $f(s)$ is the atomic form factor determined from Hartrees atom model. The value $B = 0.009$, which was determined from this formula for the oxygen atoms in oxalic acid dihydrate, is in the best accordance with the previously determined value $B = 0.010$.

As mentioned above, the procedure first described for the determination of B is based directly upon the experimental structure factors, and is certainly the more correct and reliable one, and should therefore in general be preferred.

SUMMARY

It is demonstrated how the images of the single atoms may be removed one by one or in groups from the density functions obtained by Fourier synthesis of a crystal lattice. The method is applied to a two-dimensional projection, but may easily be extended to comprise also the three-dimensional case.

By the subtraction of the atom images it is essential to adjust the atom model in such a way that the image fits to the corresponding image in the experimental synthesis. Different methods for such adjustment are described. One of the methods is based on the intensities in a plane of the reciprocal lattice. It is, however, understood that an application of all the intensities in the whole reciprocal lattice certainly should increase the reliability of the results considerably.

If it is of special importance to remove the outer part of the image, *i. e.* the diffraction effect, then the conformity of the theoretical and experimental structure factors must be the best possible for greater values of s . By our method such a conformity of the atomic form factors of the different atoms is secured in the outer parts of the reciprocal lattice, and this means again a conformity of the theoretical and experimental structure factors.

We have shown that there probably exists a certain threshold value for the experimental intensity measurement, which means that in the Fourier synthesis of the different atom images, all the terms which are not observed in the

experimental intensity measurement, should be left out. It means that the limits of summation must be the same both for the synthesis based on the experimental intensities and for the synthesis of each atom image.

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