

The Optical Derivation of Structure Amplitudes

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A method is described of simulating a zone of structure amplitudes for a proposed structure by the diffraction pattern of a mask representing the projected contents of four unit cells. The peaks of the pattern can be made sharper by separating the unit cells by some integral multiple of the appropriate cell dimension, and atoms of different scattering powers can be represented by placing extra holes for the heavier atoms in some of the intermediate unit cells. The contents of one unit cell can be distributed among two or more unit cells in order to avoid overlapping of atoms, or to facilitate relative motion of one molecule with respect to a neighbouring one while the diffraction pattern is observed. The method provides a good degree of qualitative agreement.

Introduction

An essential operation in the trial-and-error method of structure determination is the comparison of the diffraction data derived from the real and from the proposed structures. The data from the proposed structure are usually calculated, although optical methods are now sometimes used, especially in the earlier stages of an investigation. One such method is that of the Fly's Eye (Bragg, 1944; Stokes, 1946; de Vos, 1948), which provides a diffraction grating corresponding to the projection of a proposed structure upon one face of the unit cell. It is customary to produce gratings with several hundred elements, although a simpler procedure has been described (Hanson & Lipson, 1952) which uses gratings with only four elements, corresponding to the projection of four adjacent unit cells. By a fairly obvious analogy this has been called a simplified Fly's Eye procedure; this is a misnomer since the four-element gratings, or masks, are produced by the use, not of a Fly's Eye, but of a pantograph punch originally built for use in Fourier-transform work. The chief advantage of the procedure is that it provides an extension of the more flexible Fourier-transform methods of Lipson & Taylor (1951). When reasonable agreement has been achieved by the latter method, comparison of the transform and the X-ray data can be simplified by the use of the four-element grating. This effectively divides the transform into reciprocal lattice points, so that the reliability of a proposed structure can usually be assessed without resort to photography. The purpose of the present paper is to describe certain improvements which should increase the scope and usefulness of the method.

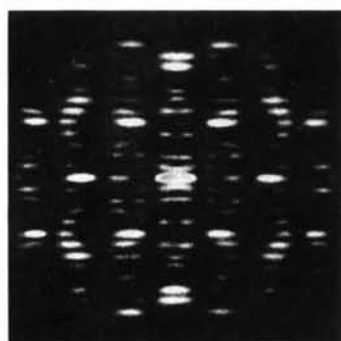
Production of sharper peaks

The practice of placing four molecules in four adjacent unit cells sometimes produces peaks which are too diffuse, particularly when the unit cell is long and

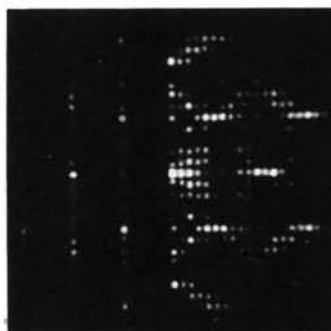
narrow. An example is given in Fig. 1(a), the diffraction pattern of the mask of Fig. 1(b) representing four molecules of di-*p*-anisyl nitric oxide (Hanson, 1953) in four adjacent cells. ('Unit cell' is taken to mean the simplest unit cell of the projection.) Sharper peaks are needed and these can be provided by placing the molecules in unit cells separated by an integral multiple of the appropriate cell dimension. This produces a finer fringe system, and consequently more peaks, only some of which correspond to reciprocal-lattice points. The effect is shown in Fig. 2(a), which is the diffraction pattern of the mask of Fig. 2(b); the presence of the extra holes between the molecules will be discussed in the next section, but is irrelevant here. On half of Fig. 2(a) the superfluous peaks have been obscured, although in direct viewing they would simply be ignored. Identification of the correct peaks can be made easier by the use of the row of calibration holes, parallel to one cell edge, also shown in Fig. 2(a). The spacing of these holes is the true cell dimension, so that the effect is to place a streak along each row of reciprocal-lattice points, as in Fig. 2(d). The holes can be covered and uncovered by the observer until each row of peaks is identified, and, if necessary, two such sets of holes, each parallel to a unit-cell edge, can be used to make identification of each peak doubly sure. The pattern can be compared either with the numerical data or with some such conventional representation as that of Fig. 2(c).

Representation of atoms of different scattering powers

Separating the molecules in the manner described above suggests a method of solving a previous difficulty, that of satisfactorily representing atoms of different scattering powers. This can be done by using extra holes to represent the heavier atoms in some of the intermediate unit cells. The relative weight to be assigned to a particular atom is taken to be proportional to the area under the curve of scattering



1 (a)



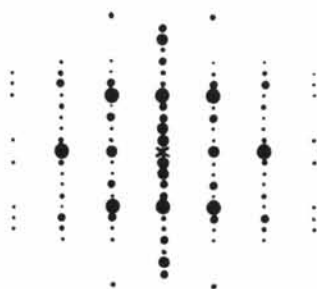
2 (a)



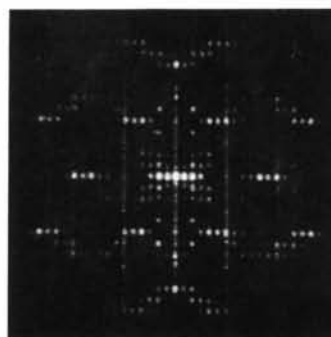
1 (b)



2 (b)



2 (c)



2 (d)

Fig. 1. (a) Diffraction pattern of mask of Fig. 1(b). (b) Mask representing four unit cells of (100) projection of di-*p*-anisyl nitric oxide.

Fig. 2. (a) Diffraction pattern of mask of Fig. 2(b). (b) Mask representing four separated unit cells of (100) projection

of di-*p*-anisyl nitric oxide. Extra holes have been added to represent oxygen and nitrogen atoms. (c) Weighted reciprocal-lattice section of (100) projection of di-*p*-anisyl nitric oxide. (d) Diffraction pattern of mask of Fig. 2(b), showing calibration streaks.

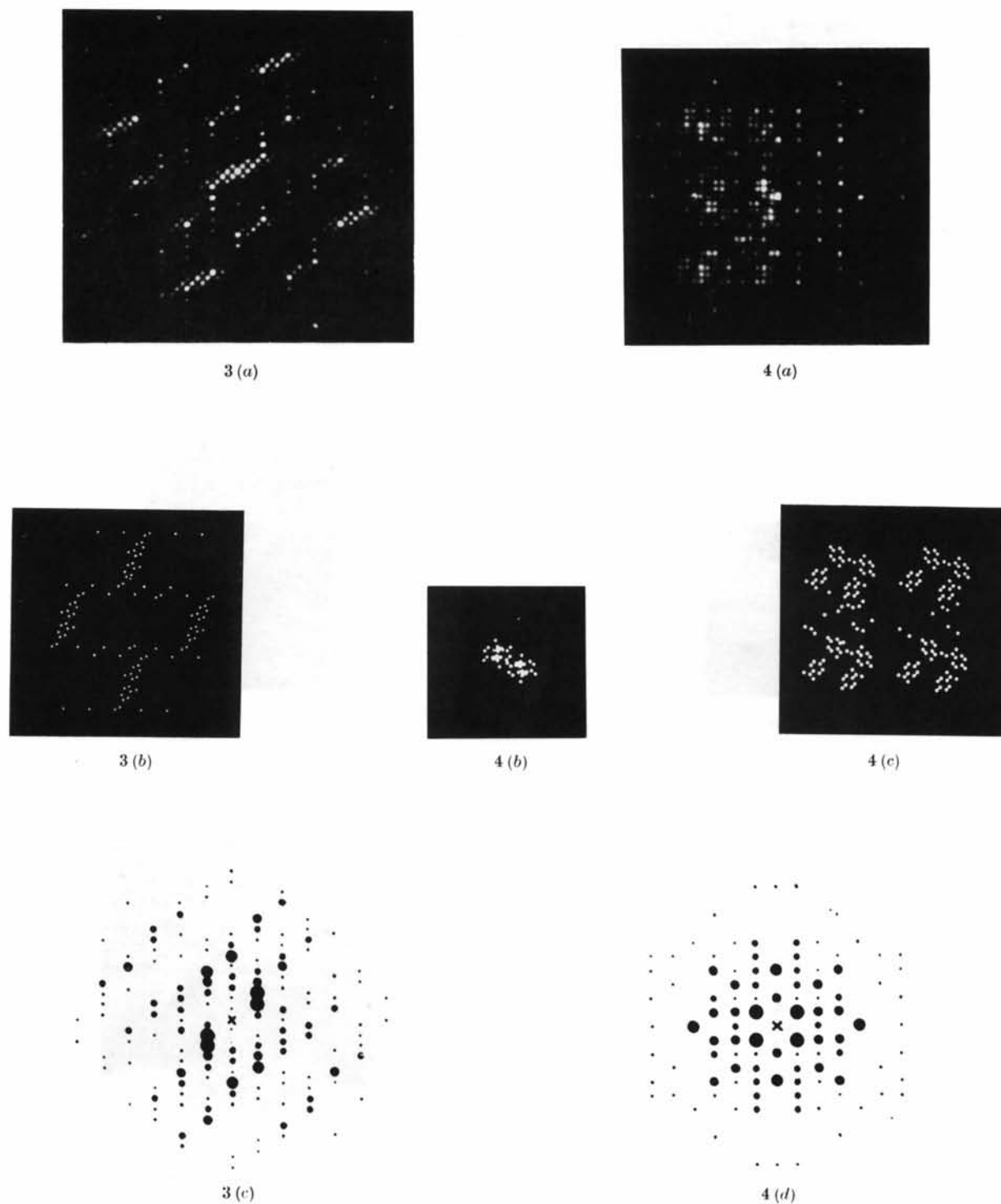


Fig. 3. (a) Diffraction pattern of mask of Fig. 3(b). (b) Mask representing four separated unit cells of (010) projection of *m*-tolidine dihydrochloride, with extra holes to allow for nitrogen and chlorine atoms. (c) Weighted reciprocal-lattice section of (010) projection of *m*-tolidine dihydrochloride.

Fig. 4. (a) Diffraction pattern of mask of Fig. 4(b). (b) Mask representing one unit cell of (100) projection of *p*-nitroaniline. (c) Mask representing four separated unit cells of (100) projection of *p*-nitroaniline, showing contents of each unit cell distributed over two unit cells. (d) Weighted reciprocal-lattice section of (100) projection of *p*-nitroaniline.

power against Bragg angle for the range in which reflexions occur. This is felt to be the best way of allowing for the different forms of the individual scattering-factor curves. Under this procedure, if a carbon atom is represented by four holes, a nitrogen atom will usually be represented by five holes (that is, one extra hole), an oxygen atom by six, and a chlorine atom by sixteen. In the example of Fig. 2, extra holes have been placed in two of the intermediate unit cells to represent the three oxygen atoms of the molecule, and in one of these unit cells to represent the single nitrogen atom. Comparison of Figs. 2(a) and 2(c) indicates that fair qualitative agreement has been achieved.

If one is concerned only with the intensity exactly at the reciprocal-lattice point, heavy atoms can be represented by extra holes placed in any available unit cells. In practice, however, the relatively large diffraction peak must be considered as a whole, and the extra holes must be so placed that the peaks due to the holes representing the heavy atoms are the same size and shape as those due to the rest of the mask. This can be done by arranging that the holes representing the heavy atoms constitute a regular lattice of the same overall size as that formed by the rest of the atoms. This is an expression of the fact that the resolving power of a grating (at given angles of incidence and diffraction) depends, not on the number of elements present, but only on the overall size. It can be seen that the condition is met exactly for the oxygen atoms of Fig. 2, but only approximately for the nitrogen atom. It is felt that such small departures as the latter will not appreciably affect the result.

Fig. 3 shows the procedure for the (010) projection of *m*-tolidine dihydrochloride (Fowweather & Hargreaves, 1950). The molecule contains, in addition to carbon atoms, two nitrogen atoms and two chlorine atoms, and the cell is centred. Fig. 3(b) shows the mask, in which the molecules have been separated by five units in the short direction and one in the long direction. Chlorine has been given a weight of sixteen, and nitrogen a weight of five. Fig. 3(a) is the diffraction pattern of the mask; the contribution of the holes representing the chlorine atoms so enhances the rows of peaks corresponding to the reciprocal-lattice points that no calibration holes are necessary. Comparison of Figs. 3(a) and 3(c) indicates good qualitative agreement.

Allowance for overlapping atoms

The final example to be considered is the (100) projection of *p*-nitroaniline (Abrahams & Robertson, 1948). Here the simplest unit cell contains four molecules, and a punched mask of the unit cell contents (Fig. 4(b)) shows serious overlapping of the atoms. The solution adopted is indicated in the mask of Fig. 4(c); two of the four molecules are placed in each of two adjacent unit cells, and the resulting array is

treated as though it were the contents of a single larger unit cell. The four arrays have been placed three units apart in one direction, and two in the other, and oxygen and nitrogen atoms have been represented as usual by extra holes. Comparison of the diffraction pattern with the weighted reciprocal-lattice section (Figs. 4(a) and 4(d)) again reveals good qualitative agreement.

Fixing the positions of molecules

It sometimes happens that the orientation and one parameter of two related molecules in a unit cell are known. Then it is sometimes possible, by a series of cuts parallel to the appropriate cell edge, to divide the mask so that all the molecules of one type are confined to one half. This allows the observer to move one molecule relative to the other in the allowed manner, while studying the diffraction pattern. The unknown parameter can often be determined very quickly in this way, but the usefulness of the method is limited by the fact that the molecules very frequently overlap or otherwise interfere with each other. The difficulty can be avoided by using the method described in the preceding section; the molecules can be placed in separate, and not necessarily adjacent, unit cells, in order to facilitate the desired partition of the mask.

Conclusions

The techniques described above seem to provide good qualitative agreement, in spite of the assumptions that a scattering-factor curve is adequately represented by the diffraction pattern of a hole, and that all scattering factor curves have the same form. A better representation could be obtained by using holes of different sizes; an oxygen atom could probably be better represented by, say, eight smaller holes than by six normal-sized ones. It is felt, however, that the slight increase in accuracy would be insufficient to justify the loss in speed and simplicity, since the accuracy obtained is probably sufficient for all but the final stages of a determination.

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