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A Non-Mathematical Introduction to X-ray Crystallography

by

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Series Preface

The long term aim of the Commission on Crystallographic Teaching in establishing this pamphlet programme is to produce a large collection of short statements each dealing with a specific topic at a specific level. The emphasis is on a particular teaching approach and there may well, in time, be pamphlets giving alternative teaching approaches to the same topic. It is not the function of the Commission to decide on the 'best' approach but to make all available so that teachers can make their own selection. Similarly, in due course, we hope that the same topics will be covered at more than one level.

The initial selection of ten pamphlets published together represents a sample of the various levels and approaches and it is hoped that it will stimulate many more people to contribute to this scheme. It does not take very long to write a short pamphlet, but its value to someone teaching a topic for the first time can be very great.

Each pamphlet is prefaced by a statement of aims, level, necessary background, etc.

C. A. Taylor
Editor for the Commission

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Teaching Aims

To help students with no previous knowledge of X-ray diffraction to understand the general principles and to give some idea of what it can do.

Level

This approach could be used at almost any level from about age 16 upwards.

Background

A general interest in science and an elementary knowledge of what can be done with a microscope and slide projectors is all that is needed.

Practical Resources

Use is made of the *Atlas of Optical Transforms* published as part of the Teaching Commission's Pilot Project (see reference at end).

Time Required for Teaching

This represents an introductory course of two or three lectures with time to study the *Atlas*.

A Non-Mathematical Introduction to X-ray Diffraction

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1. Introduction

In my view the basic problem in presenting X-ray diffraction to non-specialist audiences is to remove some of the atmosphere of mathematical difficulty and mysticism and to show, first of all, that the processes involved are, in principle, identical with those of microscopy.

My suggested approach to this problem is to use optical analogues at quite an early stage: the mathematics can be filled in easily enough once the essential ideas have been grasped—or of course it may be that a non-specialist group will not need the mathematics anyway. I shall illustrate this pamphlet by referring to illustrations in the Atlas of Optical Transforms which was published in 1975 by Bell for the Unesco pilot project of the Teaching Commission, which really initiated the idea of these pamphlets.

I usually begin by drawing attention to the basic steps that occur in all processes of image formation: the first is scattering of the radiation and the second is recombination of the scattered beams. The basic idea can be illustrated with an ordinary $2'' \times 2''$ slide projector. If the lens is removed so that a diffuse patch of light is seen on the screen even though a slide is in place, it will be clear to an audience that all the information that is contained in the slide must be available in the patch of light on the screen although it is not readily decipherable. Clearly the lens cannot 'know' anything about the slide and yet as soon as it is placed in the correct position the nature and detail of the slide are revealed. All that the lens can do is to rearrange the information so that it is immediately understandable to the eye and brain.

2. The Problem of Focusing

The operation which we call 'focusing' is a very sophisticated one which we take very much for granted. But how do we actually perform it? Even a very brief thought will make it clear that what we really do is to make the image look as we think the object is meant to look. We assume, for example, that if in one position of the lens all the junctions between black and white areas are sharply defined, then it is probably 'in focus'. The assumption clearly is that the junctions really *are* sharp. If on the other hand the object on the slide already had *diffuse* junctions it would be correspondingly more difficult for the projectionist to focus the slide. In the event of real difficulty we may focus on a hair, or on some specks of dust, which we assume should have 'sharp edges' and hope that when they look right the whole slide will be right. There are in fact, whether we like it or not, only two ways of focusing; one is to calculate the precise position of lens, slide, screen, etc., on the basis of geometrical optics and the other is to work on the basis of some preknowledge about the nature of the object. We shall return to the implications of this statement for X-ray diffraction at a later stage.

With visible light we can usually solve the focusing problems fairly easily and images of extremely small objects may be produced in the optical microscope. One severe limitation however, is the wavelength of light and detail below this size cannot be imaged. One alternative is to use electrons whose wavelength is quite small enough, but the practical problems of lens designs for the electron microscope provide an experimental limit before the resolution of individual atoms can be achieved.

X-rays have a suitable wavelength and would provide a simple solution if they could be focused experimentally. Unfortunately this is not possible except with systems of curved mirrors which are capable of only very limited magnification. To achieve the full benefits of the small wavelength some alternative approach must be adopted.

3. The Essence of X-ray Diffraction

In principle one could say that the whole development of X-ray diffraction techniques really amounts to the development of alternatives to the focusing of X-ray images. The point is that the first stage of the imaging process, illustrated by the projector with no lens, can be performed but the crystallographer has no lens to put back in the projector and must try to make sense out of the diffuse patch in some other way.

If the problem were strictly analogous to this it is unlikely that any structures would ever have been solved. Fortunately there are two significant ways in which the X-ray crystallographer's case differs from that of the projectionist with no lens for his projector. First of all the projector uses white light with a broad frequency band which is also spatially incoherent and is produced from a large source. In the X-ray case it is usual (except under the special circumstances of Laue photographs with which we are not concerned here) to use monochromatic radiation which, as a result of travelling through a long, fine hole or slit has quite a high degree of spatial coherence. The second point is that the object usually exhibits some degree of regularity or crystallinity.

These two facts lead to the production of patterns which consist not of a diffuse patch but rather of a series of discrete spots (though there may well be diffuse spots and patches if the object is not sufficiently regular).

The parallel with the projector which most nearly matches the X-ray case would be a gas-phase laser beam falling on a regular grating (e.g. a finely woven handkerchief or a piece of gauze); the beam is scattered or diffracted into a number of well defined beams or spots arranged in a regular way. The optical diffractometer used in the preparation of the plates in the Atlas is merely a sophisticated development from this simple experiment.

The difference in the patterns of regular and irregular objects, all illuminated by monochromatic coherent radiation is illustrated in Plates 16 and 17 of the Atlas.

The process carried out by the lens of the projector or by the objective of the microscope and which needs to be carried out artificially by the X-ray crystallographer involves the mathematical operation of Fourier Synthesis. We shall however attempt to illustrate the process without resort to mathematics.

If the scattering (or diffraction pattern as it tends to be called if it consists of regular spots) is completely determined then it should, in principle, be possible to transform the beam into an image by the purely mathematical process of Fourier Synthesis. Unfortunately, however, it has so far proved quite impossible to record the relative phases: this immediately invalidates the direct mathematical process. The reason why the phase cannot be recorded becomes clear if one calculates the frequency of X-rays; determination of phase would, in effect, involve time measurements corresponding to a fraction of one period. If we assume X-rays of wavelength 1.5 Å (1.5×10^{-10} m) the frequency is about 2×10^{18} and hence to measure a phase difference of (say) $\frac{1}{5}$th of a cycle would involve a time measurement of about 10^{-19} s which is certainly beyond our present resources. Perhaps one day a means of adding a coherent beam, as in optical-laser holography may become available and then the whole situation would change!

Let us first of all consider in a little more detail the relationships between an object and its scattering or diffraction pattern—regardless, for the moment, of whether we are dealing with light or with X-rays. Suppose that the object consists of two points only. Plate 1 of the Atlas shows that the result is a set of fringes whose spacing varies inversely with that of the points. These are the well known 'Young's' or 'Double-slit' fringes and can be shown to vary cosinusoidally in amplitude with alternate fringes π out of phase with the rest. For the moment we will ignore the effects of the size of the scattering points and assume that they are mathematically small. The fringes will then, in principle, be of infinite extent and without the ring patterns superimposed as in Plate 1; the centre region will be the only one of interest. If we now add further pairs of points in different orientations, fringes of different orientation and spacing will be added and the resultant pattern becomes more complex (Plate 2). If the basic arrangement of points forming the object is repeated in any kind of regular way, further fringes are introduced and a two-dimensional 'crystal' produces a pattern of regular spots (Plate 11). It will be clear from a study of plates 1, 2 and 11 that we can now separate two quite distinct variables. First the size and shape of the lattice (strictly the *reciprocal* lattice) in which the spots of the diffraction pattern are arranged depends solely on the size and shape of the lattice on which the groups of scatterers are arranged. And secondly the relative intensity of the spots depends on the arrangement of scatterers in each individual group. In the crystalline case the 'individual group' is the unit cell contents.

4. The Fundamental Problem of Reconstructing an X-ray Image

In the terms of this pamphlet we are now faced with the problem of deriving the arrangements shown on the left hand page of Plate 11, given the scattering patterns on the right hand of Plate 11.

Now let us consider the nature of the problem of recombining the scattered information to produce an image and we will start by once more considering the case of two point scatterers only. As we have seen, the diffraction or scattering pattern is a set of cosinusoidal fringes whose spacing is inversely related to that of the point. This looks very like a diffraction grating which if *itself* placed in a coherent monochromatic beam of light will give orders of diffraction. A good experiment at this point is to provide a few coarse diffraction gratings which can be placed in a laser beam and give a single row of regularly spaced sharp spots and it is easy to demonstrate the reciprocal relationship between the slit spacing of the grating and the space between the orders. If we now substitute for the ordinary diffraction grating (which has sharp transparent and opaque slits, i.e. has a square wave function) one with a cosinusoidal function determining its transparency variation we shall find only three orders: a bright centre one and a single weaker one on each side. Of course our grating really has a transparency distribution of $(1 + \cos \theta)$ since we have not provided for negative transmission. If, using phase changing tricks with polarised light and mica, the details of which need not concern us here, we make a true representation of the cosine distribution with alternative strips in opposite phase, we arrive at a diffraction pattern with just two orders, one on either side of the original line of the beam. A logical development of this train of thought then is to see that if we were to place the patterns of (say) the *right* hand side of Plate 2 in a coherent monochromatic beam of light, then we should produce an image like the *left* hand page. In other words we can achieve the recombination trick merely by using a representation of the diffraction pattern itself as another diffracting object. The problem of representing the phase remains however and needs special consideration.

This reverse process is illustrated in Plate 29. On the left we have a series of pairs of points which build up in 29.8 Left to a representation of the complete scattering pattern in two dimensions of a crystal of Rhodium phthalocyanine derived using X-rays. The relative intensities of the spots are represented by varying the size of the holes. The diffraction pattern of this, 29.8 Right, is a reasonable reconstruction of an image of a Rhodium phthalocyanine molecule and one can see in the earlier figures on this page how the successive pairs of holes add further fringes to build up the pattern. This, as one might guess, is a very special case in which it just happens that the Rhodium atom at the centre is just sufficient to scatter enough coherent background over the whole pattern to bring the maximum *negative* regions to zero, and make corresponding enhancements of the positive regions (this principle is further explored in Plate 5). In this case therefore the phase problem does not cause difficulties. Such examples are, however, rare.

Following this line of argument with further examples we should be able to establish experimentally that the process of recombination is identical with that of scattering and that, under certain circumstances, the diffraction pattern of the diffraction pattern is an image of the object again. The mathematics could be introduced at this stage if it is desired but is not essential for non-specialists.

5. Some Practical Questions

We now need to try to answer a series of questions that should arise.

(a) What happens in the general case if we ignore the phase and try to recombine with just the intensities?

In order to answer this question we need to think back once more to the object consisting of two points and its diffraction pattern which is a cosinusoidally varying fringe pattern. Suppose now that the object is translated in its own plane (which is assumed perpendicular to the light beam). It is well known that the fringes will *not* move laterally. (This can be demonstrated easily if a distant street lamp is viewed through a piece of fabric such as a handkerchief or an umbrella: the diffraction pattern does not move on the retina when the fabric is translated.) It is clear however that *some* representation of the translation must be encoded in the diffraction pattern, since, if we allowed the fringes to fall on a lens and be recombined to form an image, the translation of the object would immediately become apparent. It can be shown that the relative phases of the light arriving at various points of the pattern change but since we cannot see or record phase we are not aware of the change. It follows logically then that if we re-combine the *intensities* of the diffraction pattern ignoring the phases, the information about *lateral* position would be missing. The pairs of points which make up the object will all be reproduced with the right separation from each other and in the right orientation but they will all be symmetrically disposed about the centre of the pattern instead of being properly distributed. In other words the resulting distribution will contain information about all the vector distances that are present between the various pairs of scattering points in the object but all will be translated so that one end of every vector is the origin.

Since it is perfectly possible to record all the intensities in an X-ray photograph and to perform this recombination mathematically using a digital computer it should not be surprising to find that such a reconstruction is one of the standard methods of trying to decipher X-ray patterns. The process is known as the calculation of a Patterson function, after A. L. Patterson of Pennsylvania, U.S.A. who first suggested the technique. The problem is how to interpret the resulting map.

Figure 1 shows a simple object consisting of three points and Fig. 2 shows an Idealised Patterson map showing how the six possible vectors **ab**, **ba**, **bc**, **cb**, **ac** and **ca** appear. The relationship between the map and the object is not difficult to see. The difficulty increases very rapidly, however, if the numbers of scattering points increases. 10 scattering points would give rise to 90 peaks (though many would overlap) and 100 would give 9900 peaks. To see how the complexity increases even with simple structures we will consider an actual example. Figure 3 is a typical map and Fig. 4 is one of the symmetrically related molecules in the crystal giving rise to this distribution. A peak marked **a** in Fig. 1 would correspond to vectors such as 6-4, 1-3, 7-2 or 9-8 and a peak such as **b** would correspond to 7-6, 1-5, 2-4, and 8-2. Even though this is quite a simple arrangement the interpretation of the Patterson map *without some knowledge of the molecule* would be very difficult if not impossible.

Fig. 1.

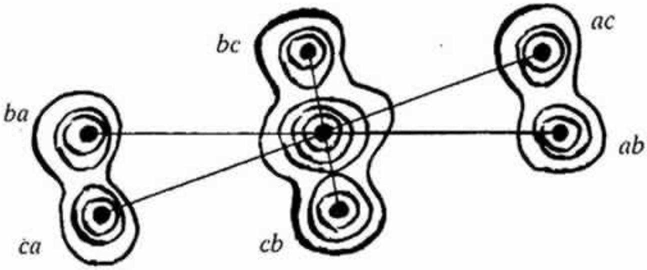

Fig. 2.

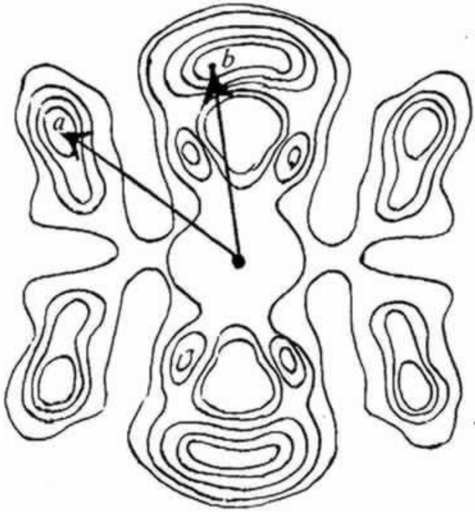

Fig. 3.

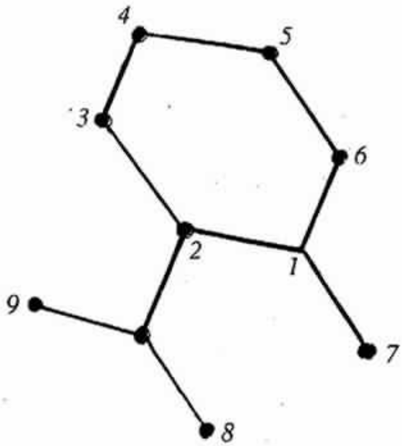

Fig. 4.

(b) How can we by-pass or otherwise solve the problem of the phases that cannot be measured?

The whole art of the crystallographer is really contained in the answer to this question. The possibilities are numerous and we shall select only four by way of illustration.

(i) We may know enough about the chemistry and stereo-chemistry to make an intelligent guess at the configuration. We may then use this to calculate the diffraction pattern that would result and our calculation will give both amplitudes and phases. If the amplitudes compare reasonably well with those observed we may then combine our *observed* amplitudes with the *calculated* phases and do a computed Fourier synthesis—or image recombination—that will be a fair representation of the required structure. This is the so-called trial and error method.

(ii) We may use the Patterson map technique already described in (a) above.

(iii) We may have available, or be able to create a series of related crystals with very similar structures but with one atom different in scattering power. For example, a material containing a chlorine atom may also exist in a very similar form with bromine replacing chlorine. A careful observation of the effect this has on the relative intensities of the diffracted beams (cf. Plate 5 of the Atlas) can lead to the determination of the relative phases necessary to reproduce this heavy atom and it can then be assumed that the same phases will not be far wrong for the whole structure.

(iv) The application of various mathematical and statistical relationships ('direct methods') between the amplitudes can lead to the direct determination of the phases of a proportion of the beams and then, by a process of successive approximations, the complete image can be built up.

(c) How can the statements made in section 2 about focusing be reconciled with the solutions of the phase problem which we have just listed and described under (b)?

The four techniques agree very well with the statements about focusing made in section 2. In (i) we clearly have to know a good deal about the object in order to focus. In (ii) (as was pointed out in the discussions of 5(a) above) we can only interpret a Patterson map if we know something about the object even if—in the simplest possible case—our only knowledge is that the object consists of discrete atoms rather than of a continuous distribution of electron density. In (iii) our heavy atom is analogous with the hair or speck of dust that we know is there: if we focus on it we can assume that the rest will be in focus. In (iv) the mathematical relationships used are all found to depend on specific assumptions about the object—usually that the scattering is everywhere real and positive and that discrete spherical atoms make up the object.

(d) What determines the accuracy of reproduction of the image?

Just as in optical microscopy the limits of accuracy are set fundamentally by the wavelength of the X-rays used and experimentally by the 'aperture' of the system. In the X-ray case the 'aperture' means the number of terms included in the Fourier synthesis. Plate 32 of the Atlas illustrates this with an optical analogue. 32.1 on the right is an object consisting of a small square cristallite of molecules of bishydroxy-duryl methane. (32.1) on the left is its diffraction pattern. If we used the whole of 32.1 on the left we could, in theory, produce—assuming that we knew both amplitudes and phases—an exact replica of 32.1 on the right. If we *restrict* the terms included in our calculation to those shown in 32.2 on the left the resulting deterioration of the image is shown in 32.2 on the right. The remainder of the plate pursues this theme in various ways and it is significant to note that in 32.6 we come back full-circle to the point that, if we only include one order of diffraction on either side of the centre (32.6 on the left) the result (32.6 on the right) is one set of sinusoidally varying fringes.

(e) What complications are introduced by the fact that crystals are three dimensional?

This is a difficult question to answer systematically without drawing on a fairly full knowledge of crystallography. In practice however it can be said that the complications in the *principles* involved are relatively few: the computation becomes necessarily greatly increased.

The important point to realise is that the relative scale of wavelength-to-object-size is quite different for light and for X-rays. For most of the objects illustrated in the Atlas the significant dimensions are a few thousand wavelengths of light. In the X-ray case however typical dimensions (e.g. a carbon–carbon bond of 1.4×10^{-10} m) are comparable with the wavelength (1.54×10^{-10} m for Cu $K\alpha$ radiation). Thus in optics all the significant scattered information is contained within very small angles, whereas in X-ray diffraction we need to take in scattering angles of up to 180° in order to extract the maximum information. The complications therefore turn out to be experimental rather than theoretical and will be dealt with in later pamphlets in the series dealing with other aspects of the subject. At the moment it will suffice to say that there is no difference in principle that need concern us, though experimentally and computationally there are significant increases in complexity on moving from two to three dimensions.

References

G. Harburn, C. A. Taylor and T. R. Welberry. *Atlas of Optical Transforms*, London: G. Bell; U.S.A.: Cornell University Press.

C. A. Taylor. 'The Patterson Function', *Physics Education*, 2 (1967) 276.

C. A. Taylor. *Images*, The Wykeham Science Series No. 46, 1978, U.K.: Taylor & Francis; U.S.A.: Crane. Russak.

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