Fourier Projection Demonstrator

Introduction

The purpose of this computer program is to demonstrate various aspects of Fourier Synthesis, a technique that crystallographers use to enable them to find the atoms in a crystal structure from the known diffraction pattern.

Note that this program only works for crystal structures with orthogonal axes, and plots two-dimensional projections down specific axes.

The left-hand window shows a plane wave corresponding to each structure factor input and the right-hand window the cumulative sum of the waves.

Background

In the case of X-ray diffraction, it is the electrons that scatter the X-rays (in neutron diffraction it is the nuclei). The diffraction pattern consists of spots of different intensities, arising from the scattering of waves. Each spot arises from a set of crystal planes of Miller Index $h,k,l$. The intensity $I(hkl)$ of each spot can be measured and is related to the amplitude $F(hkl)$ by

$$I(hkl) \propto |F(hkl)|^2$$

It can be seen from this that from the intensity measurements of the scattered waves we only know the wave amplitudes, not the phase relationships between the waves. The electron density at any point $x,y,z$ in space is given by the formula
\[ \rho(x, y, z) \propto \sum_{hkl} F(hkl) \cos \left[ 2\pi (hx + ky + lz) + \phi_{hkl} \right] \]

where \( \phi_{hkl} \) is the phase angle.

To obtain a map of the density representing the contents of the unit cell in a crystal structure it is necessary to add together all of the waves described by structure amplitudes \( |F(hkl)| \) together with their phases \( \phi_{hkl} \). As a simple example consider the Fig 1 where we sketch the effect of adding four plane waves together all with phase angle \( \phi_{hkl} = 0^\circ \):

![Diagram showing the addition of plane waves](image)

Fig 1. Example of addition of planes waves in Fourier synthesis of electron density
In Fig 1(a) the plane wave for the 100 reflection is sketched. In this case the peaks lie on the (100) planes with the troughs halfway between. The amplitude $|F(hkl)|$ is a measure of the height of this wave, represented by the amount of shading. In (b) the plane wave for the 010 reflection has been added, in (c) the wave corresponding to the 110 reflection, and finally in (d) the wave for the 110 reflection. It can be seen that just with these four reflections it is already apparent that density is being built up on the corners of the unit cell with a weaker component at the centre of the unit cell. In (e) the phases for the 110 and 110 reflections have been changed by 180°. By shifting the maxima of these two waves density is now seen to form halfway along the unit cell axes, with little density at the centre of the unit cell, a completely different structure from before.

In Fig 2 is sketched what might be the result of summing the Fourier series over a very large number of hkl reflections starting from Fig. 1(d) and (e). The effect is to concentrate the density into the atomic positions with little or no observable density between. We end up with something resembling a photograph of the atoms in the structure. The main difference obtained between the two structures shows that it is the phases that are crucial for correct structure determination, rather than simply the structure amplitudes.

Before the advent of computers, various clever photographic techniques were invented to perform Fourier syntheses in this way. The author is sufficiently advanced in years to have used one called the "von Eller photosommateur" during his graduate studies (Fig 3).
Fig 3  Schematic diagram of von Eller photosommateur.

This consisted of a cylindrical light-tight can. At one end a lamp illuminated a glass mask on which were a set of cosinusoidal fringes. The light then passed on to a photographic plate outside the can to which was taped a scale drawing of the reciprocal lattice. By rotating the photographic plate (and reciprocal lattice) at the same time by winding a cursor up and down it was possible to position the cursor directly onto a reciprocal lattice point. This had the effect of orienting the image of the cosine mask with the relevant planes. At the same time the mask moved forwards or backwards thus changing the fringe spacing on the photographic plate. Left and right movements of the mask enabled the correct phase to be set up. The light was then exposed for a number of seconds proportional to the structure amplitude for the relevant reflection, and the whole process repeated for the next reciprocal lattice point. The result was effectively a photograph of the crystal structure. Fig 4 shows the result of this technique from a publication on the crystal structure of N-oxyphenazine. Although one would not dream of using such a method today, it was nevertheless a wonderfully fun way to learn about Fourier syntheses.
Before the general use of computers became standard, prior to the mid 1960’s, many different and cunning techniques like this were devised in order to locate the atomic positions from the data, even though the intensities of the reflections were often simply estimated by eye on an arbitrary scale!

For instance, in the early days of crystal structure determination, Kathleen Lonsdale (née Yardley), a student of W.H. Bragg (Fig 5), solved the structure of a crystal of hexamethyl benzene with little more than a mechanical calculator, thus proving for the first time that aromatic carbon rings were flat. Some year later, as an aid to adding together all the sine and cosine terms for Fourier synthesis Charles Beevers and Henry Lipson produced boxes of paper strips on which the trigonometric terms were printed and boxes of the Beevers-Lipson strips were exported around the world. The strips did help to simplify the process of obtaining Fourier maps but it was still tedious. I recall myself trying this out on hexamethyl benzene and it took over a week to get an acceptable projection of the structure. With the advent of computers all that changed. In the Figure is one of the early computers that were used. The Ferranti-Pegasus Mark II computer was one that I used as a graduate student. It had 16K of store on a magnetic drum, consisted of two huge units (designed by Rolls-Royce!) and read 5-hole paper tape. This very computer has recently been restored and can now be seen in working condition in the computer gallery of the Science Museum in London.
as the only working example of a valve computer. With such machines one could obtain more precise and detailed Fourier maps, such as is shown in Fig 6.

Today, with modern computers and new methods of collecting data, it is commonplace to determine crystal structures routinely with literally hundreds or even thousands of atoms in the unit cell. To do this of course, one has first of all to deal with the phase problem. Many techniques for doing this have been developed over the last decades.

Fig 5  Top left: Dame Kathleen Lonsdale; top right: hexamethyl benzene; bottom left: Beevers-Lipson strips (this is in fact one of the prototype boxes, currently at the Clarendon Laboratory, Oxford; bottom right: Ferranti Pegasus Mark II 'modern' computer.
Open a file containing structure factors and phases. The file should consist of

1st Line: Text e.g. name of compound
2nd line unit cell parameters a b c alpha beta gamma
All following lines

h  k  l  F(hkl)  \(\phi_{hkl}\)

As the file is read in the plane waves are added to the two windows. Clicking on Enter halts the reading, which can be continued by a further Enter key.

Interrupt (Ctrl+I)

Interrupt the process.

Clear (Ctrl+Z)

Clear the two charts.
Set Printer
Set up the printer.

Print (Ctrl+P)
Send the right-hand chart to the printer.

Exit (Ctrl+X)

Single Reflections
Here you can enter individual reflections one by one and manually build up a Fourier summation. Note that only orthogonal axes are assumed and since only h and k can be entered the Fourier map is built from hk0 reflections to form a c-axis projection.
The Parameters dialog box allows various quantities to be set.

**Resolution**

The number of x,y terms in the Fourier map. The lower the number the faster the program runs, but decreases the resolution of the map. The maximum is 200.

**A Axis  B Axis C Axis**

The axis of projection can be selected here.

**A Repeat  B Repeat C Repeat**

Specify the number of unit cells (can be less than 1) in the projection.

**Scale Width, Height**

Change the dimensions of the right-hand window.
**Patterson, Random Phases, Constant F’s**
Choose between different modes. Patterson creates a Patterson map in which the squares of the structure factors are used and all phases set to 0. Clicking on Random phases demonstrates the map obtained when the phases are randomized. Constant F’s show what happens when all structure factors are set to be the same. These demonstrations show nicely that the most important quantities needed to obtain a successful Fourier map are the phases, rather than the structure factors.

**Palettes**
Choose between different palettes. Grayscale is the default

**Contours**
Either show no contours, add contours to palette, only contours (but no palette).

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**Examples**
Choice of example files. The examples are

- **Cubane**
- **Hexamethyl benzene**
- **Naphthalene**
- **Perovskite**
- **Potassium benzoyl penicillin**
- **Sodium lithium sulfate**
- **Urea**
- **Zinc sulfide**

**The first structure by Kathleen Lonsdale**
**Best projection is b-axis**
**Dorothy Hodgkin’s 1945 structure of penicillin**

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**Help**

**Guide**
Opens this help file
Investigating Single Reflections

Click on the menu item Single Reflections. Enter integer values of h and k indices, structure factors and phases. For example $h = 1$, $k = -2$, $F = 50$, phase = 45.

Now input $h = 3$, $k = 3$, $F = 15$, phase = 0

In the Parameters dialog box choose Rainbow.
**Complete projection maps**

From the `File (Ctrl F)` menu select a file. For example we shall choose the file `Penicillin.txt`. This contains the structure factors for Dorothy Hodgkin’s potassium benzoyl penicillin structure. The Fourier map that she obtained is on exhibit in the Oxford Museum of History of Science.
This shows a set of Perspex sheets on which sections of a 3-dimensional Fourier synthesis was plotted. We shall simulate this map as seen on projection through the set of sheets.

Below is a plot of the projection with potassium (pink), sulphur (yellow) and nitrogen (blue).
The file Penicillin contains a text header followed by a list of \( h k l \) \( F(hkl) \) and Phase. The program automatically reads the file and in real time build up the final map. The process can be interrupted at any time by CTRL-I.

In order to obtain the relevant Fourier projection, in the Parameters dialog box select the following:

- **B-Axis**
- 0.5 \( C \) Repeat
- 1.62 Scale Width

Now select the file Penicillin.txt. The final result looks like this
Superimposing the structure we can see the fit:
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Using the Rainbow palette:
Include contours and palette