

# Patterson syntheses for structure determination

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## 8.1 Introduction: the Patterson synthesis

$|F_o|$  with correct phases  $\rightarrow$  electron density

$$\rho(xyz) = \frac{1}{V} \sum_{h,k,l} |F(hkl)| \cdot \exp[i\phi(hkl)] \cdot \exp[-2\pi i(hx + ky + lz)]$$

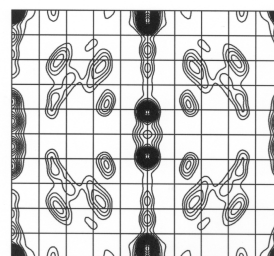
*but we don't know the phases! What can we do?*

$F_o^2$  with all phases = 0  $\rightarrow$  Patterson synthesis

$$P(uvw) = \frac{1}{V} \sum_{h,k,l} |F_o(hkl)|^2 \cdot \cos[2\pi(hu + kv + lw)]$$

All required information is known, so this can be done.

What is the result? Not the electron density (one reason for using different symbols for the coordinates), but something related to it.



A Patterson map looks rather like an electron density map, with peaks of positive density in various positions.

## 8.2 What the Patterson synthesis means

Fourier synthesis peaks correspond to atomic positions  
(relative to the unit cell origin)

Patterson synthesis peaks correspond to vectors between  
pairs of atoms (atoms relative to each other)

For every pair of atoms at  $(x_1, y_1, z_1)$  and  $(x_2, y_2, z_2)$ , there is a  
peak in the Patterson map at

$$(x_1 - x_2, y_1 - y_2, z_1 - z_2)$$

and another of the same size at

$$(x_2 - x_1, y_2 - y_1, z_2 - z_1)$$

### Alternative view:

For every peak in the Patterson map, e.g. at  $(u, v, w)$ , there must be two atoms in the structure whose  $x$  coordinates differ by  $u$ , whose  $y$  coordinates differ by  $v$ , and whose  $z$  coordinates differ by  $w$ .

The Patterson map is a weighted sum of  $N$  copies of the electron density, with each of the unit cell's  $N$  atoms placed in turn at the origin (weight = atomic number)

Patterson peaks show where atoms lie **relative to each other**, not where they lie **relative to the unit cell origin** (which is what we really want to know). But at least this is a start...

How can we extract the true atomic positions from a knowledge of vectors between them?

In an electron density map, the size of peaks is proportional to atomic numbers (number of electrons in each atom) [ignoring effects of atomic vibration].

In a Patterson map, the size of peaks is proportional to the product of the atomic numbers of the two atoms concerned.

Patterson peaks are similar in shape to electron density peaks, but about twice as broad.

These, and the definition of the Patterson synthesis, lead to the following important properties of a Patterson map.

1. For  $N$  atoms in the unit cell, there are  $N^2$  pairs; every atom makes a vector to every atom (including itself).  $N$  of these vectors have zero length and lie at (0,0,0), which is always the largest peak.
2. A Patterson map is always centrosymmetric, because every pair of atoms gives two equal and opposite vectors,  $A \rightarrow B$  and  $A \leftarrow B$ . In fact, the symmetry of the Patterson map is the same as the symmetry of the diffraction pattern.

All glide planes give mirror planes in the Patterson.  
All screw axes give pure rotation axes in the Patterson.  
So only 24 Patterson space groups are possible  
(combination of 11 Laue groups with appropriate unit cell centring in each crystal system)

3. Patterson peaks are similar to electron density peaks, but about twice as broad. Many peaks overlap and are not resolved, so there tend to be large featureless regions.
4. Vectors between pairs of heavy atoms give large peaks, which stand out above the rest of the map. For a structure containing a few heavy atoms among lots of light atoms, there will be a small number of large Patterson peaks due to the heavy atoms.
5. Vectors between pairs of symmetry-equivalent peaks may give peaks with special values of coordinates, depending on the space group.

Example: for bis(benzene)chromium,  $[\text{Cr}(\text{C}_6\text{H}_6)_2]$

Relative heights of peaks for vectors:

Cr—Cr	$24 \times 24 = 576$
Cr—C	$24 \times 6 = 144$
C—C	$6 \times 6 = 36$

(even smaller for vectors involving H)

Ratio of these is 16:4:1

So the few Cr—Cr peaks (arising from several molecules in the unit cell) stand out clearly from all others and are easily identified.

### 8.3 Finding heavy atoms from a Patterson map

Solving a Patterson map for a structure with a small number of heavy atoms is like doing a crossword puzzle or a mathematical brain-teaser.

The aim is to find the heavy atoms (in many cases, just one heavy atom in the asymmetric unit). These can then be used as a model structure from which approximate phases can be calculated for Fourier syntheses to develop the model further.

Here are some examples and recipes for common space groups. Similar methods apply to other space groups.

#### One heavy atom in the asymmetric unit of $P\bar{1}$

$P\bar{1}$	$x, y, z$	$-x, -y, -z$
$x, y, z$	0, 0, 0	$-2x, -2y, -2z$
$-x, -y, -z$	$2x, 2y, 2z$	0, 0, 0

2 atoms give 4 vectors

e.g.  $2x = 0.4 \Rightarrow x = 0.2$

but  $-2x = 0.4 \Rightarrow x = -0.2$

both are equally correct!

These are not the only possible solutions...

$$2x = 0.4 \Rightarrow x = 0.2$$

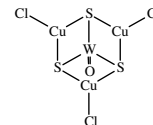
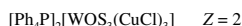
$$\text{but } 2x = 1.4 \Rightarrow x = 0.7$$

both are equally correct!

$\frac{1}{2}$  can be added to or subtracted from any coordinate, corresponding to choice of a different possible unit cell origin.

There are 16 possible solutions, all equally correct. This ambiguity is unimportant if there is only one heavy atom to be found, but it matters if there is more than one; see later!

Example



Peak number	x	y	z	Peak height	Vector length (Å)
1	0.000	0.000	0.000	999	0.00
2	0.532	0.851	0.369	272	9.12
3-8				~190	~2.60 (3) and 3 longer ones
9-11				~118	~2.25

Peak 2 is probably the W...W vector, since it is the largest non-origin peak.

From it, the position of the unique W atom is easily obtained, by dividing all 3 coordinates by 2:

W at 0.266, 0.426, 0.185

### One heavy atom in the asymmetric unit of $P2_1/c$

$P2_1/c$	x, y, z	-x, -y, -z	x, $\frac{1}{2}-y$ , $\frac{1}{2}+z$	-x, $\frac{1}{2}+y$ , $\frac{1}{2}-z$
x, y, z	0, 0, 0	-2x, -2y, -2z	0, $\frac{1}{2}-2y$ , $\frac{1}{2}$	-2x, $\frac{1}{2}$ , $\frac{1}{2}-2z$
-x, -y, -z	2x, 2y, 2z	0, 0, 0	2x, $\frac{1}{2}$ , $\frac{1}{2}+2z$	0, $\frac{1}{2}+2y$ , $\frac{1}{2}$
x, $\frac{1}{2}-y$ , $\frac{1}{2}+z$	0, $\frac{1}{2}+2y$ , $\frac{1}{2}$	-2x, $\frac{1}{2}$ , $\frac{1}{2}-2z$	0, 0, 0	-2x, 2y, -2z
-x, $\frac{1}{2}+y$ , $\frac{1}{2}-z$	2x, $\frac{1}{2}$ , $\frac{1}{2}+2z$	0, $\frac{1}{2}-2y$ , $\frac{1}{2}$	2x, -2y, 2z	0, 0, 0

4 atoms give 16 vectors

4 coincide at (0,0,0)

$2 \times 2$  coincide at related (0,v, $\frac{1}{2}$ ) positions

$2 \times 2$  coincide at related (u, $\frac{1}{2}$ ,w) positions

4 lie at related general (u,v,w) positions

Origin peak (very large)

2 Harker line peaks (double weight)

2 Harker plane peaks (double weight)

4 general peaks (single weight)

$P2_1/c$	x, y, z	-x, -y, -z	x, $\frac{1}{2}-y$ , $\frac{1}{2}+z$	-x, $\frac{1}{2}+y$ , $\frac{1}{2}-z$
x, y, z	0, 0, 0	-2x, -2y, -2z	0, $\frac{1}{2}-2y$ , $\frac{1}{2}$	-2x, $\frac{1}{2}$ , $\frac{1}{2}-2z$
-x, -y, -z	2x, 2y, 2z	0, 0, 0	2x, $\frac{1}{2}$ , $\frac{1}{2}+2z$	0, $\frac{1}{2}+2y$ , $\frac{1}{2}$
x, $\frac{1}{2}-y$ , $\frac{1}{2}+z$	0, $\frac{1}{2}+2y$ , $\frac{1}{2}$	-2x, $\frac{1}{2}$ , $\frac{1}{2}-2z$	0, 0, 0	-2x, 2y, -2z
-x, $\frac{1}{2}+y$ , $\frac{1}{2}-z$	2x, $\frac{1}{2}$ , $\frac{1}{2}+2z$	0, $\frac{1}{2}-2y$ , $\frac{1}{2}$	2x, -2y, 2z	0, 0, 0

All columns and all rows are equivalent by symmetry  
(Patterson space group  $P2_1/m$ )

Match the predictions from one column/row with the observed Patterson peak positions.

Obtain x and z from a Harker plane peak

Obtain y from a Harker line peak

Confirm x,y,z from (the largest?) general peak

Don't forget the  $\pm\frac{1}{2}$  ambiguity!

### One heavy atom in the asymmetric unit of $P2_12_12_1$

$P2_12_12_1$	x, y, z	$\frac{1}{2}+x$ , $\frac{1}{2}-y$ , -z	$\frac{1}{2}-x$ , -y, $\frac{1}{2}+z$	-x, $\frac{1}{2}+y$ , $\frac{1}{2}-z$
x, y, z	0, 0, 0	$\frac{1}{2}$ , $\frac{1}{2}-2y$ , -2z	$\frac{1}{2}-2x$ , -2y, $\frac{1}{2}$	-2x, $\frac{1}{2}$ , $\frac{1}{2}-2z$
$\frac{1}{2}+x$ , $\frac{1}{2}-y$ , -z	$\frac{1}{2}$ , $\frac{1}{2}+2y$ , 2z	0, 0, 0	-2x, $\frac{1}{2}$ , $\frac{1}{2}+2z$	$\frac{1}{2}-2x$ , 2y, $\frac{1}{2}$
$\frac{1}{2}-x$ , -y, $\frac{1}{2}+z$	$\frac{1}{2}+2x$ , 2y, $\frac{1}{2}$	2x, $\frac{1}{2}$ , $\frac{1}{2}-2z$	0, 0, 0	$\frac{1}{2}$ , $\frac{1}{2}+2y$ , -2z
-x, $\frac{1}{2}+y$ , $\frac{1}{2}-z$	2x, $\frac{1}{2}$ , $\frac{1}{2}+2z$	$\frac{1}{2}+2x$ , -2y, $\frac{1}{2}$	$\frac{1}{2}$ , $\frac{1}{2}-2y$ , 2z	0, 0, 0

4 atoms give 16 vectors

Patterson space group  $Pmmm$

4 contribute to the origin peak

All others are in Harker planes, single weight  
(4 equivalents of each; 3 unique peaks)

$\frac{1}{2}, v, w$	gives y and z
$u, \frac{1}{2}, w$	gives x and z
$u, v, \frac{1}{2}$	gives x and y
then check for consistency	

Example  $[\text{Rh}(\text{Ph}_2\text{PCH}_2\text{PPh}_2)(\text{C}_{12}\text{H}_8\text{BO}_4)]$

Peak number	x	y	z	Peak height	Vector length (Å)
1	0.000	0.000	0.000	999	0.00
2	0.500	0.788	0.800	173	8.21
3	0.094	0.500	0.300	169	9.38
4	0.594	0.288	0.500	158	11.29

From peak 2:  $y = 0.144$   $z = 0.400$

From peak 3:  $x = 0.047$   $z = -0.100$

From peak 4:  $x = 0.047$   $y = 0.144$

x and y agree OK. What about z? Peak 3 at 0.094, 0.500, 0.300 can also be considered as 0.094, 0.500, 1.300 (the same in the next unit cell), from which the calculation now gives  $z = 0.400$ . In cases like this (where a coordinate is obtained by dividing by 2),  $\frac{1}{2}$  can always be added to or subtracted from the answer and this gives an equally valid result; it just corresponds to choosing a different allowed unit cell origin.

So we have found the Rh atom at 0.047, 0.144, 0.400 (or one of several other possible, equally good answers).

### One heavy atom in the asymmetric unit of $Pbca$

8 atoms give 64 vectors !

$P2_12_12_1$  plus an inversion centre (automatically produces the glide planes also)

First column of table

$Pbca$	$x, y, z$
$x, y, z$	0, 0, 0
$\frac{1}{2}+x, \frac{1}{2}-y, -z$	$\frac{1}{2}, \frac{1}{2}+2y, 2z$
$\frac{1}{2}-x, -y, \frac{1}{2}+z$	$\frac{1}{2}+2x, 2y, \frac{1}{2}$
$-x, \frac{1}{2}+y, \frac{1}{2}-z$	$2x, \frac{1}{2}, \frac{1}{2}+2z$
$-x, -y, -z$	$2x, 2y, 2z$
$\frac{1}{2}-x, \frac{1}{2}+y, z$	$\frac{1}{2}+2x, \frac{1}{2}, 0$
$\frac{1}{2}+x, y, \frac{1}{2}-z$	$\frac{1}{2}, 0, \frac{1}{2}+2z$
$x, \frac{1}{2}-y, \frac{1}{2}+z$	$0, \frac{1}{2}+2y, \frac{1}{2}$

Origin peak  
6 Harker line peaks (2 on each of 3 lines), weight 4  
12 Harker plane peaks ( $4 \times 3$  sections), weight 2  
8 general peaks (all symmetry equivalent)

Each Harker line peak (3 of these) gives one coordinate  
Each Harker plane peak (3) gives two coordinates  
The general peak confirms all three coordinates

### One heavy atom in the asymmetric unit of $P2_1$

$P2_1$	$x, y, z$	$-x, \frac{1}{2}+y, -z$
$x, y, z$	0, 0, 0	$-2x, \frac{1}{2}, -2z$
$-x, \frac{1}{2}+y, -z$	$2x, \frac{1}{2}, 2z$	0, 0, 0

2 atoms give 4 vectors

Origin peak

2 equivalent peaks in the Harker plane ( $u, \frac{1}{2}, w$ ) — give  $x$  and  $z$

No information on  $y$ , because none is needed!

**Polar space group:**  $y$  origin is arbitrary

### Two heavy atoms in the asymmetric unit of $P\bar{1}$

Atoms at  $\pm(x, y, z)$  and  $\pm(X, Y, Z)$

4 atoms give 16 vectors

Let  $\Sigma x = x + X$  and  $\Delta x = x - X$  etc.

	$x, y, z$	$-x, -y, -z$	$X, Y, Z$	$-X, -Y, -Z$
$x, y, z$	0, 0, 0	$-2x, -2y, -2z$	$-\Delta x, -\Delta y, -\Delta z$	$-\Sigma x, -\Sigma y, -\Sigma z$
$-x, -y, -z$	$2x, 2y, 2z$	0, 0, 0	$\Sigma x, \Sigma y, \Sigma z$	$\Delta x, \Delta y, \Delta z$
$X, Y, Z$	$\Delta x, \Delta y, \Delta z$	$-\Sigma x, -\Sigma y, -\Sigma z$	0, 0, 0	$-2X, -2Y, -2Z$
$-X, -Y, -Z$	$\Sigma x, \Sigma y, \Sigma z$	$-\Delta x, -\Delta y, -\Delta z$	$2X, 2Y, 2Z$	0, 0, 0

Origin peak

Single weight peaks for vectors between symmetry-equivalent atoms

Double weight peaks for vectors between inequivalent atoms (cross-vectors)

Similar approach in other space groups;  
when Harker sections/lines are present, it is easier.

### Other aspects of heavy-atom Patterson syntheses

General peaks may fortuitously lie on Harker planes or Harker lines, leading to ambiguity: two heavy atom solutions are possible, both consistent with the Patterson, but only one is correct.

— caused by values of atom coordinates close to 0,  $\frac{1}{4}$ ,  $\frac{1}{2}$ , etc. This is not an uncommon occurrence for coordination complexes.

One heavy atom in  $P2_1$  gives a model structure with too much symmetry ( $P2_1/m$ ) and problems in deriving phases for structure expansion; similar problems can occur in other space groups.

Heavy atoms in special positions give fewer vectors than those in general positions; different vector tables are needed. Example of  $P2_1/c$  with  $Z = 4$ : one unique atom in a general position, or two lying on inversion centres? In the second case, all heavy-atom vectors have coordinates of 0 and  $\frac{1}{2}$  in the Patterson.

Harker peaks can help to distinguish between alternative space groups with the same (or indistinct) systematic absences; a different use of Pattersons.

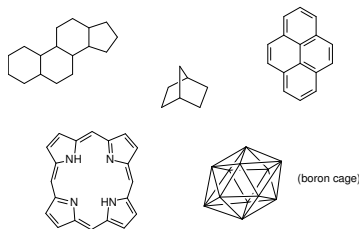
Automatic programs for Patterson map interpretation are not infallible!

### 8.4 Patterson search methods

A completely different use of Patterson syntheses, not requiring heavy atoms.

Match the expected pattern of vectors for a known structural fragment with the observed Patterson synthesis.

The fragment must have known or predictable geometry.



### Two stages are involved in most cases.

#### 1. Rotation search

Find the orientation of the fragment by matching its internal vector pattern with peaks relatively close to the Patterson map origin (short vectors, mainly intramolecular).

Systematic search over all possible different orientations (not a complete sphere search, and the extent of the search depends on the crystal system and on the molecular fragment symmetry).

For each orientation, examine the values of the Patterson function at the ends of all the model vectors and compare with what is expected. Look for the best match(es).

## 2. Translation search

(Not necessary for space group  $P1$  !)

Find the positions of the oriented fragments relative to the symmetry elements of the space group.

Systematic search over all possible positions (space-group dependent) for the oriented fragment.

Generate intermolecular vectors for symmetry-equivalent fragments, and compare with observed Patterson peaks.

(Most Patterson search programs actually do something more sophisticated than this, but the principle is the same.)

If the search fragment represents a significant proportion of the total electron density of the asymmetric unit, the result is a reasonable model structure for further development.