

6. Patterson

Patterson definition

Measured diffracted intensities, with appropriate experimental corrections, allows determination of the squared magnitudes of the structure factors $|F_H|^2$. Assume the unit-cell dimensions are known, one could then use those as the coefficients in a Fourier series. The resulting function is called the Patterson:

$$P(\mathbf{r}) = \frac{1}{v} \sum_H |F_H|^2 \cdot e^{-2\pi i \mathbf{r}_H^* \cdot \mathbf{r}}$$

We hope to extract information from the patterson about the electron density, given by:

$$\rho(\mathbf{r}) = \frac{1}{v} \sum_H F_H \cdot e^{-2\pi i \mathbf{r}_H^* \cdot \mathbf{r}}$$

We notice that

$$P(\mathbf{r}) = \frac{1}{v} \sum_{H,H'} F_{H'}^* \cdot F_H \cdot e^{-2\pi i \mathbf{r}_H^* \cdot \mathbf{r}} \cdot \Delta_{\mathbf{r}_H^* - \mathbf{r}_{H'}^*}$$

where

$$\Delta_{\mathbf{r}_H^* - \mathbf{r}_{H'}^*} = \lim_{V \rightarrow \infty} \frac{1}{V} \int_{\mathbf{r} \in V} d^3 r \cdot e^{-2\pi i (\mathbf{r}_H^* - \mathbf{r}_{H'}^*) \cdot \mathbf{r}}$$

Now

$$P(\mathbf{r}) = \lim_{N \rightarrow \infty} \frac{1}{N} \int_{\mathbf{r}' \in Nv} d^3 r' \left(\frac{1}{v} \sum_H F_H \cdot e^{-2\pi i \mathbf{r}_H^* \cdot \mathbf{r}'} \right) \cdot \left(\frac{1}{v} \sum_{H'} F_{H'} \cdot e^{-2\pi i \mathbf{r}_{H'}^* \cdot (\mathbf{r} - \mathbf{r}')} \right)$$

This can be written

$$\begin{aligned} P(\mathbf{r}) &= \lim_{N \rightarrow \infty} \frac{1}{N} \int_{\mathbf{r}' \in Nv} d^3 r' \cdot \rho(\mathbf{r}') \cdot \rho[-(\mathbf{r} - \mathbf{r}')] \\ &= \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{n=1}^N \int_{\mathbf{r}' \in Nv} d^3 r' \cdot \rho_m(\mathbf{r}' - \mathbf{r}_n) \cdot \rho[-(\mathbf{r} - \mathbf{r}')] \\ &= \lim_{V \rightarrow \infty} \int_{\mathbf{r}'} d^3 r' \cdot \rho_m(\mathbf{r}') \cdot \rho[-(\mathbf{r} - \mathbf{r}')] \end{aligned}$$

$$P(\mathbf{r}) = \rho_m(\mathbf{r}) * \rho(-\mathbf{r})$$

We can identify the integral as a convolution of $\rho_m(\mathbf{r})$ with the inverted electron density $\rho(-\mathbf{r})$. This is sometimes written as

$$P(\mathbf{r}) = \rho(\mathbf{r}) * \rho(-\mathbf{r})$$

with the understanding that each point in the unit cell is paired with every other point in the unit cell.

Patterson interpretation

The derivation above did not invoke the atomic nature of matter, but the interpretation of the patterson is more clear if we think of isolated, point-like atoms within a relatively large unit cell. Let's describe the

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unit cell by a discrete collection of atoms. Say the electronic density of atom j is described by delta functions with weight Z_j . For one unit cell

$$\rho_m(\mathbf{r}) = \sum_j \rho_j(\mathbf{r} - \mathbf{r}_j) = \sum_j Z_j \cdot \delta(\mathbf{r} - \mathbf{r}_j)$$

The electron density in all space is

$$\rho(\mathbf{r}) = \sum_n \rho_m(\mathbf{r} - \mathbf{r}_n) = \sum_j Z_j \cdot \delta(\mathbf{r} - \mathbf{r}_j - \mathbf{r}_n)$$

Then we have

$$\begin{aligned} P(\mathbf{r}) &= \rho_m(\mathbf{r}) * \rho(-\mathbf{r}) = \int_{r'} d^3 r' \cdot \rho_m(-\mathbf{r}') \cdot \rho(\mathbf{r} - \mathbf{r}') \\ &= \sum_n \int_{r'} d^3 r' \cdot \rho_m(-\mathbf{r}') \cdot \rho(\mathbf{r} - \mathbf{r}' - \mathbf{r}_n) \\ &= \sum_n \int_{r'} d^3 r' \cdot \left[\sum_j Z_j \cdot \delta(-\mathbf{r}' - \mathbf{r}_j) \right] \cdot \left\{ \sum_{j'} Z_{j'} \cdot \delta[(\mathbf{r} - \mathbf{r}') - \mathbf{r}_{j'} - \mathbf{r}_n] \right\} \\ &= \sum_n \sum_{j,j'} Z_j \cdot Z_{j'} \cdot \int_{r'} d^3 r' \cdot \delta(\mathbf{r}' - \mathbf{r}_j) \cdot \delta[(\mathbf{r} + \mathbf{r}') - \mathbf{r}_{j'} - \mathbf{r}_n] \\ P(\mathbf{r}) &= \sum_n \sum_{j,j'} Z_j \cdot Z_{j'} \cdot \delta[\mathbf{r} - (\mathbf{r}_{j'} - \mathbf{r}_j) - \mathbf{r}_n] \end{aligned}$$

We see that the patterson is a set of delta functions at positions given by the differences $\mathbf{r}_j - \mathbf{r}_{j'}$ between each pair of atoms in the unit cell, with weights of $Z_j \cdot Z_{j'}$. We can also write this in the form

$$P(\mathbf{r}) = \sum_n \sum_j Z_j \cdot \rho(\mathbf{r} + \mathbf{r}_j - \mathbf{r}_n)$$

Since the patterson is periodic, we really only need to evaluate it within a single unit cell.

$$P_m(\mathbf{r}) = \sum_j Z_j \cdot \rho(\mathbf{r} + \mathbf{r}_j)$$

which is

$$P_m(\mathbf{r}) = \sum_{j,j'} Z_j \cdot Z_{j'} \cdot \delta[\mathbf{r} - (\mathbf{r}_j - \mathbf{r}_{j'})]$$

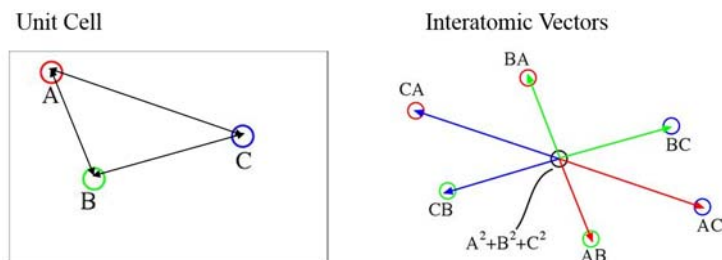
However, these expressions require translation of the vectors $\mathbf{r}_j - \mathbf{r}_{j'}$ that point outside of the unit cell back into the unit cell.

The patterson can be generated by superposing the charge density once for each atom in the unit cell, shifing by the atom location \mathbf{r}_j and weight by its atomic number Z_j .

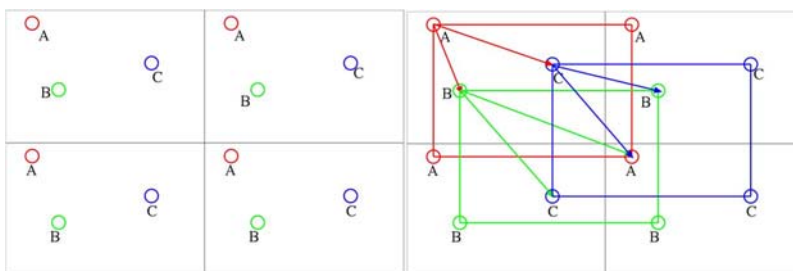
If there are N atoms in the unit cell, the Patterson would contain N^2 peaks. However, N of these arise from each atom paired with itself, which always occurs at $\mathbf{r} = \mathbf{0}$. So we should subtract off N and add 1. Thus, there are in general $N^2 - N + 1$ peaks in the patterson unit cell. The distribution gets increasingly crowded at a rate $O(N^2)$. On the other hand, the individual peaks get sharper, assuming a normal distribution of electron density in each atom.

2-D example

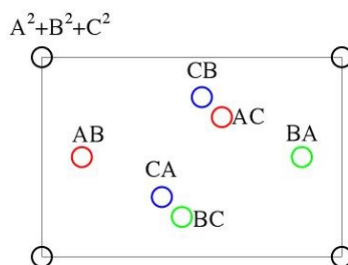
Consider a 2-D unit cell with three atoms - A, B, and C - where the labels also represent the atomic numbers Z_j . We find the vector \mathbf{r}_{ij} connecting each pair of atoms. We label the point $0 + \mathbf{r}_{ij}$ by its weight, given by the product $Z_j Z_{j'}$. The origin contains the sum of each atoms paired with itself $\sum_j Z_j^2$. Translation will replicate these points within the unit cell.



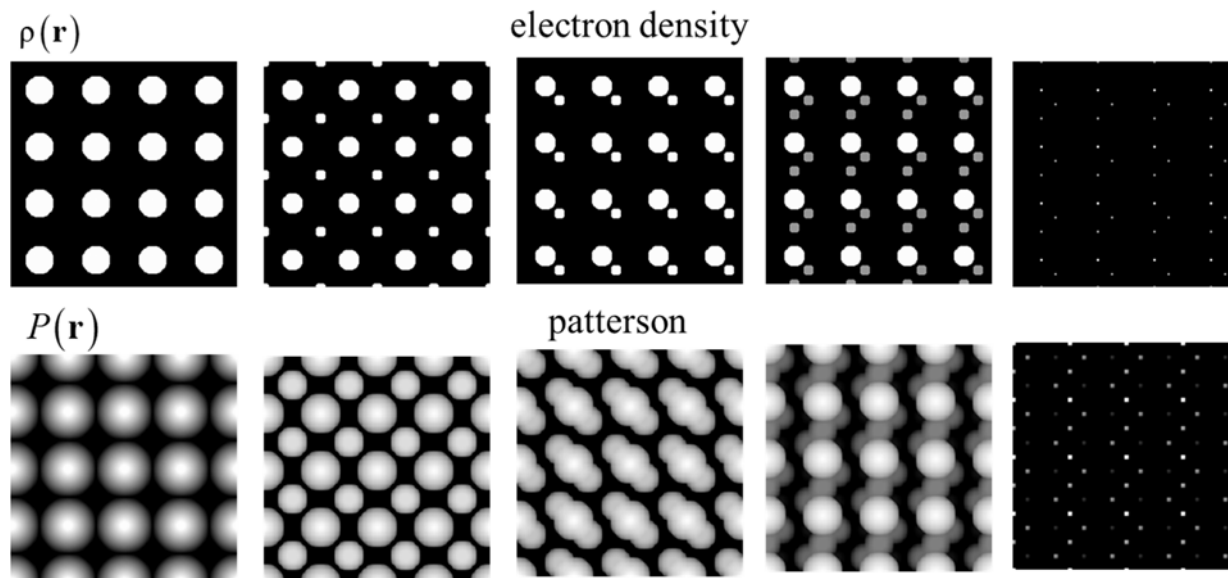
The origin of the vectors may be more obvious when consider adjacent unit cells. If a vector pointing from the origin terminates outside the unit cell, translation vectors should be added to it to bring it back within the cell. In the example below, the point AB has the same weight as BA, but falls in a different position within the unit cell of the patterson.



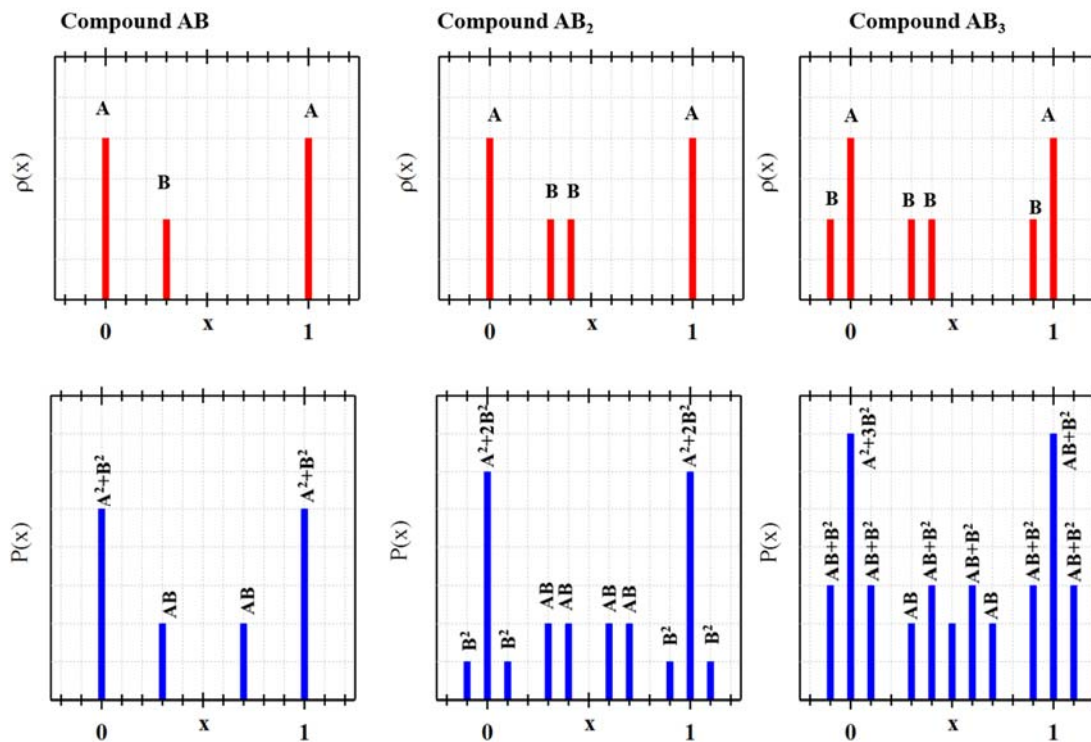
The unit cell of the patterson has the same dimensions as that of the crystal, but always contain an inversion center.



Some computed examples are shown below:



It is seldom possible to determine completely a crystal structure based on the patterson without building on additional information. Suppose we have a 1-D crystal with point-like atoms. We know the structure of compound AB. It has the larger atom A at the origin ($x_A = 0.0$) and an atom B_1 at $x_{B_1} = 0.3$. We observe that $A = 2B$, so $A^2 = 4B^2$ and $AB = 2B^2$. Its patterson will have a peak of height $A^2 + B^2$ at $x = 0.0$. We have $|x_{B_1} - x_A| = 0.3$, so peaks of height $AB = 2B^2$ are present at $x = 0.3$ and $x = -0.3 + 1.0 = 0.7$. We can label these peaks accordingly.



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It is useful to tabulate this information, as shown below:

Compound AB

Peaks	Height	Notes	Positions
$x = 0.0$	$5B^2 = A^2 + B^2$		$x_A = 0.0$
$x = 0.3$	$2B^2 = AB$		$x_{B_1} = 0.3$

Now the material is modified to incorporate a second B atom in the unit cell. Based on other information, we expect the positions of A and B_1 to remain unchanged. We do diffraction experiments and evaluate the patterson. Is the patterson sufficient determine the location x_{B_2} of atom B_2 ?

Compound AB₂

Peaks	Height	Notes	Positions
$x = 0.0$	$6B^2 = A^2 + 2B^2$	expected	$x_A = 0.0$
$x = 0.1$	B^2	must be a B-B	$x_{B_1} = 0.3$
$x = 0.3$	$2B^2 = AB$	unchanged	$x_{B_2} = 0.4$
$x = 0.4$	$2B^2 = AB$	new, must be an A-B	

We can see that $|x_{B_2} - x_A| = 0.4$, so either $x_{B_2} = 0.4$ or $x_{B_2} = 0.6$. We also see that $|x_{B_2} - x_{B_1}| = 0.1$, in which case either $x_{B_2} = 0.2$ or $x_{B_2} = 0.4$. The only way both conditions are satisfied is if $x_{B_2} = 0.4$. We can then identify the peak at $x = 0.4$ as an AB.

A third atom - B_3 - is now added, with the other coordinates remaining unchanged. The resulting table is shown below:

Compound AB₃

Peaks	Height	Notes	Positions
$x = 0.0$	$7B^2 = A^2 + 3B^2$	expected	$x_A = 0.0$
$x = 0.1$	$3B^2 = AB + B^2$	changed	$x_{B_1} = 0.3$
$x = 0.3$	$2B^2 = AB$	unchanged	$x_{B_2} = 0.4$
$x = 0.4$	$3B^2 = AB + B^2$	increased by a B-B	$x_{B_3} = 0.9$
$x = 0.5$	$2B^2$	new, double peak, must be B-B	

We see that the peak at $x = 0.1$ was increased by AB, so $|x_{B_3} - x_A| = 0.1$. Then either $x_{B_3} = 0.1$ or $x_{B_3} = 0.9$. We then have two possibilities to consider: If $|x_{B_3} - x_{B_1}| = 0.4$ and $|x_{B_3} - x_{B_2}| = 0.5$, then we can have $x_{B_3} = 0.9$. But if $|x_{B_3} - x_{B_1}| = 0.5$ and $|x_{B_3} - x_{B_2}| = 0.4$, we cannot have either $x_{B_3} = 0.1$ or $x_{B_3} = 0.9$. So the correct assignment is $x_{B_3} = 0.9$.

Harker lines and sections

In real crystals, we may know the space group, but wish to accurately determine the values of the free variables that specify the general position of some particular atom or molecule. Assume our crystal has multiple, symmetry-equivalent copies of particular atom of weight A, and that we are able to construct the

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patterson for this crystal from diffraction data. We have already assigned positions to symmetry elements in our unit cell and wish to find the location of A.

Say we know the space group is Pc and we have specified that the c_b glide plane passes through the origin. The symmetry is

$$\rho(\mathbf{r}) = \rho(m_b \cdot \mathbf{r} + \mathbf{c}/2) \quad //c_b @ \mathbf{0}$$

The general Wyckoff position has multiplicity 2.

$$1: (x, y, z) \text{ R}$$

$$2: (x, \bar{y}, \frac{1}{2} + z) \text{ L}$$

The patterson shows differences in these coordinates:

$$2-1: (0, -2y, \frac{1}{2}) = (0, 1-2y, \frac{1}{2})$$

$$1-2: (0, 2y, -\frac{1}{2}) = (0, 2y, \frac{1}{2})$$

It is best to name the coordinates of the Patterson as (u, v, w) , so not to confuse them with the general position coordinates. We expect a peak in the Patterson at $(u, v, w) = (0, 1-2y, \frac{1}{2})$. A second peak will also appear at $(u, v, w) = (0, 2y, \frac{1}{2})$, which is equivalent to the first. These peaks will appear in a linear trace through the patterson, called a Harker line, along $(0, v, \frac{1}{2})$. If the atomic number is A , these peaks will have height A^2 . We can find the coordinate using $y = v_{\max}/2$

