

Structure solution by Patterson and dual space methods

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Introduction to the problem of structure solution

The diffraction experiment provides only the amplitude of the complex structure factors, but not their phases. Knowledge of the amplitudes *and* phases, or equivalently the knowledge of the electron density of the crystal, is a starting point for the build-up of a model of the crystal structure. The central task of structure solution is to use the available information about the expected structure to derive the phases (or directly the positions of the atoms) from the structure-factor amplitudes.

Patterson method

While the atomic positions cannot be obtained directly from the experimental intensities, it is possible to obtain information about the interatomic vectors. To understand how, let us investigate the properties of an autoconvolution of the electron density.

The convolution of functions $f(\mathbf{r})$ and $g(\mathbf{r})$ is denoted as $f(\mathbf{r}) \otimes g(\mathbf{r})$ and the convolution function is defined as:

$$c(\mathbf{u}) = f(\mathbf{r}) \otimes g(\mathbf{r}) = \int f(\mathbf{r})g(\mathbf{u} - \mathbf{r})d^3\mathbf{u}$$

Now if we take $f(\mathbf{r}) = \rho(\mathbf{r})$, and $g(\mathbf{r}) = \rho(-\mathbf{r})$, we obtain an autoconvolution of $\rho(\mathbf{r})$:

$$P(\mathbf{u}) = \rho(\mathbf{r}) \otimes \rho(-\mathbf{r}) = \int \rho(\mathbf{r})\rho(\mathbf{u} + \mathbf{r})d^3\mathbf{r}$$

If $\rho(\mathbf{r})$ is a function with pronounced peaks, the function $P(\mathbf{u})$ will have peaks wherever a peak in $\rho(\mathbf{r})$ overlaps with a peak in $\rho(\mathbf{u} + \mathbf{r})$. This condition is fulfilled for every interatomic vector \mathbf{u} (Fig. 1). Thus, the function $P(\mathbf{u})$ will exhibit peaks at all interatomic vectors of the structure. In crystallography the function P is called the *Patterson function*, but generally it is known as an autocorrelation function (Fig. 1).

The convolution theorem says that the Fourier transform of a convolution of two functions is equal to the product of the Fourier transforms of the individual functions. Using this theorem we can write:

$$\begin{aligned} \mathcal{F}(P(\mathbf{u})) &= \mathcal{F}(\rho(\mathbf{r}) \otimes \rho(-\mathbf{r})) = \\ &= \mathcal{F}(\rho(\mathbf{r})) \cdot \mathcal{F}(\rho(-\mathbf{r})) = \\ &= F_{\mathbf{h}} F_{\mathbf{h}}^* = |F_{\mathbf{h}}|^2 \end{aligned}$$

Here $F_{\mathbf{h}}^*$ denotes the complex conjugate of $F_{\mathbf{h}}$ and \mathcal{F} represents the Fourier transform.

We see that the Fourier transform of the Patterson function is the square of the structure-factor amplitude, which is a quantity proportional to the diffracted intensities. We immediately see that the Patterson function can be obtained as an inverse Fourier transform of the diffracted intensities:

$$P(\mathbf{u}) = \mathcal{F}\left(|F_{\mathbf{h}}|^2\right)$$

Thus, we can obtain direct information about the direction and length of the interatomic vectors by taking a Fourier transform of the diffracted intensities and extracting peaks from the resulting Patterson map.

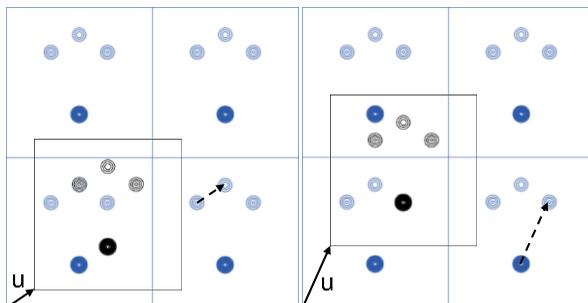


Figure 1. Generating the Patterson function. The Patterson function will be large for such a shift \mathbf{u} (black arrow) that a peak in the electron density $\rho(\mathbf{r})$ (blue, four unit cells shown) overlaps with another peak in the density $\rho(\mathbf{u} + \mathbf{r})$ (black, one unit cell shown). This happens for all interatomic vectors in the structure (dashed arrow).

The height of a peak in the Patterson function is proportional to the product of the atomic numbers of the atoms forming that peak. Therefore the peaks corresponding to the overlap of two heavy atoms will be much higher than peaks from two light atoms. This makes it possible to assign the peaks in the Patterson map to the interatomic vectors of specific atomic species. An example of a Patterson map is shown in Fig. 2.

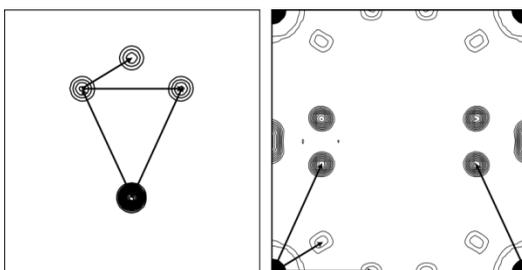


Figure 2. Section of the electron density of sodium nitrite with some interatomic vectors indicated by arrows (left), and the corresponding Patterson map (right, the same interatomic vectors indicated). Note the correspondence of the peak height in the Patterson map and the peak height of the constituent atoms.

For a vector \mathbf{r}_{AB} from atom A to atom B there will always exist a vector $\mathbf{r}_{BA} = -\mathbf{r}_{AB}$, each peak in the Patterson function will have its counterpart at $-\mathbf{r}$. Thus the Patterson function is always centrosymmetric regardless of the symmetry of the crystal structure.

The Patterson map becomes complicated if the number of atoms in the structure becomes large, because the number of Patterson peaks grows with the square of the number of atoms. The situation becomes much simpler if the structure contains one or a few heavy atoms. The highest Patterson peaks can be assigned to the overlap of these atoms and their positions can thus be determined.

Dual space iterative methods

While Patterson method can be considered a predominantly direct-space method and direct methods work mostly in the Fourier (reciprocal) space, in the class of dual-space methods neither of the two spaces play a dominant role – neither the operation in direct space nor in the Fourier space is, even in principle, capable of solving the structure alone, and it is their combination that makes the solution possible.

The operation of dual space algorithms can be described in the language of constraints, projections and iteration schemes. A constraint is a property that an electron density must fulfil. The two principal constraints in crystallography are the amplitude constraint and the positivity constraint. The amplitude constraint is defined in Fourier space – it is the requirement that the Fourier coefficients of the electron density have amplitudes equal to the experimentally determined amplitudes. The positivity constraint is defined in the direct-space – it is the requirement that the density is everywhere positive. This constraint can have a range of variants. A projection is an operation that transforms an arbitrary electron density into a density that satisfies one of the constraints. The positivity projection consists from a simple operation: set all pixels with negative density value to zero. Applying the amplitude projection requires the following steps:

- Calculate a Fourier transform of the starting electron density
- Replace the amplitudes of the structure factors by the experimentally determined amplitudes
- Calculate the new electron density by inverse Fourier transform of the modified structure factors

These projections can be combined into more or less complicated iteration schemes. Different dual-space algorithms use different types of projections and different iterations schemes.

The most well-known representative of the dual-space phasing algorithms is the *charge flipping* algorithm (Oszlányi & Sütő, 2004). A schematic flowchart of the algorithm is shown in Fig. 3. The iteration is initialized by assigning random phases to the experimental structure-factor amplitudes. From this trial solution an electron density is calculated by inverse Fourier transform. This electron density is modified in such a way, that all grid points with density below a certain positive threshold δ are multiplied by -1 (flipped). New temporary structure factors are calculated by Fourier transform of this modified density. The phases of these temporary structure factors are combined with the experimental amplitudes and such a set of structure factors enters the next cycle of iteration. δ is the only parameter of the whole algorithm. In the language of projections, the charge flipping algorithm is a repeated application of the amplitude projection, and a positivity “reflection”. A reflection is an operation defined as $R=2P-I$, where P is the projection operation and I is an identity. (Note that this reflection has nothing to do with the reflection in the context of diffraction.)

Other algorithms from this family are the low-density elimination method (Shiono & Woolfson, 1992) the method of iterated overprojections (Elser, 2003) and also the recently published algorithm used in the SHELXT program (Sheldrick 2014). A detailed overview of the field of dual space iterative algorithms can be found in the review article by Palatinus (2013).

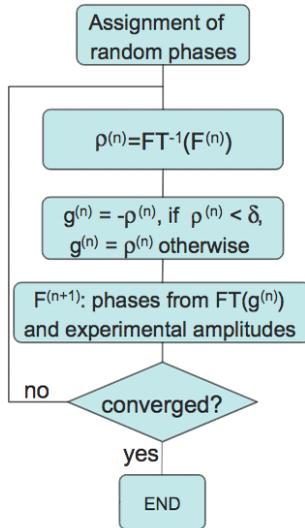


Figure 3. Schematic flowchart of the operation of the charge-flipping algorithm. FT stands for Fourier transform.

References

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