Diffraction Methods in Chemistry

University of Cambridge Part II Natural Sciences Tripos

Yue Wu

Yusuf Hamied Department of Chemistry
Lensfield Road,
Cambridge, CB2 1EW

yw628@cam.ac.uk

Acknowledgements

Nothing in these lecture notes is original. They are largely based on the notes by Dr. Andrew Bond, who lectured this course in 2025. They are nowhere near accurate representations of what was actually lectured, and in particular, all errors are almost surely mine.

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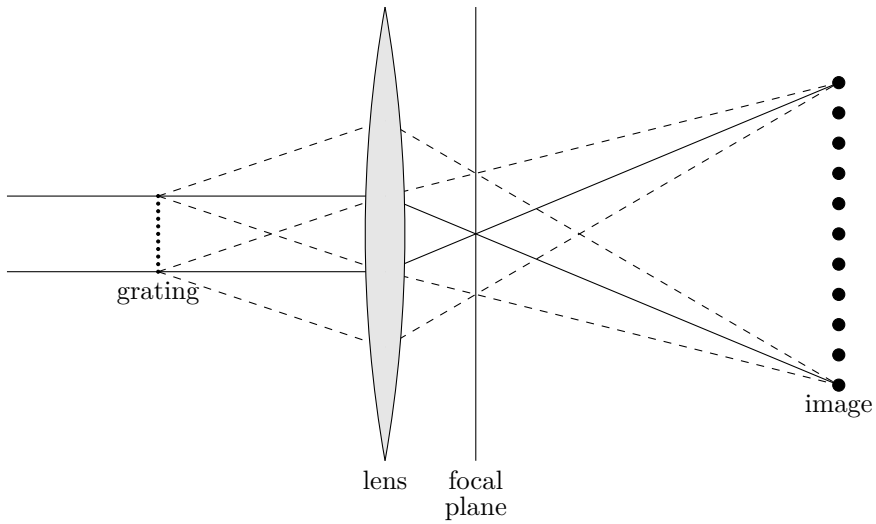


Figure 1.1: A magnified image of the diffraction grating is formed using a convex lens to focus the diffraction pattern.

1 Diffraction

It might be familiar from physics that if you shine a beam of light on a diffraction grating, then a diffraction pattern will emerge. If you put a lens after the diffracted beam, they may be brought to a focus, and a magnified image of the diffraction grating will be seen, as shown in the figure.

Atoms in a crystal are, in some sense, very fine gratings. Can we use a similar method to image the atoms in a crystal directly? However, to form a diffraction pattern, we need the wavelength of the light to be in roughly the same length scale as the pattern we are trying to image. The atoms are in the length scales of Angstroms 10^{-10} m, therefore, we need to use X-ray for diffractions at atomic length scales. However, there is no lens for X rays (because lenses are made of atoms too), so the imaging process does not work. What we have to do is to measure the intensity of the diffracted beams at different directions, and infer the atomic structure mathematically.

This is, however, a hard thing to do. We will spend the vast majority of our lectures on how to translate the diffracted beam intensities to atomic structure.

1.1 Addition of Electromagnetic Waves

X-rays are electromagnetic waves, so they are described by Maxwell's equations, from which we can infer that the electromagnetic fields are essentially just oscillating electric and magnetic fields, travelling in some direction $\mathbf{k}$ (the magnitude of $\mathbf{k}$ also encodes the wavelength via $|k| = 2\pi/\lambda$) with the speed of light c.[1] We will label the distance as x along the direction of propagation of the electromagnetic wave $\mathbf{k}$, and consider

[1] In free space, $\rho = 0$ and $\mathbf{J} = 0$, so by Maxwell's equations

$$\boldsymbol{\nabla} \times (\boldsymbol{\nabla} \times \mathbf{E}) = -\boldsymbol{\nabla} \times \frac{\partial \mathbf{B}}{\partial t} = -\frac{\partial}{\partial t}(\boldsymbol{\nabla} \times B) = -\frac{\partial}{\partial t}\left(\mu_0 \epsilon_0 \frac{\partial \mathbf{E}}{\partial t}\right) = -\mu_0 \epsilon_0 \frac{\partial^2 \mathbf{E}}{\partial t^2}\,. \tag{1.1}$$

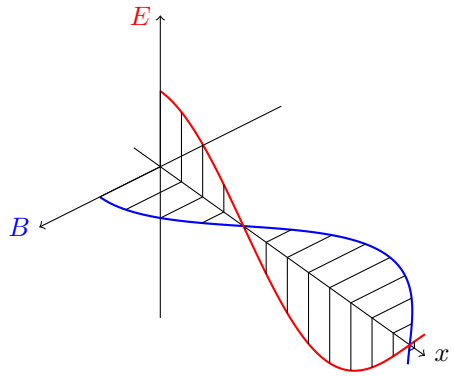


Figure 1.2: Electromagnetic wave propagating in space.

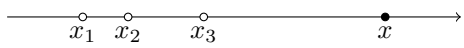
the wave at some fixed time t. Then the electric (or equivalently the magnetic) field strength is given by

$$\psi(x) = A \sin\left(\frac{2\pi x}{\lambda} + \phi\right), \tag{1.7}$$

where the real number A is the amplitude and ϕ is the phase offset. However, it turns out that when considering oscillations, it is always easier to use complex numbers, so we will alternatively see the electric field as the real part of the complex wave

$$\psi(x) = A \exp\left(\frac{2\pi i x}{\lambda}\right), \tag{1.8}$$

where $A = |A|\, e^{i\phi}$ is now complex and includes both the amplitude $|A|$ and the initial phase offset ϕ.



Now what happens if we have multiple sources, each sending off magnetic waves of the same frequencies but with different amplitudes and phases? Let's consider the simple 1D case, where n sources are located at x_j. We will let all three sources to have

By vector calculus identities, we also have

$$\boldsymbol{\nabla} \times (\boldsymbol{\nabla} \times \mathbf{E}) = \boldsymbol{\nabla}(\boldsymbol{\nabla} \cdot \mathbf{E}) - \nabla^2 \mathbf{E} = -\nabla^2 \mathbf{E}, \tag{1.2}$$

and hence

$$\nabla^2 \mathbf{E} = \mu_0 \epsilon_0 \frac{\partial^2 \mathbf{E}}{\partial t^2}. \tag{1.3}$$

This is the wave equation, with wave speed $c = 1/\sqrt{\mu_0 \epsilon_0}$, with general complex solution

$$\mathbf{E} = \mathbf{E}_0 e^{i(\mathbf{k}\cdot\mathbf{r} - \omega t)} \tag{1.4}$$

for $\mathbf{E} \in \mathbb{C}$ and $\mathbf{k}^2 c^2 = \omega^2$. By Maxwell's equations, we also have

$$\frac{\partial \mathbf{B}}{\partial t} = -\boldsymbol{\nabla} \times \mathbf{E} = -i\mathbf{k} \times \mathbf{E}, \tag{1.5}$$

and so

$$\mathbf{B} = \frac{\mathbf{k}}{\omega} \times \mathbf{E}. \tag{1.6}$$

Therefore, $\mathbf{E}$ and $\mathbf{B}$ are both transverse wave that are in the same phase but perpendicular to each other.

a zero initial phase[2], so that the resulting wave at point x due to source j is given by

$$\psi_j(x) = A_j \exp\left(\frac{2\pi i(x - x_j)}{\lambda}\right) , \tag{1.9}$$

where A_j is real because we have a zero initial phase. We will denote the phase of the wave due to source j at x as

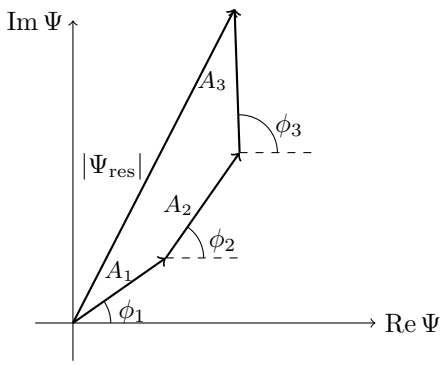
$$\phi_j = \frac{2\pi(x - x_j)}{\lambda} . \tag{1.10}$$

Then to work out the total wave, we only need to sum up the contributions from each sources to get

$$\Psi_{\text{res}}(x) = \sum_j A_j \exp\left(i\phi_n\right) . \tag{1.11}$$

It is easy to see that the phase angle of the resultant amplitude is

$$\Phi_{\text{res}} = \tan^{-1}\left[\frac{\sum_j A_j \sin\phi_j}{\sum_j A_j \cos\phi_j}\right] . \tag{1.12}$$



Now what if we move the measuring point x by an amount of δx? This will increase the phases of the wave from all the sources by

$$\delta\phi = \frac{2\pi\delta x}{\lambda} . \tag{1.13}$$

The net result is that the resultant magnitude of the combined wave does not change, but the phase changes by $\delta\phi$, as

$$\Psi'_{\text{res}}(x) = \sum_j A_j \exp(i(\phi_n + \delta\phi)) \tag{1.14}$$

$$= e^{i\delta\phi} \sum_j A_j \exp(i\phi_n) . \tag{1.15}$$

What if we change the position of one of the sources x_k? This will in general lead to a change in the phase ϕ_k. Now both the phase and the amplitude of the resulting wave is different.

[2]It is a trivial generalisation for the sources to have different non-zero initial phases. We make such assumption because this is the only situation we will need for later discussion, and it makes my diagram cleaner. It is actually also trivial to generalise it to 3D by replacing $x - x_j$ with $\|\mathbf{x} - \mathbf{x}_j\|$ in all the expressions below.

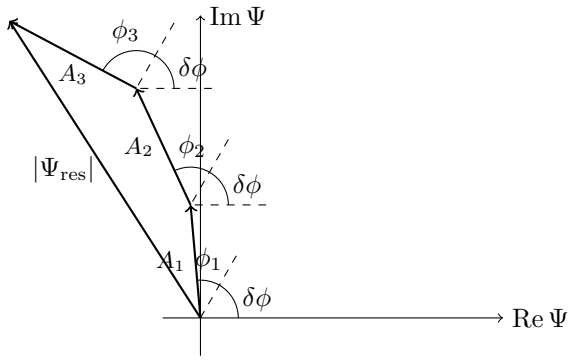


Figure 1.3: Movement of the measuring point results in a change of measured phase only.

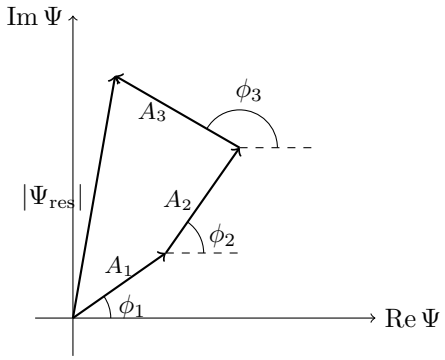


Figure 1.4: A change in the position of one of the sources leads to a change in both the magnitude and the phase measured.

1.2 Diffraction of an Object

We would now like to consider the diffraction of an extended object. Suppose we have parallel incident beams from the direction $\hat{\mathbf{s}}_0$ illuminating the whole object, and we are measuring the diffracted beam at some distant point Q. The dimension of this object is small compared to its distance to the measuring point Q so we can sensibly say that Q is at direction $\hat{\mathbf{s}}$ for all points in the object. To produce the diffraction pattern, we need to sum up the radiation scattered from all the points in the object. To do this, we first pick an arbitrary origin O in the object, and we need to figure out the intensity and phase difference between the beams diffracted in direction $\hat{\mathbf{s}}$ from O and from any other point P with position vector $\mathbf{r}$.

From figure 1.5, it is easy to see that the beam diffracted from P and O has a path difference

$$\Delta x = \mathbf{r} \cdot \hat{\mathbf{s}}_0 - \mathbf{r} \cdot \hat{\mathbf{s}} \,. \tag{1.16}$$

In particular, a positive path difference means that the beam from P falls behind the beam from O, leading to a negative phase difference, so

$$\Delta\phi = -\frac{2\pi\Delta x}{\lambda} = \frac{2\pi \mathbf{r} \cdot (\hat{\mathbf{s}} - \hat{\mathbf{s}}_0)}{\lambda} \,. \tag{1.17}$$

The amplitude of the beam diffracted from O and P may also be different, since the object may be inhomogeneous. Let $A(\mathbf{r})$ be a real function representing the diffraction

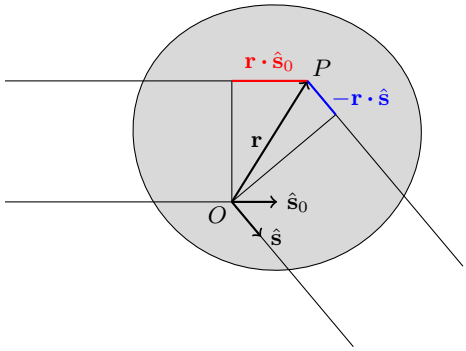


Figure 1.5: Path difference for diffractions in a general object.

amplitude, then by integrating over all points, the wave measured at point Q is

$$\Psi(\hat{\mathbf{s}}) = \int \mathrm{d}^3\mathbf{r}\, A(\mathbf{r}) \exp\left(\frac{2\pi i \mathbf{r}\cdot(\mathbf{s}-\mathbf{s}_0)}{\lambda}\right) . \tag{1.18}$$

We can define the *scattering vector* $\mathbf{S}$ by

$$S := \frac{\hat{\mathbf{s}} - \hat{\mathbf{s}}_0}{\lambda} . \tag{1.19}$$

It is a vector bisecting the incident and diffracted beam, as shown in the figure below. If we define the angle of deflection to be 2θ, then the length of the scattering vector is

$$\|\mathbf{S}\| = \frac{2\sin\theta}{\lambda} . \tag{1.20}$$

The scattering vector has dimension $[\mathrm{L}]^{-1}$, so it exists in the reciprocal space, which might be familiar from Part IB Chemistry A.[3] This allows us to simplify our expression

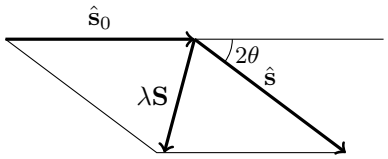


Figure 1.6: Construction of the scattering vector.

of the measured wave as

$$\Psi(\mathbf{S}) = \int \mathrm{d}^3\mathbf{r}\, A(\mathbf{r}) \exp\left(2\pi i \mathbf{r}\cdot\mathbf{S}\right) . \tag{1.22}$$

1.3 Diffraction of X-rays from Electrons

We will now consider how X-rays interacts with matter. The interaction generally fall into two categories.

[3] In some derivation, one uses *momentum transfer vector* $\mathbf{Q}$ defined by

$$\mathbf{Q} = \frac{2\pi(\hat{\mathbf{s}} - \hat{\mathbf{s}}_0)}{\lambda} . \tag{1.21}$$

instead of $\mathbf{S}$.

- *Elastic scattering.* This is our main focus. In an *elastic scattering*, or *Thomson scattering*, there is no net transfer of energy from the photon to the material. It can be think of as some kind of resonance of the atomic electrons. When X-rays pass through the material, the oscillating electric field causes the atomic electrons to oscillate, which in turn emit X-rays in all directions. The incoming and outgoing rays retain a non-random phase relationship and are said to be *coherent*.

- *Inelastic processes. Inelastic processes* involve energy transfer from the incoming X-rays to electrons in atoms. The simplest example is photoelectron emission, where an X-ray photon providing energy for an atom to eject a core-shell electron. The photons are then re-emitted with lower energy in an incoherent fashion. This incoherence means that they cannot interfere with each other to produce diffraction patters. Other processes of this type may result from interaction with valence shell electrons or vibrations, all being incoherent. We are therefore not interested in inelastic processes at this stage.

The quantitative description of Thomson scattering strictly only applies to free electrons, but the results are found to be generally applicable to crystals under normal scattering conditions. Crucially, the amplitude of X-rays diffracted from some point is proportional to the local electron density $\rho(\mathbf{r})$. Therefore,

$$\Psi(\mathbf{S}) = \int \mathrm{d}^3\mathbf{r}\, \sigma\rho(\mathbf{r}) \exp(2\pi i \mathbf{r}\cdot\mathbf{S})\,, \tag{1.23}$$

where σ is the scattering power of a single electron. We can divide through this constant of proportionality to obtain the *structure factor* $F(\mathbf{S})$ given by

$$F(\mathbf{S}) = \int \mathrm{d}^3\mathbf{r}\, \rho(\mathbf{r}) \exp\left(2\pi i \mathbf{r}\cdot\mathbf{S}\right)\,. \tag{1.24}$$

Mathematically, $F(\mathbf{S})$ is the *Fourier transform* of the electron density $\rho(\mathbf{r})$.

Definition 1.1. Let $f : \mathbb{R}^n \to \mathbb{C}$ be a function. The *Fourier transform* of f is $\mathcal{F}[f] \equiv \tilde{f} : \mathbb{R}^n \to \mathbb{C}$ given by[4]

$$\tilde{f}(\mathbf{k}) \coloneqq \int \mathrm{d}^n\mathbf{x}\, f(\mathbf{x}) e^{2\pi i \mathbf{k}\cdot\mathbf{x}}\,. \tag{1.26}$$

Theorem 1.2. Let $\tilde{f}(\mathbf{k})$ be the Fourier transform of $f(\mathbf{x})$. The *inverse Fourier transform* that converts $\tilde{f}$ back to f is given by

$$f(\mathbf{x}) = \mathcal{F}^{-1}[\tilde{f}(\mathbf{k})] \coloneqq \int \mathrm{d}^3\mathbf{k}\, \tilde{f}(\mathbf{k}) e^{-2\pi i \mathbf{k}\cdot\mathbf{x}}\,. \tag{1.27}$$

[4]You might be more familiar with the Fourier transform defined as

$$\tilde{f} = \frac{1}{\sqrt{2\pi}} \int \mathrm{d}x\, f(x) e^{-ikx}\,, \tag{1.25}$$

where the normalisation factor of $1/\sqrt{2\pi}$ may or may not be there. It is just a matter of convention. However, this difference in convention is annoying since it results in slight tweaks in a lot of formulae.

Proof.

$$\begin{aligned}\mathcal{F}[\tilde{f}](\mathbf{x}) &= \int \mathrm{d}^n\mathbf{k}\, e^{-2\pi i\mathbf{k}\cdot\mathbf{x}} \int \mathrm{d}^3\mathbf{s}\, e^{2\pi i\mathbf{k}\cdot\mathbf{s}} f(\mathbf{s}) \\ &= \int \mathrm{d}^n\mathbf{s}\, f(\mathbf{s}) \int \mathrm{d}^n\mathbf{k}\, e^{2\pi i k\cdot(\mathbf{s}-\mathbf{x})} \\ &= \int \mathrm{d}^n\mathbf{s}\, f(\mathbf{s})\delta(\mathbf{s}-\mathbf{x}) \\ &= f(\mathbf{x})\,. \end{aligned} \tag{1.28}$$

□

Hence to convert the $F(\mathbf{S})$ back to $\rho(\mathbf{r})$, one simply needs to perform the inverse Fourier transform

$$\rho(\mathbf{r}) = \int \mathrm{d}^3\mathbf{S}\, F(\mathbf{S}) \exp(-2\pi i\mathbf{r}\cdot\mathbf{S})\,. \tag{1.29}$$

This means that if we can determine the $F(\mathbf{S})$, then we can easily reconstruct the electron density in a material, no matter how complex the structure is. (1) Measure the phases and the amplitudes of the diffracted beams. (2) Divide by single-electron scattering power σ to get $F(\mathbf{S})$. (3) Do the inverse Fourier transform to obtain $\rho(\mathbf{S})$. Simple as that! Three steps to solve any chemical structure in the world!

This is the happy ending of our story on X-ray diffraction.

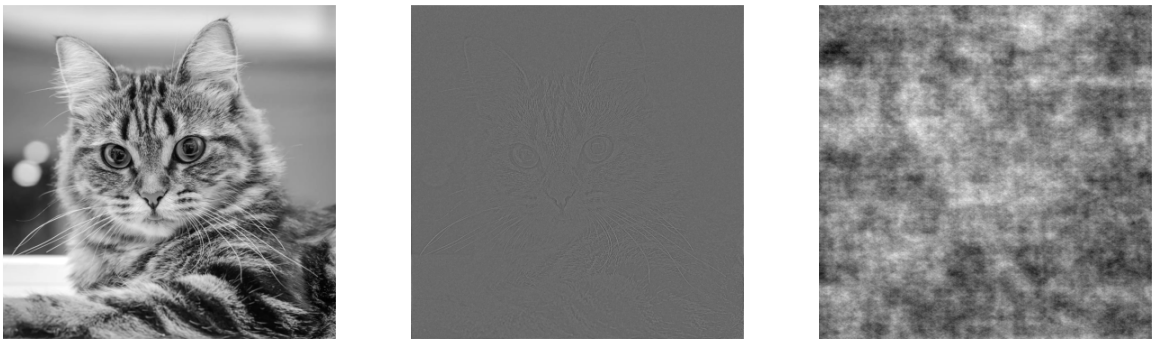
1.4 The Phase Problem

If the problem is really as simple as this, then this would be a one-lecture course instead of a 12-lecture one. There is a huge issue. We cannot measure the phase of an X-ray.

To measure the magnitude and the phase of an electromagnetic wave, we would use an antenna. However, this would require the antenna to have its dimensions comparable to the radiation wavelength. The X-ray we used for diffraction is at atomic length scale — that's why we can see the diffraction, but it is impossible to make an antenna at atomic length scale since antennas should be made from atoms! All we can measure in a diffraction experiment is the number of X-ray photons encountered in a given time, which is the diffracted *intensity*. This is proportional to $I = |F(\mathbf{S})|^2$. The phase information is completely lost.

Now the question is: is getting the correct phase important? If using a wrong phase of the diffracted beam has little impact on the electron density calculated, then this would not be a huge problem. We can calculate the modulus of $F(\mathbf{S})$ by taking the square root of the intensity, and just plug in some random phases to calculate $\rho(\mathbf{r})$. However, it turns out that getting the correct phase is extremely important — it even plays a more important role than the magnitude to some extent. This can be illustrated by the following little experiment.

Instead of doing Fourier transform of a electron density function, we do a Fourier transform on a picture. A black and white picture is also a function of the pixels, where the values of the function is the gray scale. We can transform it into the frequency domain, and then transform it back, and we get the original image. However, if we use some randomly generated phase values to replace the correct phase values in the Fourier transform of the image, and we transform it back, we see a complete mess. This is what will happen if we use random phase value for the structure factor — we will get no valuable information. If fact, if we use some random value for the magnitudes of the Fourier transform, with the correct phase values, we can still vaguely see the shape of a cat.



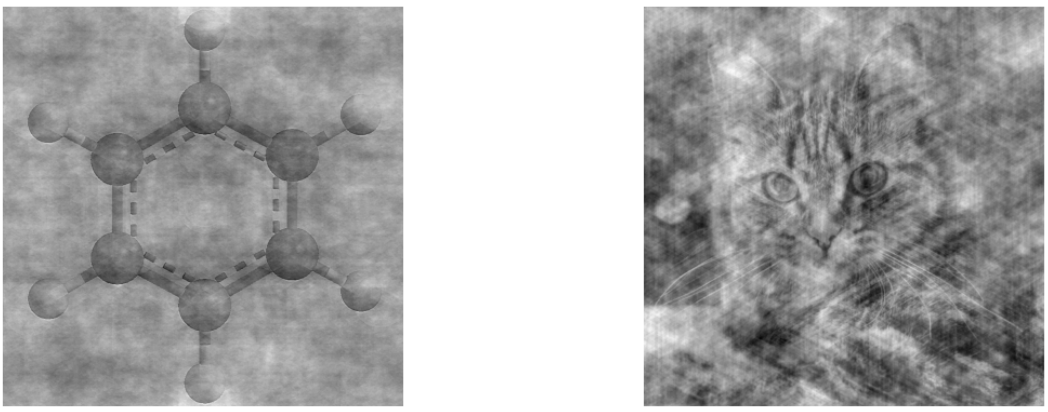
(a) Correct magnitude + correct phase

(b) Random magnitude + correct phase

(c) Correct magnitude + random phase

Figure 1.7: The effect of using the wrong phases and magnitudes in an inverse Fourier transform.

Just for fun, we can extend this experiment further. We have two images: one is a benzene and one is a cat. What will happen if we use the magnitude value of one figure with the phase value of the other?



(a) Magnitude of cat + phase of benzene

(b) Magnitude of benzene + phase of cat

Figure 1.8: Phases govern what we see in an inverse Fourier transform. If you use the phases of a benzene, you see a benzene. If you use the phases of a cat, you see a cat.

Moral: phase is important, but we can't measure it. The main task of structure determination using X-ray diffraction is to deduce the phases of the structure factor. This is what we will spend the remaining 11-lectures worths of time on.

1.5 Patterson Function

Since all what we can get from measuring a diffraction pattern is the intensity $I(\mathbf{S}) = |F(\mathbf{S})|^2$, let's see what its inverse Fourier transform gives us anyway.

Before doing that, let's first introduce convolution and correlation.

Definition 1.3. For two functions $f, g : \mathbb{R}^n \to \mathbb{C}$, their *convolution* is

$$(f * g)(\mathbf{x}) := \int \mathrm{d}^n\mathbf{s}\, f(\mathbf{s}) g(\mathbf{x} - \mathbf{s})\,, \tag{1.30}$$

and their *correlation* is

$$(f \otimes g)(\mathbf{x}) := \int \mathrm{d}^n\mathbf{s}\, f(\mathbf{s})^* g(\mathbf{x} + \mathbf{s})\,. \tag{1.31}$$

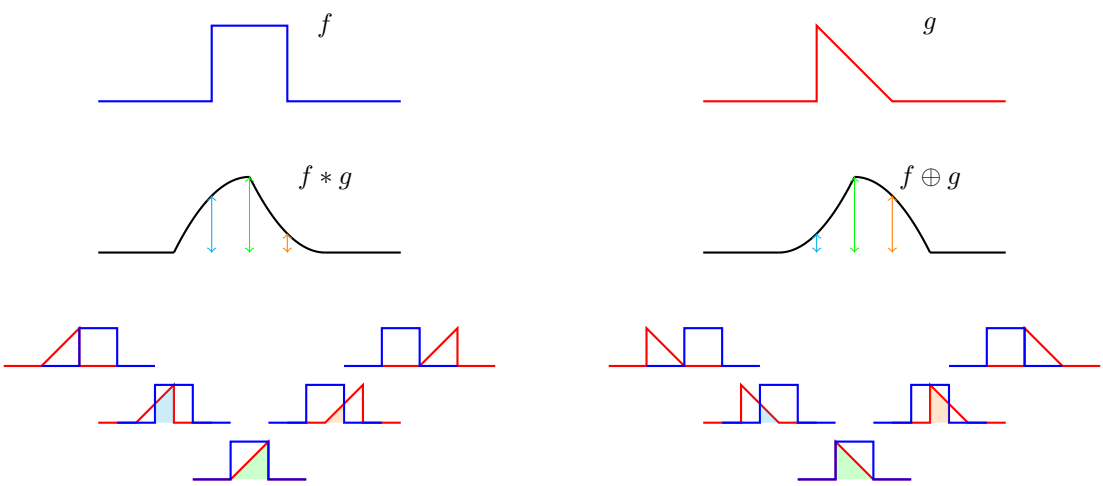


Figure 1.9: Graphic explanation of convolution and correlation.

Theorem 1.4 (Convolution theorem). The Fourier transform of a convolution if the product of Fourier transform.

$$\mathcal{F}[f * g] = \mathcal{F}[f]\mathcal{F}[g]\,. \tag{1.32}$$

Proof.

$$\begin{aligned}
\mathcal{F}[f * g](\mathbf{k}) &= \int \mathrm{d}^n\mathbf{x}\, e^{2\pi i \mathbf{k}\cdot\mathbf{x}} \int \mathrm{d}^n\mathbf{s}\, f(\mathbf{s}) g(\mathbf{x} - \mathbf{s}) \\
&= \int \mathrm{d}^n\mathbf{s}\, f(\mathbf{s}) \int \mathrm{d}^n\mathbf{x}\, e^{2\pi i \mathbf{k}\cdot\mathbf{x}} g(\mathbf{x} - \mathbf{s}) \\
&= \int \mathrm{d}^n\mathbf{s}\, f(\mathbf{s}) \int \mathrm{d}^n\mathbf{u}\, e^{2\pi i \mathbf{k}\cdot(\mathbf{u}+\mathbf{s})} g(\mathbf{u}) \qquad \text{define } \mathbf{u} = \mathbf{x} - \mathbf{s} \\
&= \int \mathrm{d}^n\mathbf{s}\, e^{2\pi i \mathbf{k}\cdot\mathbf{s}} f(\mathbf{s}) \int \mathrm{d}^n\mathbf{u}\, e^{2\pi i \mathbf{k}\cdot\mathbf{u}} g(\mathbf{u}) \\
&= \tilde{f}(\mathbf{k})\tilde{g}(\mathbf{k})\,.
\end{aligned} \tag{1.33}$$

□

Theorem 1.5. Conversely, the Fourier transform of a product fg is the convolution of their fourier transforms

$$\mathcal{F}[fg] = \mathcal{F}[f] * \mathcal{F}[g]\,. \tag{1.34}$$

Proof.

$$\begin{aligned}
\mathcal{F}[fg](\mathbf{k}) &= \int \mathrm{d}^n\mathbf{x}\, e^{2\pi i \mathbf{k}\cdot\mathbf{x}} f(\mathbf{x}) g(\mathbf{x}) \\
&= \int \mathrm{d}^n\mathbf{x}\, e^{2\pi i \mathbf{k}\cdot\mathbf{x}} f(\mathbf{x}) \int \mathrm{d}^n\boldsymbol{\ell}\, e^{-2\pi i \boldsymbol{\ell}\cdot\mathbf{x}} \tilde{g}(\boldsymbol{\ell}) \\
&= \int \mathrm{d}^n\boldsymbol{\ell}\, \tilde{g}(\boldsymbol{\ell}) \int \mathrm{d}^n\mathbf{x}\, e^{2\pi i \mathbf{x}\cdot(\mathbf{k}-\boldsymbol{\ell})} f(\mathbf{x}) \\
&= \int \mathrm{d}^n\boldsymbol{\ell}\, \tilde{g}(\boldsymbol{\ell}) \tilde{f}(\mathbf{k}-\boldsymbol{\ell}) \\
&= \tilde{f} * \tilde{g}(\mathbf{k})\,.
\end{aligned} \tag{1.35}$$

□

We see a beautiful duality here. Product in the real domain is the convolution in the Fourier domain, and *vice versa*.

Theorem 1.6 (Wiener–Khinchin theorem). The Fourier transform of the autocorrelation of a function is its *power spectral intensity*.

$$\mathcal{F}[f \otimes f] = \left|\tilde{f}\right|^2\,. \tag{1.36}$$

Proof.

$$\begin{aligned}
\mathcal{F}[f \otimes f](\mathbf{k}) &= \int \mathrm{d}^n\mathbf{x}\, e^{2\pi i \mathbf{k}\cdot\mathbf{x}} \int \mathrm{d}^n\mathbf{s}\, f^*(\mathbf{s}) f(\mathbf{x}+\mathbf{s}) \\
&= \int \mathrm{d}^n\mathbf{s}\, f^*(\mathbf{s}) \int \mathrm{d}^n\mathbf{x}\, e^{2\pi i \mathbf{k}\cdot\mathbf{x}} f(\mathbf{x}+\mathbf{s}) \\
&= \int \mathrm{d}^n\mathbf{s}\, f^*(\mathbf{s}) \int \mathrm{d}^n\mathbf{u}\, e^{2\pi i \mathbf{k}\cdot(\mathbf{u}-\mathbf{s})} f(\mathbf{u}) \qquad \text{define } \mathbf{u} = \mathbf{x}+\mathbf{s} \\
&= \int \mathrm{d}^n\mathbf{s}\, e^{-2\pi i \mathbf{k}\cdot\mathbf{s}} f^*(\mathbf{s}) \int \mathrm{d}^n\mathbf{u}\, e^{2\pi i \mathbf{k}\cdot\mathbf{u}} f(\mathbf{u}) \\
&= \tilde{f}^*(\mathbf{k}) \tilde{f}(\mathbf{k}) = \left|\tilde{f}(\mathbf{k})\right|^2\,.
\end{aligned} \tag{1.37}$$

□

Finally, if we apply both sides on the Wiener–Khinchin theorem, we get

$$\mathcal{I}\left[|\tilde{f}|^2\right] = f \otimes f\,. \tag{1.38}$$

We can apply this to our diffraction intensity! We previously identified the structure factor to be the Fourier transform of the electron density, $F(\mathbf{S}) = \mathcal{F}[\rho(\mathbf{x})]$, and the diffraction intensity is exactly $I(\mathbf{S}) = |F(\mathbf{S})|^2$. Therefore, the inverse Fourier transform of the diffraction intensity is exactly the autocorrelation of the electron density!

$$\mathcal{F}^{-1}[I(\mathbf{S})] = \rho \otimes \rho(\mathbf{r})\,. \tag{1.39}$$

We often call this the *Patterson function*, denoted $P(\mathbf{r})$.