

PREFACE

Function Algebra — an Important Bridge between Diffraction Experiments and their Evaluation

Two of the most important parameter integrals for the mathematical description of nature are the Fourier integral and the convolution integral. While the Fourier integral transforms a certain function from one space into another one the convolution integral describes the interaction of two functions. The human beings are living in the so-called physical space but observation in the Fourier space can give hints about things happening in the physical space. The transform can be performed in both directions and so one can assume, that both spaces are equivalent in some sense and that the same laws are valid in both of them.

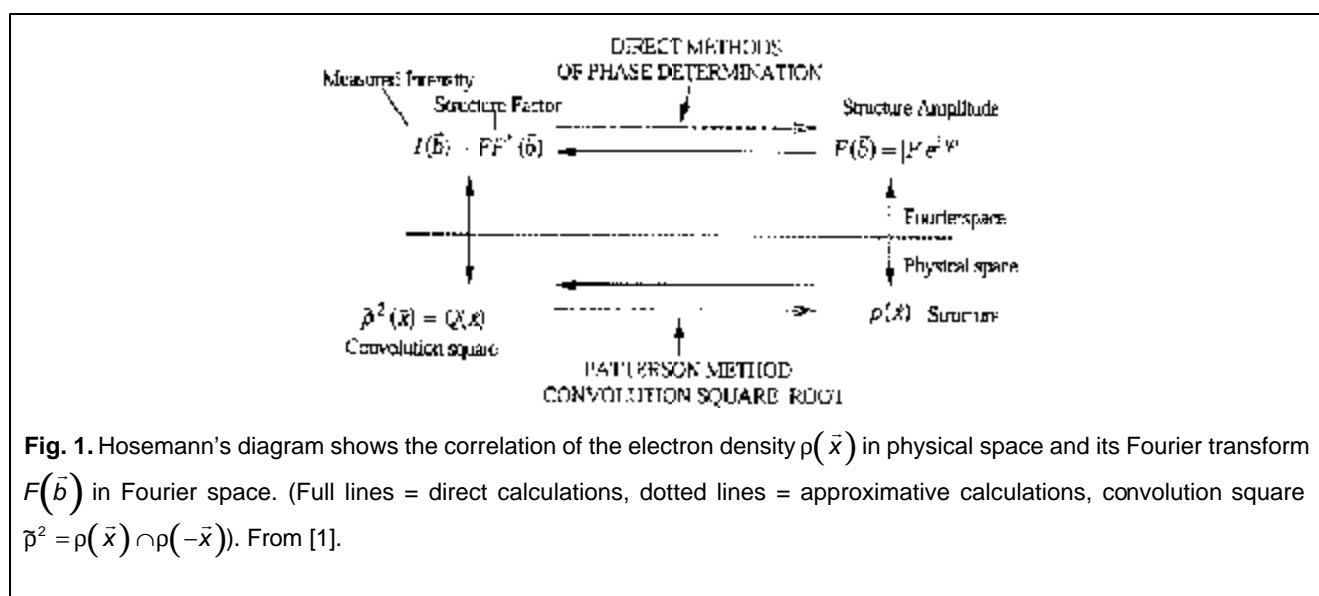
In the early 20th century very important discoveries and developments have been made in the field of diffraction. It could be shown, that X-rays are of wave nature and at the same time that crystals have a periodic structure. The names M. v. Laue, P. P. Ewald, W. H. and W. L. Bragg may be mentioned here.

The kinematic theory of X-ray diffraction led finally to the knowledge, that if a sample is present in the physical space, its diffraction can be represented in the Fourier space (Fig. 1). This knowledge opens up many possibilities to correlate diffraction experiments with the nature of the sample. One problem, however, remains until today: Measurements of X-rays are measurements of intensities: the phases are getting lost. It took many years to overcome this “phase problem of crystallography” at least by approximative calculations.

Let us now familiarize with a little mathematics. The convolution integral of two functions f_1 and f_2 is defined by

$$f_1 \circ f_2 = f_1 \circ f_2(\bar{x}) = \int_{\infty} f_1(\bar{\xi}) \cdot f_2(\bar{x} - \bar{\xi}) dV_{\bar{\xi}}^{*1)}$$

\bar{x} are the parameters of the integral, the sign \circ means one function “convoluted with” the other one.



* 1) Here and later on holds $\bar{x} = x, y, z$; $\bar{b} = b_1, b_2, b_3$; $\bar{\xi} = \xi, \eta, \zeta$; $dV = dx dy dz$; $dV_b = db_1 db_2 db_3$; $dV_{\bar{\xi}} = d\xi d\eta d\zeta$

As can easily be shown the integral obeys the rules of algebraic multiplications, which are valid in both spaces:

Commutative law: $f_1 \cap f_2 = f_2 \cap f_1$;

Associative law: $f_1 \cap (f_2 \cap f_3) = (f_1 \cap f_2) \cap f_3$;

Distributive law: $(f_1 + f_2) \cap f_3 = f_1 \cap f_3 + f_2 \cap f_3$.

Furthermore let us introduce a “neutral” element, the so called point- or δ -function with

$$\int_{\infty} \delta(\vec{x}) dV_x = 1 \text{ (normalization)}$$

and
$$\delta(\vec{x}) = \begin{cases} \neq 0 \text{ if } |\vec{x}| \approx 0, 0, 0 & *2) \\ = 0 \text{ in all other points} \end{cases}$$

Obviously for any function $f(\vec{x})$

$$f \cap \delta = \delta \cap f = \int_{\infty} \delta(\vec{\xi}) \cdot f(\vec{x} - \vec{\xi}) dV_{\xi} \text{ is valid.}$$

Because f is (almost) constant in the range of δ (in the point $\vec{\xi} \approx (0, 0, 0)$), it can be drawn before the integral and then one gets

$$\delta \cap f = f(\vec{x}) \cdot \int_{\infty} \delta(\vec{\xi}) dV_{\xi} = f(\vec{x}).$$

This arithmetical behaviour can be used together with the arithmetic rules of the Fourier transform later on to simplify evaluations of diffraction measurements.

The Fourier transform is a parameter integral

$$F(\vec{b}) = FT[\rho(\vec{x})] = \int_{\infty} \rho(\vec{x}) e^{-2\pi i \vec{b} \cdot \vec{x}} dV_x, \quad *3)$$

as well as its inverse transformation

$$\rho(\vec{x}) = FT^{-1}[F(\vec{b})] = \int_{\infty} F(\vec{b}) e^{+2\pi i \vec{b} \cdot \vec{x}} dV_b,$$

where \vec{x} defines the physical space and \vec{b} the Fourier space (cp. Fig. 1).

Trying to transform as an example a Gaussian sphere one gets the result that a Gaussian leads to a Gaussian again, but the width is inverted, “the thick one will be thin in the other space” and reverse. This relationship led to the nomination “reciprocal space”.

Setting in the Fourier transform formula $|\vec{b}|=0$ and in the inverse transformation formula $|\vec{x}|=0$ one gets immediately the relationship that the value at the zeropoint of one space is the weight of the transformed function in the other space while the weight is equal to $\int_{\infty} \rho(\vec{x}) dV_x$.

Several theorems could be derived, which are very useful for the diffraction evaluation and for several other applications.

*2) Dirac's δ -function is not suited, because our point function has to be well defined in every point of the space, so everybody can use his own pointfunction, if it is zero outside a certain precision interval. The best suited function is a very small Gaussian sphere.

*3) $\vec{b} \cdot \vec{x} = |\vec{b}| \cdot |\vec{x}| \cos \angle(\vec{b}, \vec{x})$ the scalar product of \vec{b} with \vec{x} .

The convolution theorem

$$FT[\rho_1 \cap \rho_2] = FT[\rho_1] \cdot FT[\rho_2]; FT[\rho_1 \cap \rho_2] = FT[\rho_1] \cap FT[\rho_2]$$

in connection with the shift theorem with \vec{x}_0 =shift vector

$$FT[\rho(\vec{x} - \vec{x}_0)] = FT[\rho \cap \delta(\vec{x} - \vec{x}_0)] = FT[\rho] \cdot FT[\delta(\vec{x} - \vec{x}_0)] = FT[\rho] \cdot e^{2\pi i \vec{b} \cdot \vec{x}_0}$$

gives the possibility to calculate the diffraction behaviour of a periodic structure (e.g. a crystal or a multilayer) and leads to the Bragg law. Evidently for such a structure necessarily $\rho(\vec{x}) = \rho(\vec{x} - \vec{d})$ holds, where $|\vec{d}|$ is the periodic distance (e.g. the lattice constant), $\vec{d}/|\vec{d}|$ its direction and $\rho(\vec{x})$ the electron density of the sample.

Using the shift and convolution theorems one gets for the Fourier transform

$$FT[\rho(\vec{x})] = FT[\rho(\vec{x} - \vec{d})] = FT[\rho \cap \delta(\vec{x} - \vec{d})] = FT[\rho] \cdot FT[\delta(\vec{x} - \vec{d})] = FT[\rho] \cdot e^{2\pi i \vec{b} \cdot \vec{d}}$$

The equation

$$FT[\rho(\vec{x})] = FT[\rho(\vec{x})] \cdot e^{2\pi i \vec{b} \cdot \vec{d}}$$

is obviously valid if either $FT[\rho(\vec{x})] = 0$ or $e^{2\pi i \vec{b} \cdot \vec{d}} = \cos 2\pi \vec{b} \cdot \vec{d} + i \sin 2\pi \vec{b} \cdot \vec{d} = 1$.

Because $FT[\rho(\vec{x})]$ is the structure amplitude (see below) the value 0 has the meaning that there is no intensity.

The second solution is possible only if at first the imaginary part disappears. Because $|\vec{b}| \neq 0, |\vec{d}| \neq 0, \sin \vec{b} \cdot \vec{d} = 0$, follows, and therefore \vec{b} must be parallel to \vec{d} .

The remaining real part $\cos 2\pi \vec{b} \cdot \vec{d} = 1$ delivers $\vec{b} \cdot \vec{d} = \pm n$, where $n=1, 2, 3, \dots$ ($n=0$ is a trivial solution). With \vec{s}_0 and \vec{s}_h unit vectors in the directions of an incident and a reflected X-ray beam and the condition $\vec{b} \parallel \vec{d}$ the experimental situation sketched in Fig. 2 results. Due to the definition $\vec{b} = (\vec{s}_h - \vec{s}_0)/\lambda$ we find

$$n = \vec{b} \cdot \vec{d} = \frac{\vec{s}_h \cdot \vec{d} - \vec{s}_0 \cdot \vec{d}}{\lambda} = \frac{|\vec{d}|}{\lambda} \left[\cos\left(\frac{\pi}{2} - \Theta\right) - \cos\left(\frac{\pi}{2} + \Theta\right) \right] = \frac{2|\vec{d}|}{\lambda} \sin \Theta,$$

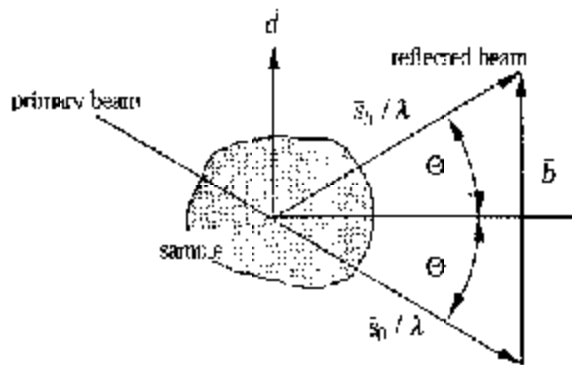


Fig. 2. Primary and reflected X-ray beam at a sample. (Wave vectors: $\vec{k}_0 = \vec{s}_0/\lambda, \vec{k}_h = \vec{s}_h/\lambda$; definition: $\vec{b} = \vec{k}_h - \vec{k}_0 = (\vec{s}_h - \vec{s}_0)/\lambda$; unit vectors: $|\vec{s}_h| = |\vec{s}_0| = 1$; Bragg angle Θ)

which is the usual form of the Bragg equation.

Obviously there is no need to consider lattice “planes”, the existence of a periodicity in the medium is sufficient to derive the equation.

A second example is the derivation of the formulae for the “Direct Methods of the Phase Determination”. It took several years to develop these formulae and their application, but a very easy derivation can be shown using the functional algebra.

For many structure evaluations the main interest is to find out the location of the atoms, neglecting their shape. Then the shape can be replaced by a “black and white” structure:

$$\rho(\vec{x}) = \begin{cases} 1 & \text{inside} \\ 0 & \text{outside} \end{cases} \text{ the atoms, no overlapping is allowed.}$$

This definition leads immediately to the equation $\rho(\vec{x}) = \rho^2(\vec{x}) = \rho^3(\vec{x}) \dots$ Its Fourier transform is using the convolution theorem:

$$\text{FT}[\rho] = \text{FT}[\rho^2] = \text{FT}[\rho] \cap \text{FT}[\rho] \dots$$

As the Fourier transform $\text{FT}[\rho]$ usually the expression $F(\vec{b})$ is taken which is called structure amplitude*⁴⁾ (Fig. 1). So we get

$$F(\vec{b}) = F(\vec{b}) \cap F(\vec{b}) = \int_{\infty} F(\vec{\beta}) \cdot F(\vec{b} - \vec{\beta}) dV_{\beta} \quad dV_{\beta} = d\beta_1 d\beta_2 d\beta_3$$

Evidently $\vec{b} = \vec{\beta} + (\vec{b} - \vec{\beta})$ holds, which is the so-called “ Σ_2 -relationship”. Because of $F(\vec{b}) = |F(\vec{b})| \cdot e^{i\varphi_b}$ (φ_b is the phase of the structure amplitude $|F(\vec{b})|$), we will get

$$|F(\vec{b})| \cdot e^{i\varphi_b} = \int_{\infty} |F(\vec{\beta})| \cdot |F(\vec{b} - \vec{\beta})| \cdot e^{i(\varphi_b + \varphi_{b-\beta})} dV_{\beta};$$

this is exactly the integral form of the Sayre equation [2], which promoted the Direct Methods. Taking the real and the imaginary parts of the Sayre equation separately according to Euler's law ($e^{i\phi} = \cos \phi + i \sin \phi$) and dividing the imaginary part by the real part we will get immediately the famous “tangent formula” [3] in integral representation:

$$\frac{\sin \varphi_b}{\cos \varphi_b} = \text{tg} \varphi_b = \frac{\int |F(\vec{\beta})| \cdot |F(\vec{b} - \vec{\beta})| \cdot \sin(\varphi_b + \varphi_{b-\beta}) dV_{\beta}}{\int |F(\vec{\beta})| \cdot |F(\vec{b} - \vec{\beta})| \cdot \cos(\varphi_b + \varphi_{b-\beta}) dV_{\beta}}$$

In the case of centrosymmetric structures the imaginary part is zero, so the “cosinus formula” [4] results:

$$\cos \varphi_b = \int |F(\vec{\beta})| \cdot |F(\vec{b} - \vec{\beta})| \cdot \cos(\varphi_b + \varphi_{b-\beta}) dV_{\beta}$$

After measuring the structure factors $|F(\vec{b})|^2$ the approximation steps of these formulae are starting with two known or suggested (φ -values (phases) which lead to a third one and so on.

A third example of the application of the function algebra is not restricted exclusively to the diffraction field.

*⁴⁾ Nomenclature of Max v. Laue.

Let us consider that a “true” function $A(\bar{x})$ may only be measured with a certain accuracy, which might be described by a known (e.g. Gaussian) error function $E(\bar{x})$. That means the result of the measurement will be $B(\bar{x}) = A(\bar{x}) \cap E(\bar{x})$: “A smeared by E”.

How can we calculate the “true” function $A(\bar{x})$? Using the convolution theorem we get

$$FT[B] = FT[A \cap E] = FT[A] \cdot FT[E],$$

$$FT[A] = \frac{FT[B]}{FT[E]} \text{ and finally } A = FT^{-1} \left[\frac{FT[B]}{FT[E]} \right]$$

Although the application of the Fourier integral is distributed widely in physics and related disciplines, the functional algebra is in use only rarely. The few examples may help to convince the reader that it might be useful to get into a closer relationship with this elegant mathematical method.

References

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