

Chapter 13-Diffracted beams

Delta function

We need some mathematical tools to develop a physical theory of electron diffraction. Ideal crystals are infinite things, so there will be some infinities lingering about. Usually, the infinite quantity only exists at a point in space - either direct or reciprocal - so we get finite numbers for things that we measure. And when we adjust our theory later for real, imperfect crystals, the infinite things become finite.

A delta function $\delta(x)$ (sometimes called a Dirac delta function), is positive infinity at just one place on the number line, where $x = 0$. It is zero every where else. But this is a somewhat intractable definition. A better definition is based on its “sampling property”. That is, whenever another function, such as $f(x)$, is multiplied by $\delta(x)$ and integrated over all, the result is $f(0)$.

$$f(0) = \int_{x=-\infty}^{\infty} f(x) \cdot \delta(x) \cdot dx$$

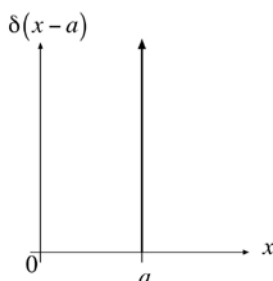
So say $f(x) = 1$. We can immediately notice a general property of $\delta(x)$:

$$1 = \int_{x=-\infty}^{\infty} \delta(x) dx$$

The integral from $-\infty$ to $+\infty$ can be thought of as a limit:

$$\int_{x=-\infty}^{\infty} \rightarrow \lim_{L \rightarrow \infty} \int_{x=-L}^L$$

Delta functions are sometimes called “unit impulse functions”.



Fourier transform

The Fourier transform $f(k)$ of a function $f(x)$ can be thought of as its frequency representation. The Fourier transform is invertible, so we can get $f(x)$ back from $f(k)$.

$$f(k) = \int_{x=-\infty}^{\infty} f(x) e^{-2\pi i k x} dx = \mathfrak{F}[f(x)] \text{ //Fourier transform}$$

$$f(x) = \int_{k=-\infty}^{\infty} f(k) e^{2\pi i k x} dk = \mathfrak{F}^{-1}[f(k)] \text{ //inverse Fourier transform}$$

We are using the \mathfrak{F} and \mathfrak{F}^{-1} symbols to represent the Fourier transform and inverse Fourier transform operations, which are both linear, meaning that $\mathfrak{F}[\alpha_1 f_1 + \alpha_2 f_2] = \alpha_1 \mathfrak{F}[f_1] + \alpha_2 \mathfrak{F}[f_2]$ for any functions f_1 and f_2 and coefficients α_1 and α_2 .

Here is an example:

$$f(x) = \delta(x-a) \Rightarrow f(k) = e^{-2\pi ika}$$

Notice that the delta function can be written as:

$$\delta(x) = \mathfrak{F}^{-1}(1) = \int_{k=-\infty}^{\infty} e^{2\pi i k x} dk$$

Here is another example with two delta functions:

$$f(x) = \frac{1}{2}[\delta(x-a) + \delta(x+a)] \Rightarrow f(k) = \cos(2\pi ka)$$

Convolution theorem

Convolutions of two functions show up when every point in one function is modified by another function:

$$f_1(x) * f_2(x) = \int_{x'=-\infty}^{\infty} f_1(x') f_2(x-x') dx'$$

Say we know the Fourier transforms of the two functions

$$f_1(k) = \mathfrak{F}\{f_1(x)\}, f_2(k) = \mathfrak{F}\{f_2(x)\}$$

The convolution theorem states that the Fourier transform of their convolution equals the product of their Fourier transforms:

$$\mathfrak{F}\{f_1(x) * f_2(x)\} = f_1(k) \cdot f_2(k)$$

Three-dimensional versions

The Fourier transform of a 3-D function f and the inverse FT are

$$f(\mathbf{k}) = \lim_{V \rightarrow \infty} \int_{\mathbf{r}}^V f(\mathbf{r}) e^{-2\pi i \mathbf{k} \cdot \mathbf{r}} d^3 r, f(\mathbf{r}) = \lim_{\Omega \rightarrow \infty} \int_{\mathbf{k}}^{\Omega} f(\mathbf{k}) e^{2\pi i \mathbf{k} \cdot \mathbf{r}} d^3 k$$

In 3-D, the delta function can still be written as an integral, and has the sampling property

$$\delta(\mathbf{r}) = \lim_{\Omega \rightarrow \infty} \int_{\mathbf{k}}^{\Omega} e^{2\pi i \mathbf{k} \cdot \mathbf{r}} d^3 k, f(\mathbf{r}_0) = \lim_{V \rightarrow \infty} \int_{\mathbf{r}}^V f(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}_0) d^3 r$$

The convolution of two 3-D functions is

$$f_1(\mathbf{r}) * f_2(\mathbf{r}) = \lim_{V \rightarrow \infty} \int_{\mathbf{r}'}^V f_1(\mathbf{r}') f_2(\mathbf{r} - \mathbf{r}') d^3 r'$$

The convolution theorem in 3-D becomes

$$\mathfrak{F}\{f_1(\mathbf{r}) * f_2(\mathbf{r})\} = f_1(\mathbf{k}) \cdot f_2(\mathbf{k})$$

Periodic functions

A Fourier series is a the representation of a periodic function by an infinite sum of harmonics:

$$f(\mathbf{r}) = \sum_{hkl} f_{hkl} e^{2\pi i \mathbf{g}_{hkl} \cdot \mathbf{r}}$$

The periodicity is guaranteed:

$$\begin{aligned}
 f(\mathbf{r} + \mathbf{r}_{uvw}) &= \sum_{hkl} f_{hkl} e^{2\pi i \mathbf{g}_{hkl} \cdot (\mathbf{r} + \mathbf{r}_{uvw})} \\
 &= \sum_{hkl} f_{hkl} e^{2\pi i \mathbf{g}_{hkl} \cdot \mathbf{r}} \cdot e^{2\pi i \mathbf{g}_{hkl} \cdot \mathbf{r}_{uvw}} \\
 &= \sum_{hkl} f_{hkl} e^{2\pi i \mathbf{g}_{hkl} \cdot \mathbf{r}} \cdot (1) \\
 f(\mathbf{r} + \mathbf{r}_{uvw}) &= f(\mathbf{r})
 \end{aligned}$$

In crystallography, we know will be summing over the RLVs by permuting the indices (hkl) among all integers, so we can adopt a shorthand notation:

$$f(\mathbf{r}) = \sum_{hkl} f_{hkl} e^{2\pi i \mathbf{g}_{hkl} \cdot \mathbf{r}} = \sum_{\mathbf{g}} f_{\mathbf{g}} e^{2\pi i \mathbf{g} \cdot \mathbf{r}}$$

In other words, the sum over the RLVs is an abbreviation for the sum over Miller indices:

$$\sum_{hkl} \rightarrow \sum_{\mathbf{g}}$$

Another delta function

It makes think clearer if we define another delta function to use in reciprocal space

$$\Delta(k) \equiv \lim_{L \rightarrow \infty} \left(\int_x^L e^{-2\pi i k x} dx \right) = \begin{cases} \infty, & k = 0 \\ 0, & \text{otherwise} \end{cases}$$

The 3-D version looks like

$$\Delta(\mathbf{k}) \equiv \lim_{V \rightarrow \infty} \left(\int_{\mathbf{r}}^V e^{-2\pi i \mathbf{k} \cdot \mathbf{r}} d^3 r \right) = \begin{cases} \infty, & \mathbf{k} = \mathbf{0} \\ 0, & \text{otherwise} \end{cases}$$

It is often more useful to define a normalized, discrete version

$$\Delta_{\mathbf{k}} \equiv \lim_{V \rightarrow \infty} \left(\frac{1}{V} \int_{\mathbf{r}}^V e^{-2\pi i \mathbf{k} \cdot \mathbf{r}} d^3 r \right) = \begin{cases} 1, & \mathbf{k} = \mathbf{0} \\ 0, & \text{otherwise} \end{cases}$$

This form avoids the puzzling infinities.

Proof of convolution theorem

Do you need proof of the convolution theorem? Here it is:

$$g(x) = f(x) * h(x) = \int_{x'} dx' f(x') h(x - x')$$

$$\begin{aligned} g(k) &= \mathfrak{T}\{g(x)\} = \int_x dx g(x) e^{-2\pi i k x} \\ &= \int_x dx \left[\int_{x'} dx' f(x') h(x - x') \right] e^{-2\pi i k x} \\ &= \int_x dx \int_{x'} dx' \left[\int_{k'} dk' f(k') e^{2\pi i k' x'} \right] \left[\int_{k''} dk'' h(k'') e^{2\pi i k'' (x - x')} \right] e^{-2\pi i k x} \\ &= \int_{k'} dk' \int_{k''} dk'' f(k') h(k'') \int_{x'} dx' e^{-2\pi i (k'' - k') x'} \int_x dx e^{-2\pi i (k - k'') x} \\ &= \int_{k'} dk' \int_{k''} dk'' f(k') h(k'') \Delta(k'' - k') \Delta(k - k'') \\ &= \int_{k''} dk'' f(k'') h(k'') \Delta(k - k'') \\ g(k) &= f(k) \cdot h(k) \end{aligned}$$

Fourier components

Say we define a normalized Fourier transform using the method for defining $\Delta_{\mathbf{k}}$:

$$f_{\mathbf{k}} = \lim_{V \rightarrow \infty} \left\{ \frac{1}{V} \int_{\mathbf{r}}^V f(\mathbf{r}) e^{-2\pi i \mathbf{k} \cdot \mathbf{r}} d^3 r \right\}$$

Assume $f(\mathbf{r})$ is periodic. Then

$$f(\mathbf{r}) = \sum_{\mathbf{g}} f_{\mathbf{g}} e^{2\pi i \mathbf{g} \cdot \mathbf{r}}$$

Evaluating the $f_{\mathbf{k}}$ gives:

$$\begin{aligned} f_{\mathbf{k}} &= \lim_{V \rightarrow \infty} \left[\frac{1}{V} \int_{\mathbf{r}}^V \left(\sum_{\mathbf{g}} f_{\mathbf{g}} e^{2\pi i \mathbf{g} \cdot \mathbf{r}} \right) e^{-2\pi i \mathbf{k} \cdot \mathbf{r}} d^3 r \right] \\ &= \sum_{\mathbf{g}} f_{\mathbf{g}} \left\{ \lim_{V \rightarrow \infty} \left[\frac{1}{V} \int_{\mathbf{r}}^V e^{2\pi i (\mathbf{g} - \mathbf{k}) \cdot \mathbf{r}} d^3 r \right] \right\} \\ f_{\mathbf{k}} &= \sum_{\mathbf{g}} f_{\mathbf{g}} \cdot \Delta_{\mathbf{g} - \mathbf{k}} \end{aligned}$$

In other words, for a periodic function, the Fourier coefficients for the RLVs are the only non-zero Fourier components.

Fourier components of crystal potential

The main function I have in mind in this discussion is the electrostatic potential, of a crystal, or crystal potential, for short. The crystal potential can be written as:

$$\Phi(\mathbf{r}) = \sum_{\mathbf{g}} \Phi_{\mathbf{g}} e^{2\pi i \mathbf{g} \cdot \mathbf{r}}$$

We can make some generalizations about the $\Phi_{\mathbf{g}}$. Let's look at the complex conjugate of $\Phi(\mathbf{r})$:

$$[\Phi(\mathbf{r})]^* = \sum_{\mathbf{g}} (\Phi_{\mathbf{g}})^* e^{-2\pi i \mathbf{g} \cdot \mathbf{r}}$$

It is usually a good starting point to assume $\Phi(\mathbf{r})$ is real. So

$$\begin{aligned}\Phi(\mathbf{r}) &= [\Phi(\mathbf{r})]^* \\ \sum_{\mathbf{g}} \Phi_{\mathbf{g}} e^{2\pi i \mathbf{g} \cdot \mathbf{r}} &= \sum_{\mathbf{g}} (\Phi_{\mathbf{g}})^* e^{2\pi i (-\mathbf{g}) \cdot \mathbf{r}} \\ \sum_{\mathbf{g}} \Phi_{\mathbf{g}} e^{2\pi i \mathbf{g} \cdot \mathbf{r}} &= \sum_{\mathbf{g}} (\Phi_{-\mathbf{g}})^* e^{2\pi i \mathbf{g} \cdot \mathbf{r}}\end{aligned}$$

So if the crystal potential is real, we can always say:

$$(\Phi_{\mathbf{g}})^* = \Phi_{-\mathbf{g}}$$

Now let's look at the what happens if we invert the crystal about the origin

$$\Phi(-\mathbf{r}) = \sum_{\mathbf{g}} \Phi_{\mathbf{g}} e^{-2\pi i \mathbf{g} \cdot \mathbf{r}}$$

If the origin is a center of inversion symmetry, then

$$\begin{aligned}\Phi(\mathbf{r}) &= \Phi(-\mathbf{r}) \\ \sum_{\mathbf{g}} \Phi_{\mathbf{g}} e^{2\pi i \mathbf{g} \cdot \mathbf{r}} &= \sum_{\mathbf{g}} \Phi_{\mathbf{g}} e^{-2\pi i \mathbf{g} \cdot \mathbf{r}} \\ \sum_{\mathbf{g}} \Phi_{\mathbf{g}} e^{2\pi i \mathbf{g} \cdot \mathbf{r}} &= \sum_{\mathbf{g}} \Phi_{-\mathbf{g}} e^{2\pi i \mathbf{g} \cdot \mathbf{r}}\end{aligned}$$

So, if the crystal potential is “centrosymmetric”, we can say:

$$\Phi_{\mathbf{g}} = \Phi_{-\mathbf{g}}$$

If the crystal potential is both real and centrosymmetric, then all of its Fourier coefficients are real:

$$\Phi_{\mathbf{g}} = \Phi_{-\mathbf{g}} = (\Phi_{\mathbf{g}})^* = \text{real}$$

Evaluating the crystal potential by convolution

The tools introduced here so far are intended to make life easier. For example consider a periodic array of delta functions, located at the lattice points of a crystal:

$$X(\mathbf{r}) = \sum_n \delta(\mathbf{r} - \mathbf{r}_n)$$

Now take the electrostatic potential $\phi(\mathbf{r})$ of just one unit cell. The convolution of these gives the crystal potential:

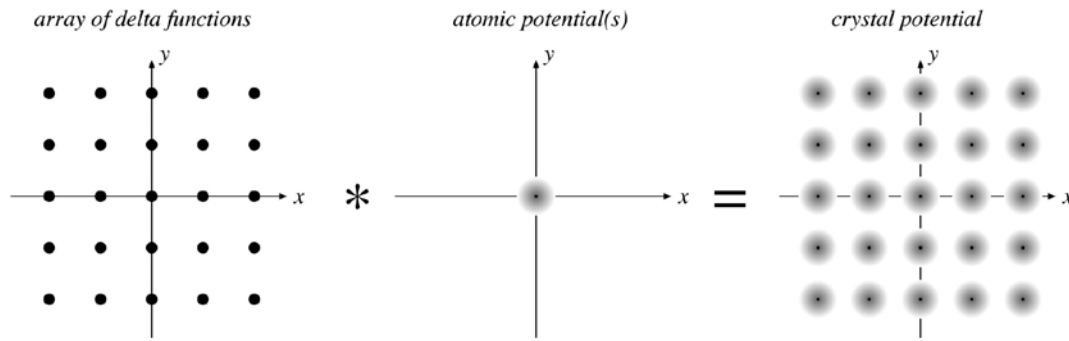
$$\Phi(\mathbf{r}) = \phi(\mathbf{r}) * X(\mathbf{r})$$

In direct space, we get back the expected sum of potentials for all unit cells

$$\Phi(\mathbf{r}) = \sum_n \phi(\mathbf{r} - \mathbf{r}_n)$$

The advantage comes in reciprocal space, where we can use the convolution theorem

$$\mathfrak{Z}[\Phi(\mathbf{r})] = \mathfrak{Z}[\phi(\mathbf{r})] \cdot \mathfrak{Z}[X(\mathbf{r})]$$



Crystal function (lattice sum)

Can we say anything else about $\mathfrak{F}[X(\mathbf{r})]$? For an infinite crystal

$$X(\mathbf{r}) = \lim_{N \rightarrow \infty} \left[\sum_{n=1}^N \delta(\mathbf{r} - \mathbf{r}_n) \right]$$

Its Fourier components are:

$$X_{\mathbf{k}} = \lim_{V \rightarrow \infty} \left\{ \frac{1}{V} \int_{\mathbf{r}} \lim_{N \rightarrow \infty} \left[\sum_{n=1}^N \delta(\mathbf{r} - \mathbf{r}_n) \right] e^{-2\pi i \mathbf{k} \cdot \mathbf{r}} d^3 r \right\} = \lim_{V \rightarrow \infty} \left\{ \frac{1}{V} \lim_{N \rightarrow \infty} \left[\sum_{n=1}^N e^{-2\pi i \mathbf{k} \cdot \mathbf{r}_n} \right] \right\}$$

We can just divide up space into unit-cell-sized regions, with one lattice point per region. If the unit cell volume is v , then $V = Nv$

$$X_{\mathbf{k}} = \lim_{N \rightarrow \infty} \left(\frac{1}{Nv} \sum_{n=1}^N e^{-2\pi i \mathbf{k} \cdot \mathbf{r}_n} \right) = \begin{cases} \frac{1}{v}, & \mathbf{k} = \text{an RLV} \\ 0, & \mathbf{k} = \text{otherwise} \end{cases}$$

So the Fourier series representation of the crystal function is very simple:

$$X(\mathbf{r}) = \sum_{\mathbf{g}} X_{\mathbf{g}} e^{2\pi i \mathbf{g} \cdot \mathbf{r}} = \left(\frac{1}{v} \right) \sum_{\mathbf{g}} e^{2\pi i \mathbf{g} \cdot \mathbf{r}}$$

Unit-cell potentials

The total crystal potential is a sum over unit-cell potentials:

$$\Phi(\mathbf{r}) = \lim_{N \rightarrow \infty} \left[\sum_{n=1}^N \phi(\mathbf{r} - \mathbf{r}_n) \right]$$

We can usually assume that the unit-cell potential is a sum over atomic potentials, with atoms located at their appropriate positions in the unit cell:

$$\phi(\mathbf{r}) = \sum_{m \text{ atoms}} \phi^{(m)}(\mathbf{r} - \mathbf{d}^{(m)})$$

We argued that the individual potentials for isolated atoms had spherical symmetry. So

$$\phi^{(m)}(g) = 4\pi \int_{r=0}^{\infty} r^2 \phi^{(m)}(r) \frac{\sin(2\pi g r)}{2\pi g r} dr$$

Thus, the Fourier transform of the unit-cell potential is:

$$\phi(\mathbf{g}) = \lim_{V \rightarrow \infty} \left\{ \int_{\mathbf{r}} \left[\sum_{m \text{ atoms}} \phi^{(m)}(\mathbf{r} - \mathbf{d}^{(m)}) \right] e^{-2\pi i \mathbf{g} \cdot \mathbf{r}} d^3 r \right\} = \sum_{m \text{ atoms}} \phi^{(m)}(\mathbf{g}) e^{-2\pi i \mathbf{g} \cdot \mathbf{d}^{(m)}}$$

The sign on the exponent of the phase factor is sometimes opposite by convention. Please bear with me.

Evaluating the Fourier components of the crystal potential

We saw that $\Phi(\mathbf{r})$ is the convolution

$$\Phi(\mathbf{r}) = \phi(\mathbf{r}) * X(\mathbf{r})$$

So $\Phi_{\mathbf{g}}$ is the product:

$$\Phi_{\mathbf{g}} = \phi(\mathbf{g}) \cdot X_{\mathbf{g}}$$

Total wave function

We often assume the wave function above the sample is described by a plane wave that represents the incident beam:

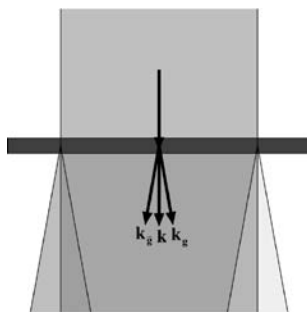
$$\psi(\mathbf{r}) = e^{2\pi i \mathbf{k} \cdot \mathbf{r}}$$

Below the sample, the total, transmitted wave function is a collection of diffracted beams, including 0, which are each plane waves with different amplitudes and traveling in different directions:

$$\psi(\mathbf{r}) = \sum_{\mathbf{g}} \Psi_{\mathbf{g}} e^{2\pi i \mathbf{k}_{\mathbf{g}} \cdot \mathbf{r}}$$

using the abbreviation

$$\mathbf{k}_{\mathbf{g}} = \mathbf{k} + \mathbf{g} + \mathbf{s}_{\mathbf{g}}$$



If we know the crystal structure and orientation, we also know the $\mathbf{k}_{\mathbf{g}}$. But we need a procedure to find the beam amplitudes $\Psi_{\mathbf{g}}$. Once we know those, the intensities of the diffraction spots will be

$$I_{\mathbf{g}} = |\Psi_{\mathbf{g}}|^2$$