

## 11. Crystal Potential

### Delta function

We need some mathematical tools to develop a physical theory of electron diffraction from crystal. 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 everywhere 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  $x$ , the result is  $f(0)$ .

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

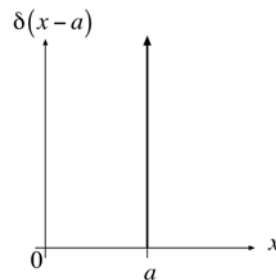
So, say  $f(x) = 1$ . We can immediately notice a general property of  $\delta(x)$ :

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

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  $\alpha_1$  and  $\alpha_2$ .

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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:

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

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  $f(\mathbf{r})$  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:

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

The periodicity is guaranteed:

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

$$f(\mathbf{r} + \mathbf{r}_{uvw}) = f(\mathbf{r})$$

When discussing crystals, we know we 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:

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

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

### 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  $\Phi(\mathbf{r})$  :

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

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:

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

### **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:

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

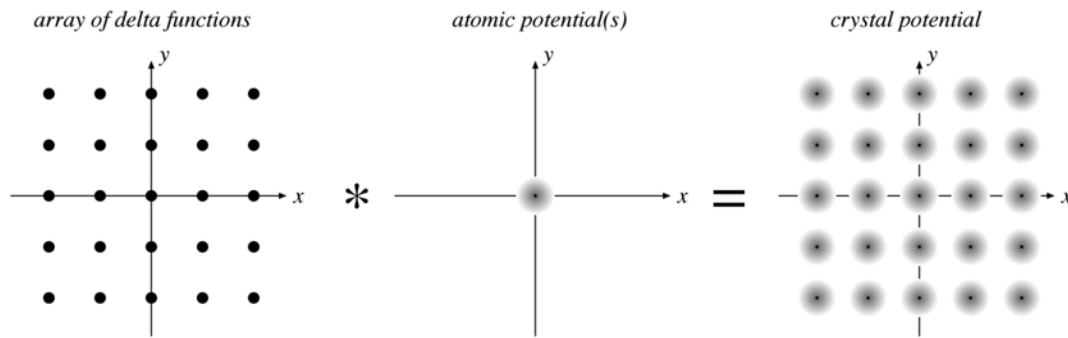
In direct space, we get back the expected sum of potentials for all unit cells

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

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

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

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### Crystal function (lattice sum)

Can we say anything in particular 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

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

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

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

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:

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