

**Bragg's Law**

$$n\lambda = 2d_{\text{unit cell}} \sin(\theta)$$

$$\lambda = 2d_{h,k,l} \sin(\theta_{h,k,l})$$

**smallest  $d_{h,k,l}$  is resolution**

$$\frac{1}{d_{h,k,l}} = \frac{2 \sin(\theta_{h,k,l})}{\lambda} \quad \text{so} \quad \frac{\sin(\theta_{h,k,l})}{\lambda} \text{ is a measure of resolution}$$

**Scalar value of amplitude equals the square root of the intensity (energy) of the wave.**

$$|F_{hkl}| = (I_{hkl})^{1/2} \quad I_{hkl} = |F_{hkl}|^2$$

“Intensity” has been corrected for polarization and other consequences of data collection method.

**A diffracted ray is the sum of contributions from all atoms.**

$$F \Rightarrow |F_{hkl}| \cdot e^{i\phi_{hkl}} = \sum_n O_n \cdot f_{n,\theta} \cdot e^{-B_n (\sin \theta / \lambda)^2} \cdot e^{i 2\pi (hx_n + ky_n + lz_n)}$$

**A diffracted ray is the sum of contributions from all electron density.**

$$|F_{hkl}| \cdot e^{i\phi_{hkl}} = \text{Volume}_{\text{(of repeating unit)}} \sum_x \sum_y \sum_z \rho_{xyz} \cdot e^{i 2\pi (hx + ky + lz)}$$

**Electron density is the Fourier transform of all diffracted rays.**

$$\rho_{xyz} = (\text{Vol})^{-1} \sum_h \sum_k \sum_\ell m_{hkl} \cdot |F_{hkl}| \cdot e^{i\phi_{hkl}} \cdot e^{-i 2\pi (hx + ky + lz)}$$

**Patterson map is the Fourier transform of the intensities.**

$$P_{xyz} = (\text{Vol})^{-2} \sum_h \sum_k \sum_\ell |F_{hkl}|^2 \cdot e^{-i 2\pi (hx + ky + lz)}$$

product of all electron densities separated by the x,y,z vector distance  
same shape and dimension unit cell

**Residuals, R-values, assess agreement between datasets. (here model vs experimental)**

$$R_{\text{cryst}} = \frac{\sum ||F_{\text{obs}}| - |F_{\text{calc}}||}{\sum |F_{\text{obs}}|}$$

$R_{\text{free}}$  calculated from  
otherwise unused 5%

$\lambda$	: wavelength of radiation
$d$	: interplanar spacing, the effective distance associated with a particular diffracted ray
$\theta_{hkl}$	: angle of incident beam to the $h, k, \ell$ Bragg plane
$h, k, \ell$	: integer index numbers of a particular Bragg Plane, a diffracted ray, a “reflection”, index of a point of the reciprocal lattice “reciprocal space”
$ F_{hkl} $	: amplitude of the $hkl^{\text{th}}$ diffracted ray
$\phi_{hkl}$	: the phase of the $hkl^{\text{th}}$ diffracted ray
$B$	: B-factor (historically the Temperature Factor, but dominated by other uncertainties)
$f_{n,\theta_{hkl}}$	: individual atomic scattering factor of the $n^{\text{th}}$ atom as a function of $\theta_{hkl}$
$x_n, y_n, z_n$	: coordinates of the $n^{\text{th}}$ atom
$m_{hkl}$	: figure of merit for phase of the $hkl^{\text{th}}$ diffracted ray
$N$	: total number of atoms in the repeating unit of the crystal
$O_n$	: occupancy of the $n^{\text{th}}$ atom.
$\text{Vol}$	: volume of the repeating unit, the unit cell
$\rho_{xyz}$	: electron density at coordinates x, y, z in the crystal “real space”
$P_{xyz}$	: Patterson function value at coordinates x,y,z : vector distances-between atom positions

## The equations: (Good-Parts version: what you really need to remember)

Bragg's law (as used to track each individual scattered ray):

$$\lambda = 2d_{h,k,l} \sin(\theta_{h,k,l}) \quad \frac{1}{d_{h,k,l}} = \frac{2 \sin(\theta_{h,k,l})}{\lambda} \quad \text{between } d_{h,k,l} \text{ and } \theta_{h,k,l}$$

Remember this equation!

Note the reciprocal relationship

d: distance, but direction only implied!

$d_{h,k,l}$  is a particular indexed distance in the crystal, and is the “resolution” of the  $h,k,l$  diffracted ray. The smaller the  $d$ , the better the resolution, thus the best resolution data is from diffracted rays with the largest angles. The index carries a lot of the “direction” information.

These “ $d$ ”s are distances between “Bragg Planes”. Bragg Planes are simply ways of dividing the unit-cells of the crystal into equally spaced intervals (the “ $d$ ” spacing). So Bragg Planes are oriented families of parallel planes with a particular separation. The  $h,k,l$  indices, along with the unit cell dimensions and shape, define both the orientation and the  $d$ -spacing of a particular set of Bragg Planes.

(The unit cell is the basic repeating unit of the crystal: the repeat is done entirely by translations, and the unit cells “tile” (completely fill) the volume of the crystal.)

The “ $\theta$ ” is the angle the ray makes to the Bragg Plane, and in the defining construction the angle of the incident ray is equal to the angle of the diffracted ray, just like a classical reflection, so the diffracted rays are often called “reflections”.

### CAVEAT:

When discussing crystallography, many people remember Bragg's law this way:

$$n\lambda = 2d \sin(\theta) \quad \text{more specifically:} \quad n\lambda = 2d_{\text{unit cell}} \sin(\theta)$$

where  $\lambda$  is the wavelength of the x-rays,  $d$  is a dimension of the unit cell of the crystal, and  $\theta$  is the angle of the scattered ray from “Bragg Planes”, and the integer  $n$  is the number of wavelengths of path difference between a ray scattered from one side of the unit cell and a ray scattered from the opposite side of the unit cell.

The “ $n$ ” formula brings to mind vibrating string harmonics. Indeed, we will see how the electron density can be thought of as a sum of standing waves in the box of the unit cell.

This  $n$ , the order of the diffraction, is useful for fiber diffraction and is reasonably convenient for small molecule crystals with very small unit cells, BUT can be very confusing when thinking about diffraction from macromolecular crystals. (For convenience, the examples drawn in text books and lecture notes show small unit cells, so drawings with the “ $n$ ” form seem to make sense. However, in real life, or with general equations, dealing with large unit cells, everything is done in terms of uniquely indexed Bragg planes, i.e. uniquely indexed diffraction events.).

## The equations: (Good-Parts version: what you really need to remember, cont'd.)

A light wave ray diffracted from a molecule in a crystal:

A wave is defined by an Amplitude  $|F_{hkl}|$  and a Phase:  $e^{i\phi_{hkl}}$

Each diffracted “wave” is a sum of contributions from ALL atoms:

$$\sum_n^N (\text{Amplitude-factors}) \cdot (\text{Phase-factor}) \quad \dots \text{the sum is over all atoms.}$$

Amplitude-factors are a property of the atom, including uncertainty about its position.

(Uncertainties are put into the B-factor. Many people think they understand the B-factor because they remember hearing about the Temperature Factor from Physics, for macromolecules the temperature part of the B-factor is only a minor part, most of the effect comes from other kinds of disorder.)

Phase-factor is just dependent on the position of the atom.

And now the equation we will derive (and that crystallographers should be familiar with):

Remember this equation for your prelim!

$$\vec{F} = |F_{hkl}| \cdot e^{i\phi_{hkl}} = \sum_n^N O_n \cdot f_{n,\theta_{hkl}} \cdot e^{-B_n (\sin\theta_{hkl}/\lambda)^2} \cdot e^{i2\pi(hx_n + ky_n + lz_n)}$$

$h, k, \ell$  : integer index numbers of a particular Bragg Plane, a diffracted ray, a “reflection”.

$\theta_{hkl}$  : angle of incident beam to the  $h, k, \ell$  Bragg plane

$|F_{hkl}|$  : amplitude of the  $hkl^{\text{th}}$  diffracted ray

$\phi_{hkl}$  : the phase of the  $hkl^{\text{th}}$  diffracted ray

B : B-factor (historically the Temperature Factor, but dominated by other uncertainties)

$f_{n,\theta_{hkl}}$  : individual atomic scattering factor of the  $n^{\text{th}}$  atom as a function of  $\theta_{hkl}$

$x_n, y_n, z_n$  : coordinates of the  $n^{\text{th}}$  atom

N : total number of atoms in the repeating unit of the crystal

$O_n$  : occupancy of the  $n^{\text{th}}$  atom. (e.g. for a half-occupied ligand, sidechain alternate rotamer, etc.)

## The equations: (Good-Parts version: segue into a trick...)

The wave equation depends on a model of the structure (i.e. atomic coordinates) --- but that is the result of the process, the whole problem is that we don't know any of the coordinates in the beginning! We really want to run that equation backwards and calculate the model from the diffracted waves. The trick is to cast the equation into the form of a Fourier Transform equation which can be reformulated backwards.

So, take this equation:

**A diffracted wave is the sum of contributions from all atoms.**

$$\vec{F} = |F_{hkl}| \cdot e^{i\phi_{hkl}} = \sum_n^N O_n \cdot f_{n,\theta_{hkl}} \cdot e^{-B_n (\sin\theta_{hkl}/\lambda)^2} \cdot e^{i2\pi(hx_n + ky_n + lz_n)}$$

And recast it in terms of continuous density instead of individual atoms:

**A diffracted wave is the sum of contributions from all electron density.**

$$|F_{hkl}| \cdot e^{i\phi_{hkl}} = \left( \begin{matrix} \text{Volume} \\ \text{of} \\ \text{unit cell} \end{matrix} \right) \sum_x \sum_y \sum_z \rho_{xyz} \cdot e^{i2\pi(hx + ky + lz)}$$

And now we can work it backwards:                      the **Trick**

**Electron density is the Fourier transform of all diffracted waves.**

$$\rho_{xyz} = (\text{Vol})^{-1} \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} m_{hkl} \cdot |F_{hkl}| \cdot e^{i\phi_{hkl}} \cdot e^{-i2\pi(hx + ky + lz)}$$

Amplitude = (Amplitude-factors) • (Phase-factors)  
(electron density has no phase)                      here the x,y,z is the point in the unit cell where we are calculating the density, if we do this for the whole unit cell, then we'll see everything that is possible to see.

So, can we do it? What is known about the factors on the right side of the equation?

$m_{hkl}$  is the figure of merit for phases, we'll get that when we figure out the phases.

$|F_{hkl}|$  is the amplitude of the  $hkl^{\text{th}}$  diffracted wave,  $|F_{hkl}| = (I_{hkl})^{1/2}$  and  $I_{hkl}$  is the Intensity of the diffracted wave, which we can measure!

$e^{-i2\pi(hx + ky + lz)}$  is easy: we know  $h,k,l$  for each wave and the  $x,y,z$  of the point being calculated.  
 $e^{i\phi_{hkl}}$  is the hooker, we do NOT know  $\phi_{hkl}$  the phase for the  $hkl^{\text{th}}$  diffracted wave.

So now we have to do some work -- find ways to recover the phase of each diffracted wave that was lost when we measured just the intensity.

**Two kinds of waves:** these last big equations are of a form:  
 (Amplitude factor) • (Phase factor) Which is just the general equation of a wave.  
 However, there are two varieties:

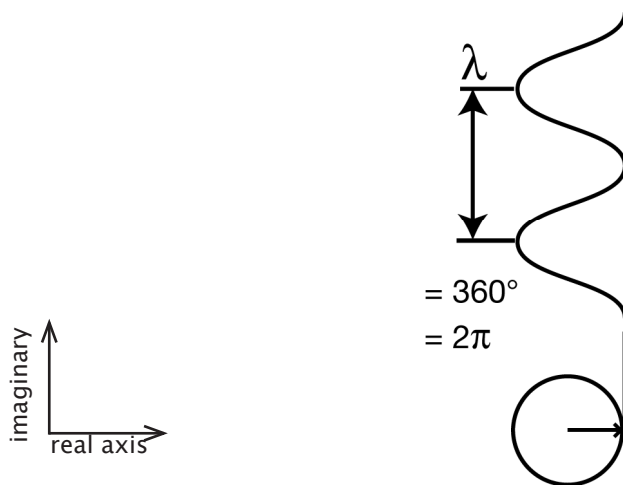
1)  $|F_{hkl}| \cdot e^{i\phi_{hkl}}$  the expression for a real x-ray, with a real, experimentally fixed, wavelength.

A resultant diffracted x-ray wave from the crystal is the sum of x-ray waves scattered from each and every atom in that crystal in a particular direction. Each resultant wave, indexed as  $h,k,l$ , travels out of the crystal in that particular direction, so we will need to learn how to combine parallel x-ray waves to form a resultant wave.

2) (amplitude factor) •  $e^{-i2\pi(hx + ky + \ell z)}$  some other kind of wave, with wavelengths that turn out to be integral fractions of the dimensions of the unit cell.

The electron density in a model of the crystal is the sum of these second kind of waves. Not only are the wavelengths of these density waves different from each other, each wave is going in its own particular direction. The wavelengths are integral fractions of unit cell dimensions (i.e. 1,2,3,... complete cycles within the bounds of the unit cell), thus they are standing waves. So we will need to learn how to combine standing waves in a box (the unit cell) to build up a density-like image.

Representing waves, the phase clock (with radius = amplitude):



$\phi$  factor ( $e^{i\phi}$ ): exponential form convenient to talk about;  $e^{i\phi} = \cos(\phi) + i \sin(\phi)$   
 $\cos()$  &  $\sin()$  form (real and imaginary components) sometimes more convenient for computation.