

Handout 6: Structure Factors

How to get more than unit cell sizes from your diffraction data

Chem 6850/8850

X-ray Crystallography

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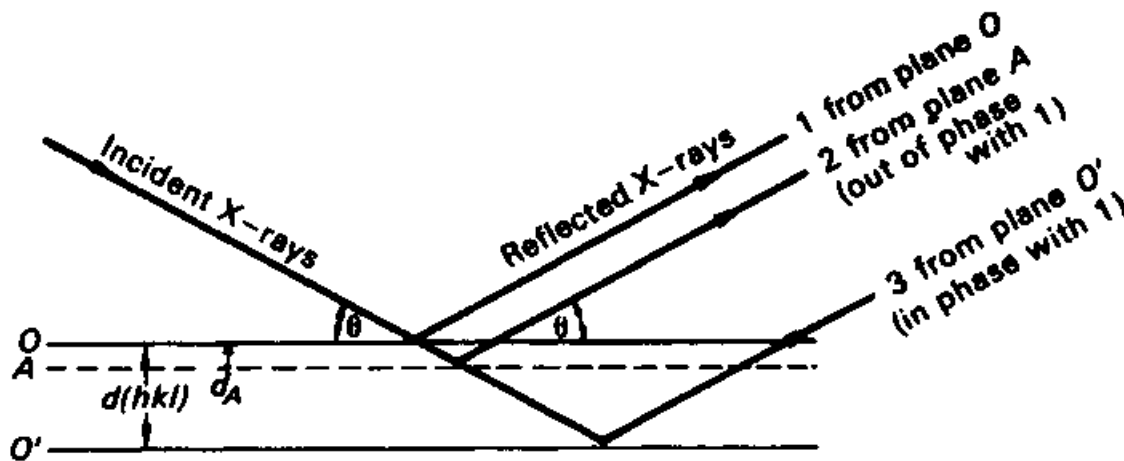
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Yet again... expanding convenient concepts

- **First concept introduced: Reflection from lattice planes**
 - facilitates derivation of Bragg's law
 - explains the location of spots on the observed diffraction pattern
- **Second concept introduced: Scattering from atoms, all the electron density was assumed to be concentrated in a “lattice point” (e.g., origin of the unit cell)**
 - gave the correct locations for spots in the diffraction pattern
- **But what about atoms that are located “between lattice planes”?**
 - any atom can scatter an X-ray that hits it
 - what does this imply for the overall scattering amplitude?

Atoms “between lattice planes”

- “Atoms between lattice planes” will always scatter X-rays so that the resulting wave is partially out of phase with X-rays scattered from the “lattice planes”
 - the “lattice planes” can be envisioned as atoms located in the plane



“Structure Determination by X-ray Crystallography”, Ladd and Palmer, Plenum, 1994.



Description of a plane

- Point P can be described by the vector \mathbf{p} , which is perpendicular to the plane LMN, or by the coordinates (X,Y,Z)

- the intercept equation of the plane is given by

$$X/a_p + Y/b_p + Z/c_p = 1$$

- this can be rearranged to

$$X \cos\chi + Y \cos\psi + Z \cos\omega = p$$

- describes family of parallel planes that are located at distance $|\mathbf{p}|$ from 0

$$a_p = p/\cos\chi, \quad b_p = p/\cos\psi, \quad c_p = p/\cos\omega \quad (4.2)$$

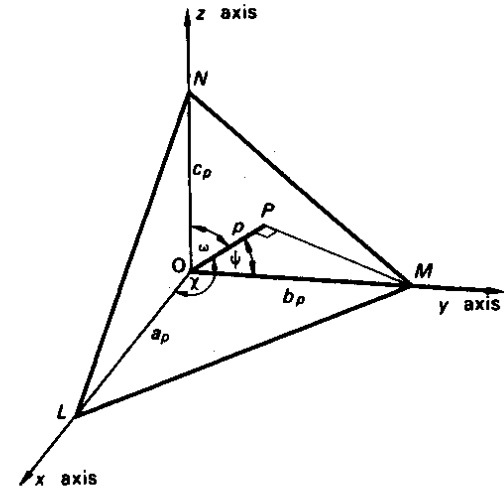


FIGURE 4.2. Plane LMN referred to general (triclinic) axes; OP of length p is the perpendicular from the origin to the plane.

“Structure Determination by X-ray Crystallography”, Ladd and Palmer, Plenum, 1994.



Path difference

$$X \cos\chi + Y \cos\psi + Z \cos\omega = p$$

For plane O': $p = d_{hkl}$; $a_p = a/h$; $b_p = b/k$; $c_p = c/l$

$$\cos\chi = d_{hkl}/(a/h); \cos\psi = d_{hkl}/(b/k); \cos\omega = d_{hkl}/(c/l)$$

For plane A: $p_A = d_A$; atom at (X_A, Y_A, Z_A)

$$\Rightarrow d_A = X_A \cdot \frac{d_{hkl}}{a/h} + Y_A \cdot \frac{d_{hkl}}{b/k} + Z_A \cdot \frac{d_{hkl}}{c/l}$$

$$d_A = (hx_A + ky_A + lz_A)d_{hkl} \quad \text{using fractional coordinates}$$

According to Bragg's law, the path difference between O and A is

$$\delta_A = 2d_A \sin\theta_{hkl} = 2d_{hkl} \sin\theta_{hkl} (hx_A + ky_A + lz_A)$$

$$\Rightarrow \delta_A = \lambda (hx_A + ky_A + lz_A)$$



Using wave equations instead

We can describe a wave as

$$W_0 = f \cdot \cos(2\pi X/\lambda) \quad \text{or} \quad W_0 = f \cdot \cos(\omega t)$$

where W_0 is the transverse displacement of a wave moving in the X direction, the maximum amplitude is f at $t=0$ and $X=0$

For other waves with a maximum at $t=t_n$ and $X=X_n$, we can write

$$W_n = f_n \cdot \cos(2\pi X/\lambda - \phi_n) \quad \text{where} \quad \phi_n = 2\pi X_n/\lambda$$

Two arbitrary waves of same frequency can then be represented as

$$W_1 = f_1 \cdot \cos(\omega t - \phi_1) = f_1 \cdot [\cos(\omega t) \cos(\phi_1) + \sin(\omega t) \sin(\phi_1)]$$

$$W_2 = f_2 \cdot \cos(\omega t - \phi_2) = f_2 \cdot [\cos(\omega t) \cos(\phi_2) + \sin(\omega t) \sin(\phi_2)]$$

Sum: $W = W_1 + W_2 = \cos(\omega t) \cdot (f_1 \cdot \cos(\phi_1) + f_2 \cdot \cos(\phi_2)) + \sin(\omega t) \cdot (f_1 \cdot \sin(\phi_1) + f_2 \cdot \sin(\phi_2))$

Wave equations continued

We know that we can write any wave as

$$W = F \cos(\omega t - \phi) = F [\cos(\omega t) \cos(\phi) + \sin(\omega t) \sin(\phi)]$$

Comparison with the equations on the last slide gives

$$F \cos(\phi) = f_1 \cos(\phi_1) + f_2 \cos(\phi_2)$$

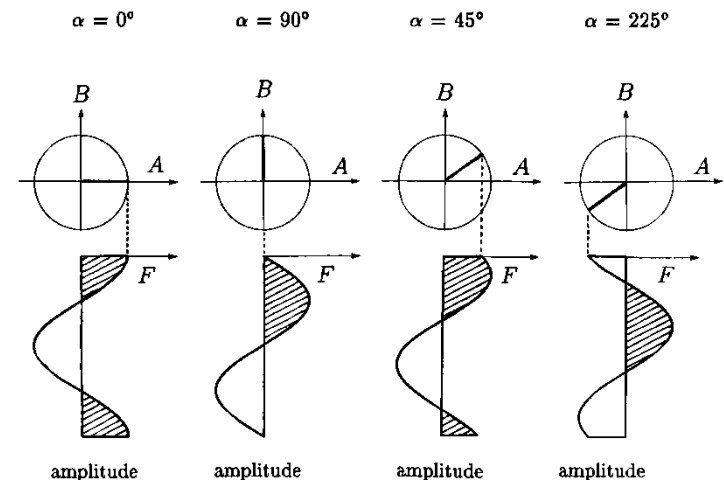
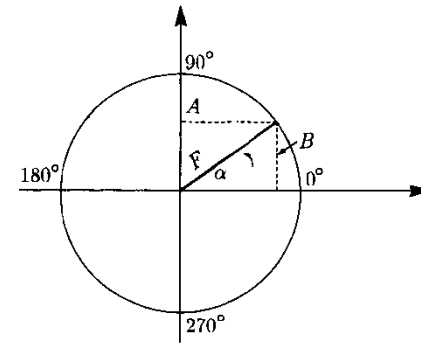
$$F \sin(\phi) = f_1 \sin(\phi_1) + f_2 \sin(\phi_2)$$

F can be calculated as

$$F = [(f_1 \cos(\phi_1) + f_2 \cos(\phi_2))^2 + (f_1 \sin(\phi_1) + f_2 \sin(\phi_2))^2]^{1/2}$$

Argand diagrams

- Waves can be represented as vectors in an Argand diagram
 - represented with real and imaginary components
 - allows for straightforward wave addition
 - For any given wave, we can write $\mathbf{F} = |\mathbf{F}| \cdot (\cos(\alpha t) + i \cdot \sin(\alpha t)) = |\mathbf{F}| \cdot e^{i\alpha t}$ (compare to slide 12 of handout 4!)



“Crystal Structure Analysis for Chemists and Biologists”, Glusker, Lewis and Rossi, VCH, 1994.

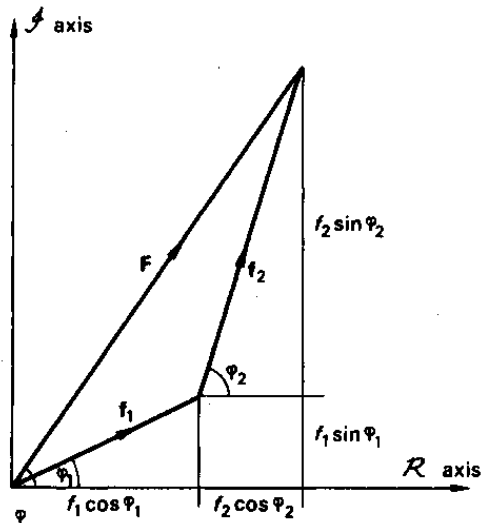


Wave addition using Argand diagrams

- Any number of waves can be added using an Argand diagram

- For N waves,
$$F \cos(\varphi) = \sum_{j=1}^N f_j \cos(\varphi_j); \quad F \sin(\varphi) = \sum_{j=1}^N f_j \sin(\varphi_j)$$

- Alternatively, we can write
$$\mathbf{F} = \sum_{j=1}^N f_j \mathbf{e}^{i\varphi_j} = |F| \mathbf{e}^{i\varphi}$$



“Structure Determination by X-ray Crystallography”, Ladd and Palmer, Plenum, 1994.

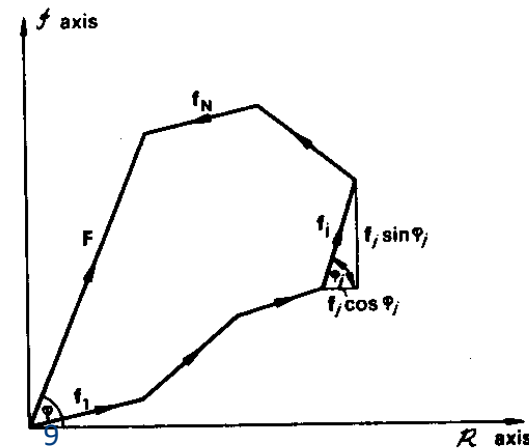


FIGURE 4.8. Combination of N waves ($N = 6$) on an Argand diagram; $\mathbf{F} = \sum_{j=1}^6 f_j \mathbf{e}^{i\varphi_j}$.

FIGURE 4.7. Combination of the two waves, $f_1 \mathbf{e}^{i\varphi_1}$ and $f_2 \mathbf{e}^{i\varphi_2}$, as vectors on an Argand diagram.

Phase difference

- From our treatment of path differences of waves scattered by arbitrary atoms, we obtained

$$\delta_A = \lambda(hx_A + ky_A + lz_A)$$

- The corresponding phase difference can be written as

$$\varphi_j = (2\pi/\lambda)\delta_j = 2\pi(hx_j + ky_j + lz_j)$$

- This implies that our expression for **F** depends on the diffraction direction as described by the Miller indices *hkl* (or the diffraction angle, if you prefer)

Structure factors

- \mathbf{F} should be more properly written as $\mathbf{F}(hkl)$ or \mathbf{F}_{hkl} to express its dependence on the diffraction angle
- There will be a unique $\mathbf{F}(hkl)$ corresponding to each reflection in a diffraction pattern
 - note – and remember! – that all atoms in a crystal contribute to every $\mathbf{F}(hkl)$.
- $\mathbf{F}(hkl)$ is called the *structure factor* for the (hkl) reflection
- Can be broken down in its real and imaginary components

$$\mathbf{F}(hkl) = A(hkl) + iB(hkl)$$

where

$$A(hkl) = \sum_{j=1}^N f_j \cos(2\pi(hx_j + ky_j + lz_j))$$

$$B(hkl) = \sum_{j=1}^N f_j \sin(2\pi(hx_j + ky_j + lz_j))$$

Atomic scattering factors

- The individual atomic components, f_j , are called *atomic scattering factors*
 - depend on nature of atom, direction of scattering, and X-ray wavelength
 - provide a measure of how efficiently an atom scatters X-rays compared to an electron
 - usually written as f_j although they should be written as $f_{j,\theta,\lambda}$
 - listed as a function of $\sin(\theta)/\lambda$ for each atom in the International Tables
 - maximum value of f_j is Z_j the number of electrons of the j^{th} atom

Intensity and structure factors

- We cannot measure structure factors, instead, we will measure the intensity of diffracted beams

$$I(hkl) \propto \mathbf{F}(hkl)\mathbf{F}^*(hkl)$$

$$\mathbf{F}^*(hkl) = |F(hkl)|e^{-i\varphi}$$

$$|F(hkl)|^2 = A^2(hkl) + B^2(hkl)$$

- The phase is given by

$$\tan(\varphi) = B(hkl)/A(hkl)$$

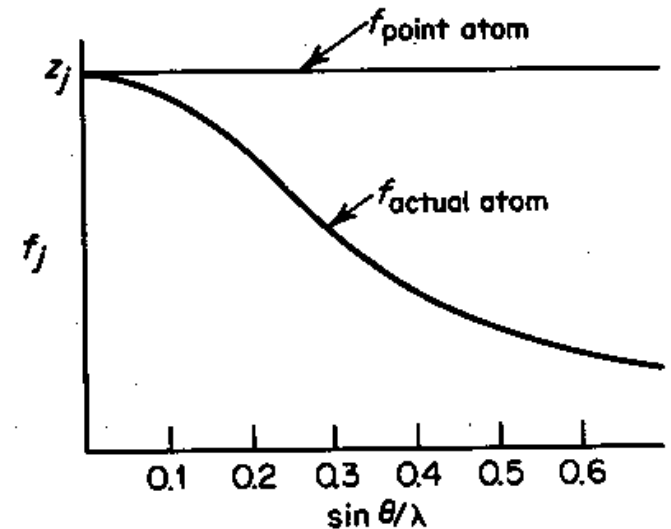
- Problem: We lose the phase information when measuring intensities!

Factors between I and F

- There are several factors between I and F that will change the measured intensity:
 - thermal vibration of the atoms: $\exp[-B_j(\sin^2(\theta)/\lambda^2)]$
 - Lorentz factor, for normal 4 circle diffractometers: $1/\sin(2\theta)$
 - absorption: $e^{-\mu t}$, where μ is the linear absorption coefficient and t the thickness of the specimen
 - polarization: $p = (1+\cos^2(2\theta))/2$
 - scale factor

Thermal vibration

- Thermal vibration “smears out” the electron cloud surrounding an atom
 - we see time average over all configurations
 - displacement of atoms leads to slight phase difference for atoms in neighboring unit cells
 - $f = f_0 \cdot \exp[-B_j(\sin^2(\theta)/\lambda^2)]$
 - $B_j = 8\pi^2 \langle u^2 \rangle$
 - $\langle u^2 \rangle$ is the mean square amplitude of displacement



Systematic absences

- Some reflections will be systematically absent from your diffraction pattern
- These absences are a result of
 - lattice centering
 - glide planes
 - screw axes
- Note that simple rotations and mirror planes do not give systematic absences!
- Space groups can be assigned based on systematic absences & Laue symmetry

Systematic absences (2)

TABLE 4.1. Limiting Conditions for Unit-Cell Type

Unit-cell type	Limiting conditions	Translations associated with the unit-cell type
<i>P</i>	None	None
<i>A</i>	<i>hkl</i> : $k + l = 2n$	$b/2 + c/2$
<i>B</i>	<i>hkl</i> : $h + l = 2n$	$a/2 + c/2$
<i>C</i>	<i>hkl</i> : $h + k = 2n$	$a/2 + b/2$
<i>I</i>	<i>hkl</i> : $h + k + l = 2n$	$a/2 + b/2 + c/2$
<i>F</i>	<i>hkl</i> : $h + k = 2n$	$a/2 + b/2$
	<i>hkl</i> : $k + l = 2n$	$b/2 + c/2$
	<i>hkl</i> : $(h + l = 2n)^a$	$a/2 + c/2$
<i>R_{hex}</i> ^b	<i>hkl</i> : $-h + k + l = 3n$ (obv)	$\begin{cases} a/3 + 2b/3 + 2c/3 \\ 2a/3 + b/3 + c/3 \end{cases}$
	<i>hkl</i> : $h - k + l = 3n$ (rev)	$\begin{cases} a/3 + 2b/3 + c/3 \\ 2a/3 + b/3 + 2c/3 \end{cases}$

^a This condition is not independent of the other two, as may be shown easily.

^b See page 70 and Table 2.3.

TABLE 4.2. Limiting Conditions for Screw Axes

Screw axis	Orientation	Limiting condition	Translation component
2 ₁	<i>a</i>	<i>h</i> 00: $h = 2n$	$a/2$
2 ₁	<i>b</i>	0 <i>k</i> 0: $k = 2n$	$b/2$
2 ₁	<i>c</i>	00 <i>l</i> : $l = 2n$	$c/2$
3 ₁ or 3 ₂	<i>c</i>	000 <i>l</i> : $l = 3n$	$c/3, 2c/3$
4 ₁ or 4 ₃	<i>c</i>	000 <i>l</i> : $l = 4n$	$c/4, 3c/4$
4 ₂	<i>c</i>	000 <i>l</i> : $l = 2n$	$2c/4(c/2)$
6 ₁ or 6 ₅	<i>c</i>	000 <i>l</i> : $l = 6n$	$c/6, 5c/6$
6 ₂ or 6 ₄	<i>c</i>	000 <i>l</i> : $l = 3n$	$2c/6, 4c/6(c/3, 2c/3)$
6 ₃	<i>c</i>	000 <i>l</i> : $l = 2n$	$3c/6(c/2)$

TABLE 4.3. Limiting Conditions for Glide Planes

Glide plane	Orientation	Limiting condition	Translation component
<i>a</i>	⊥ <i>b</i>	<i>h</i> 0 <i>l</i> : $h = 2n$	$a/2$
<i>a</i>	⊥ <i>c</i>	<i>h</i> <i>k</i> 0: $h = 2n$	$a/2$
<i>b</i>	⊥ <i>a</i>	0 <i>k</i> <i>l</i> : $k = 2n$	$b/2$
<i>b</i>	⊥ <i>c</i>	<i>h</i> <i>k</i> 0: $k = 2n$	$b/2$
<i>c</i>	⊥ <i>a</i>	0 <i>k</i> <i>l</i> : $l = 2n$	$c/2$
<i>c</i>	⊥ <i>b</i>	<i>h</i> 0 <i>l</i> : $l = 2n$	$c/2$
<i>n</i>	⊥ <i>a</i>	0 <i>k</i> <i>l</i> : $k + l = 2n$	$b/2 + c/2$
<i>n</i>	⊥ <i>b</i>	<i>h</i> 0 <i>l</i> : $h + l = 2n$	$a/2 + c/2$
<i>n</i>	⊥ <i>c</i>	<i>h</i> <i>k</i> 0: $h + k = 2n$	$a/2 + b/2$

“Structure Determination by X-ray Crystallography”, Ladd and Palmer, Plenum, 1994.

