

X-ray Scattering and Structure Factors

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Developing a Theory of X-ray Diffraction by Crystals

- What do we mean by “theory” or “theoretical model” in X-ray crystallography?

Developing a Theory of X-ray Diffraction by Crystals

- What do we mean by “theory” or “theoretical model” in X-ray crystallography?
- In physical science a theory is:
 - A mathematical model (an equation or several equations) which both accounts for observed phenomena and gives accurate and precise predictions for that phenomenon.
 - Mathematical models are quantitative (we use numbers to evaluate how well our model fits observations)

Theoretical Development of Crystals and X-ray Diffraction by Crystals

Observable	Theoretical Model	Accounts for
Lattice of diffraction maxima	Lattice and basis vectors, transformations to “reciprocal space”	Geometry of overall observed diffraction pattern
Individual diffraction maxima	Bragg's Law, Laue equations	Position (angular deviation) of diffraction maxima relative to source X-ray beam
Diffraction symmetry	Point Group Theory	Symmetry in the intensity weighted reciprocal lattice
Systematic absences in diffraction pattern	Space Group Theory	Systematically absent reflections due to translational symmetry
Intensity distribution in diffraction pattern	Structure Factor Theory	Diffraction intensity as a function of atomic (electron) density distribution in crystal

X-ray Interactions with Matter

- X-rays photons interact with matter in 2 ways:
 - Absorption of photon
 - Scattering (deflection of photon from its path by encountering another particle)
 - We are primarily concerned with X-ray photons being scattered by electrons
 - Compton Scattering (Inelastic Scattering)
 - Thomson Scattering (Elastic Scattering)

Theoretical Treatment of X-ray Scattering

- Use Quantum Electrodynamics (QED) for the rigorous quantum mechanical treatment of scattering of X-ray photons by electrons
- QED is complicated
- Fortunately, the classical equations for Compton and Thomson scattering are recovered from QED treatment
- See, for example:
<https://sites.ualberta.ca/~gingrich/courses/phys512/node102.html>

Classical Theory of X-ray Scattering

- We won't treat X-rays as photons, but as electromagnetic radiation with oscillating E (electric) and B (magnetic) fields.
- Electrons will be treated as charged particles of known mass and charge.

And now for something completely different ...
a brief mathematical interlude

Brief Review: Waves, Vectors, Complex Numbers

- The sinusoidal motion is traced out by vector \mathbf{f} rotating around the origin.
- f is the amplitude of the vector
- ϕ designates the orientation of the vector
- OB is the projection of \mathbf{f} along the horizontal axis as it rotates about the origin. $OB = f \cos(\phi)$
- If \mathbf{f} is rotating at a constant angular velocity, plotting OB as a function of ϕ traces out a cosine (or sin) wave

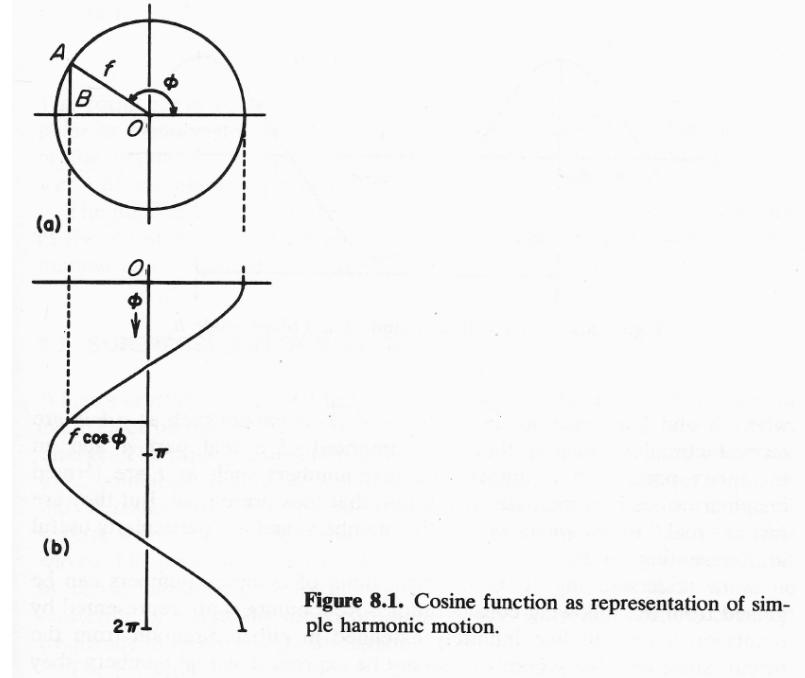


Figure 8.1. Cosine function as representation of simple harmonic motion.

Brief Review: Phase Angles

- A phase angle arises if the wave traced out by our rotating \mathbf{f} vector is shifted along the φ axis by an amount δ
- We can think of the phase angle as the relationship between our rotating vector, \mathbf{f} , and a rotating reference vector when the reference vector is oriented along the horizontal axis
- To characterize \mathbf{f} we need both $|\mathbf{f}|$ and δ

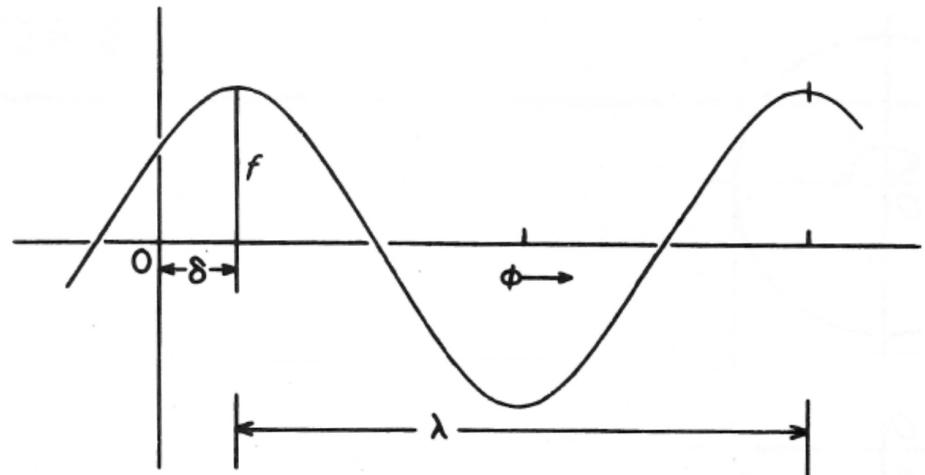


Figure 8.2. Wave with amplitude f and phase angle δ .

Brief Review: Complex Numbers

- Complex number has the form:
- $z = x + iy$
- $i = \sqrt{-1}$
- Complex conjugate: $z^* = x - iy$
- In this context “*” means complex conjugate
- The real axis is usually the horizontal axis
- Vertical axis is the imaginary axis
- Together these axes form the “complex plane”
- Squaring a complex number means “multiply by complex conjugate”, therefore:
- $z^2 = a^2 + b^2$
- In physical science, complex numbers are not observables, **only real values are observables** (imaginary component must be zero for an observed value)
- How this plays out in crystallography: We can't observe diffracted amplitudes, but we can observe diffracted intensities because the intensity is the square of the amplitude.

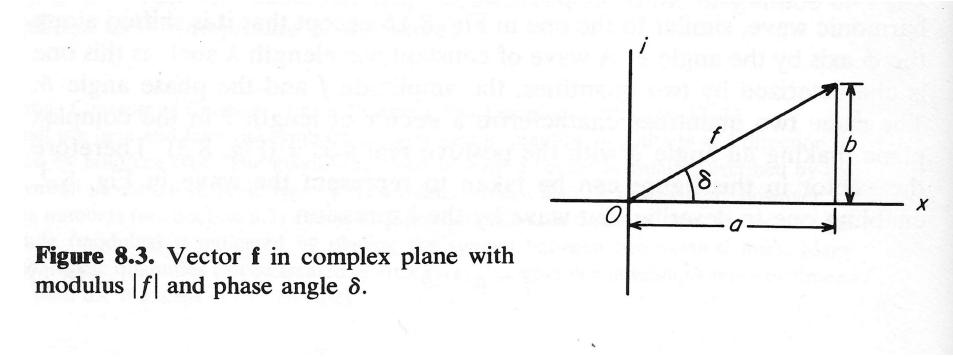


Figure 8.3. Vector f in complex plane with modulus $|f|$ and phase angle δ .

Brief Review: Vectors as Complex Quantities

- Using the complex plane, a vector can be expressed in either

Rectangular form:

$$\mathbf{f} = a + ib$$

Polar (trigonometric form):

$$\mathbf{f} = |f|(\cos(\delta) + i\sin(\delta))$$

- $a + ib = |f|(\cos(\delta) + i\sin(\delta))$

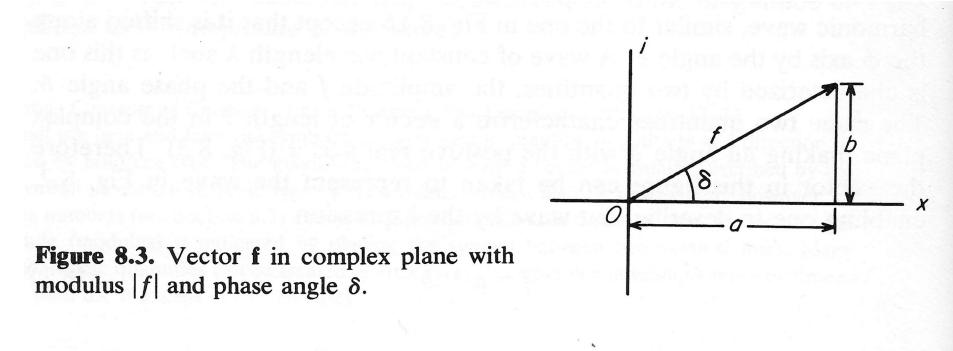


Figure 8.3. Vector \mathbf{f} in complex plane with modulus $|f|$ and phase angle δ .

Brief Review: The Euler Relation

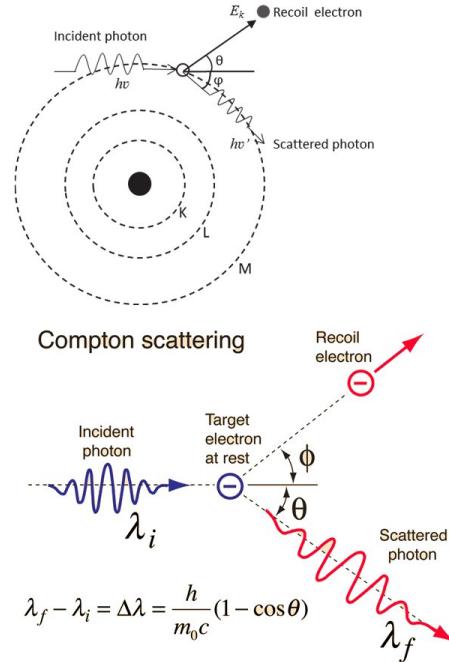
- $e^{i\varphi} = \cos(\varphi) + i\sin(\varphi)$
- when the angle is π or 2π :
- $e^{i\pi} = -1$ and $e^{i2\pi} = 1$
- A vector with a magnitude of $|F|$ can be written:
- $F = |F|e^{i\varphi}$
- $e^{i\varphi}$ can also be written as $\exp(i\varphi)$

Brief Review: Elastic and Inelastic Collisions

- **Elastic collision:** a particle's kinetic energy is not lost in the collision
- **Inelastic collision:** at least a portion of a particle's kinetic energy is lost in a collision

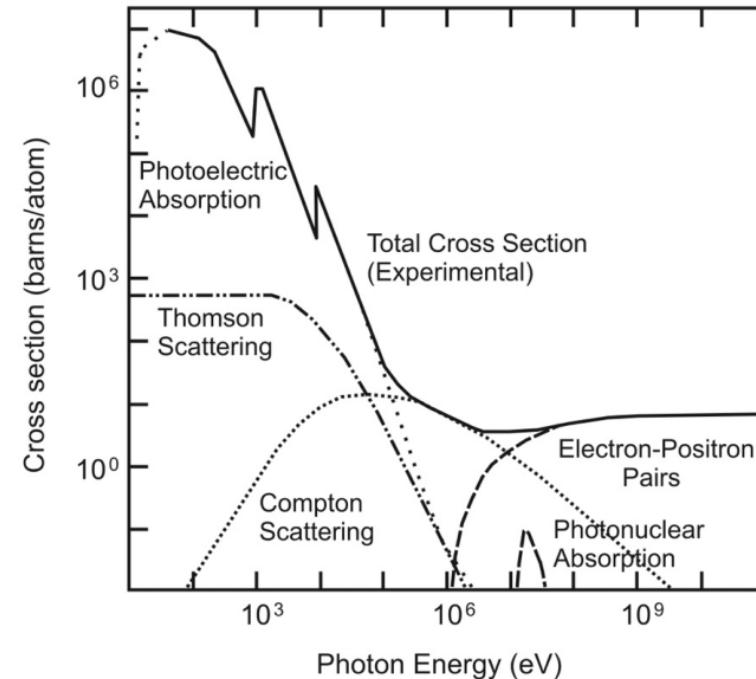
Compton Scattering

- The inelastic scattering causes the X-ray photons to lose energy
- $\lambda_{\text{Compton}} > \lambda_{\text{source}}$
- More important at higher energies
- For our X-ray diffraction experiment Thomson scattering dominates
- Image:
<https://www.quora.com/What-is-Compton-scattering>



Relative Importance of Thomson versus Compton Scattering

- Energies of laboratory X-rays:
 - MoK α : 17.45 keV
 - CuK α : 8.05 keV
- For these energies Thomson scattering is much more important than Compton scattering.
- Image:
<https://physics.stackexchange.com/questions/480996/is-the-compton-effect-observed-during-regular-x-ray-diffraction>

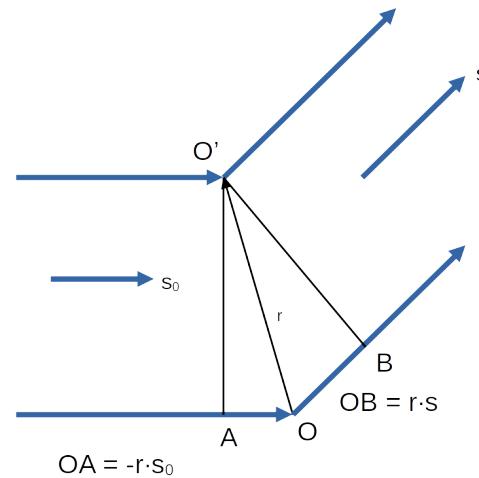


Thomson Scattering (Single Electron)

- The oscillating electric field of the X-ray beams induce an oscillating motion in the electron
- The oscillating electron becomes an emitter of spherical waves of electromagnetic radiation with the same wavelength as the impinging X-rays.

Scattering from Two Electrons

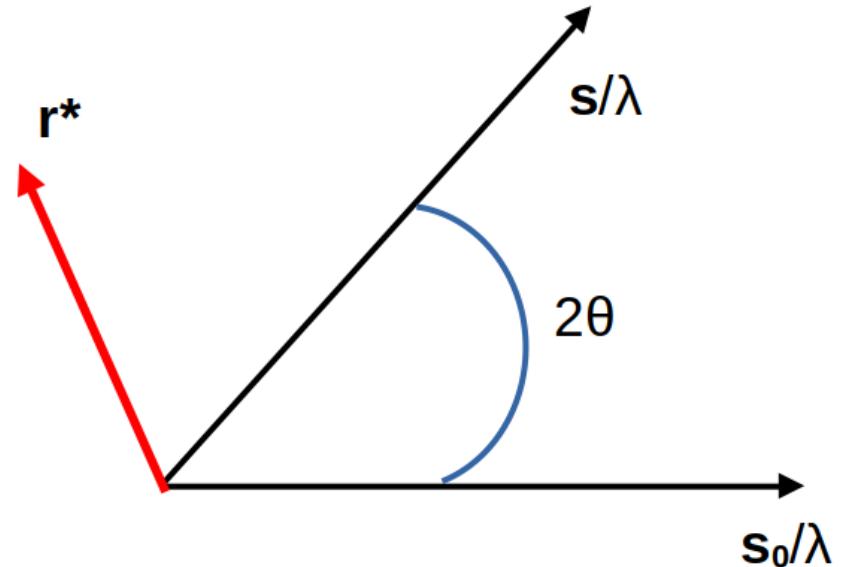
- s_0 is the source X-ray and s is the scattered X-ray observed at an angle deviating from the main beam
- s_0 and s are unit vectors
- Electrons at O and O' are separated by vector r and scatter X-rays as spherical waves
- The difference in the phase angle depends on the difference in the path lengths of the scattered waves at the angle of observation.
- The phase difference is: $(2\pi/\lambda)[(s - s_0) \cdot r]$



$$\begin{aligned}\text{Path length difference} &= OA + OB \\ &= -r \cdot s_0 + r \cdot s \\ &= r \cdot s - r \cdot s_0 \\ &= (s - s_0) \cdot r\end{aligned}$$

Scattering Vector

- Phase difference = $(2\pi/\lambda)[(\mathbf{s}-\mathbf{s}_0) \cdot \mathbf{r}]$
- Define $\mathbf{r}^* = (\mathbf{s}-\mathbf{s}_0)/\lambda$
- \mathbf{r}^* is called the “scattering vector”
- The scattering vector points in the direction of the bisector between \mathbf{s} and $-\mathbf{s}_0$.
- $|\mathbf{r}^*| = 2\sin(\theta)/\lambda$
- Phase difference in terms of scattering vector = $2\pi(\mathbf{r}^* \cdot \mathbf{r})$



Scattering from Multiple Electrons (an Atom)

- For N discrete electrons we can write the sum of the scattering as:

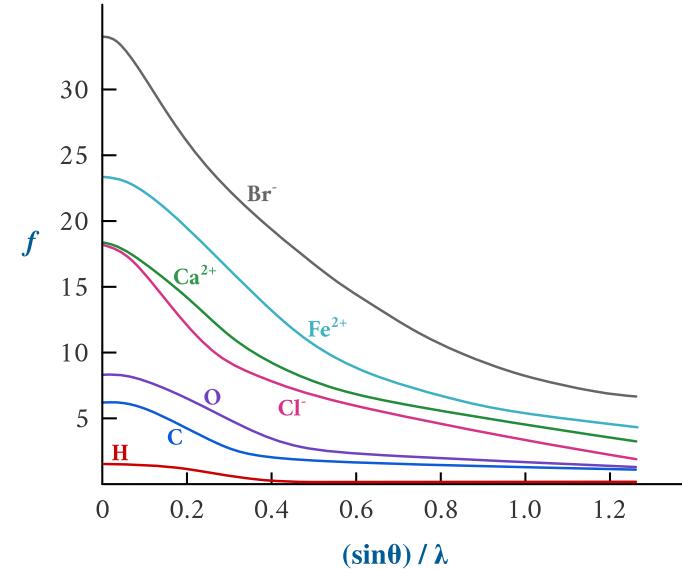
$$F(\mathbf{r}^*) = \sum_{j=1}^N A_j \exp(2\pi i \mathbf{r}^* \cdot \mathbf{r})$$

- For a continuous electron density distribution, $\rho(\mathbf{r})$, we can write:
- We can treat scattering from N electrons in an atom as a singular scattering source of finite width

$$F(\mathbf{r}^*) = \int \rho(\mathbf{r}) \exp(2\pi i \mathbf{r}^* \cdot \mathbf{r}) d\mathbf{r}$$

Atomic Scattering Factor

- In general, the term $F(r^*)$ is called the **structure factor**
- and represents the amplitude of a scattered wave in a certain direction
- In general the structure factor is a continuous complex function
- The structure factor is the **Fourier transform** of an electron density distribution
- The Fourier transform of the electron density distribution in an atom is called the **atomic scattering factor**, f
- An atomic scattering factor is a type of structure factor (but the terminology can be confusing)
- Atomic scattering factors are assumed to be transferable between structures
- At $\sin\theta/\lambda = 0$, the value of f equals number of electrons in the atom (or ion).
- The magnitude of f decreases with increasing $\sin\theta/\lambda$ because of mutual interference of the scattering by the individual electrons within the atom (or ion).



Calculation of Atomic Scattering Factors

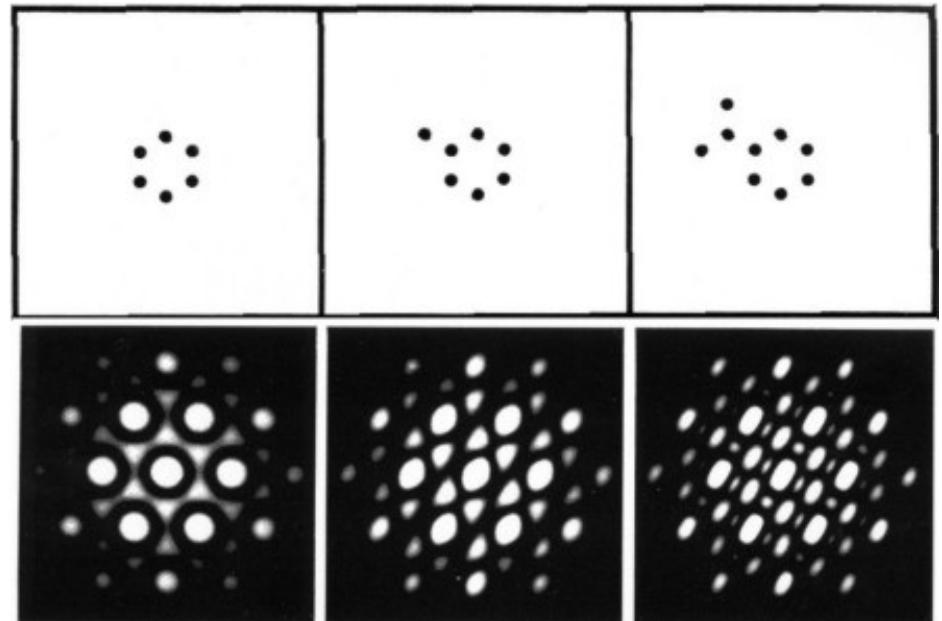
- Calculate the electron density distribution for an isolated atom
- Currently, quantum mechanical calculations are not done “on the fly” during the crystallographic structure refinement
- We use tabulated values (from the International Tables for Crystallography)
- The tabulated values are coefficients from a polynomial fit of the scattering factor curve
- Approximations: We assume atoms is neutral and has spherical symmetry

$$f(\mathbf{r}^*) = \int U_e(r) \sin\left(\frac{2\pi r^* \cdot \mathbf{r}}{2\pi r^* \cdot \mathbf{r}}\right) dr$$

where $U_e(r) = 4\pi r^2 \rho(r)$ is the radial distribution function for the atom

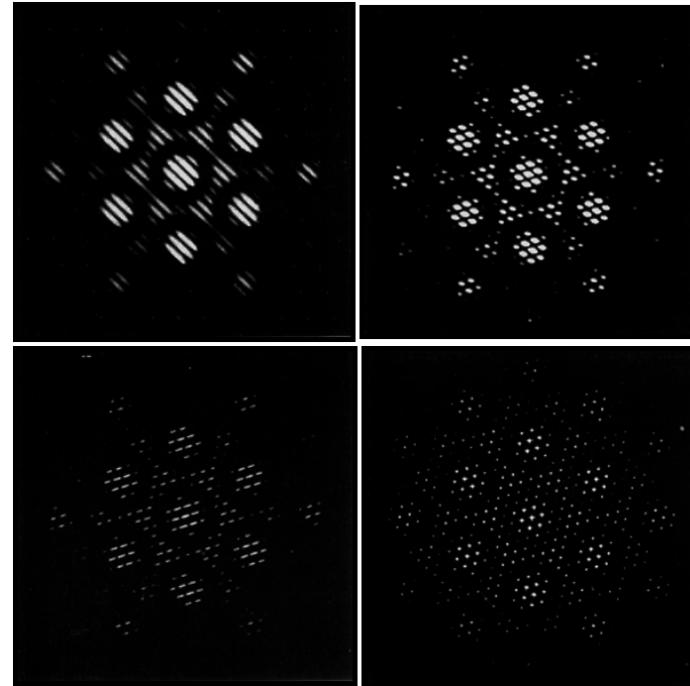
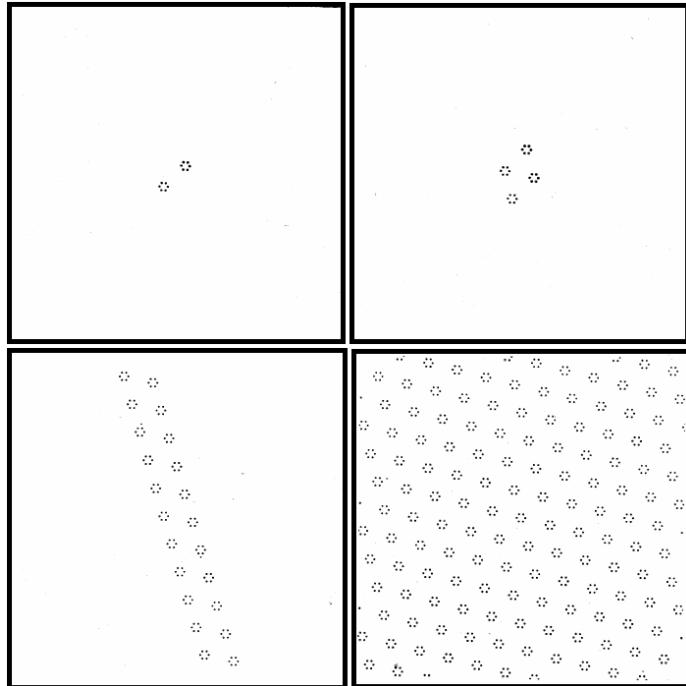
Molecular Transform

- We can calculate Fourier transform of a molecule's electron density distribution
- These molecular transforms can be depicted by creating an optical transform
- Examples: benzene, toluene, and nitrobenzene
- In general molecular transforms are continuous functions
- Our X-ray diffraction pattern is a molecular transform sampled at reciprocal lattice points
- Image from:
https://www.xtal.iqf.csic.es/Cristalografia/parte_05_3-en.html



Lattice periodicity increases sharpness of molecular transform

(from Atlas of Optical Transforms: <https://iubemcenter.indiana.edu/doc/atlas-of-optical-transforms.pdf>)



Developing the Structure Factor Equation (1)

- The lattice, through Bragg's Law, imposes a quantization of momentum
- We can only sample the molecular transform via X-ray diffraction at reciprocal lattice points
- Scattering vector, \mathbf{r}^* , is identical to the reciprocal lattice vector
- We relabel \mathbf{r}^* to \mathbf{H} (the reciprocal lattice vector) to emphasize the quantized nature of the scattering
- The vector components for reciprocal lattice points are the Miller indices h , k , and l
- $$\mathbf{H} = h \hat{\mathbf{a}}^* + k \hat{\mathbf{b}}^* + l \hat{\mathbf{c}}^*$$

Structure Factor for Atoms in a Lattice

- For N discrete atoms we can write the sum of the scattering using atomic scattering factors as:

$$F(\mathbf{H}) = \sum_{j=1}^N f_j \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_j)$$

- For a continuous electron density distribution, $\rho(\mathbf{r})$, we can write:

$$F(\mathbf{H}) = \int \rho(\mathbf{r}) \exp(2\pi i \mathbf{H} \cdot \mathbf{r}) d\mathbf{r}$$

- The exponential factor is:

$$2\pi i(hx_j + ky_j + lz_j)$$

Superposition of Waves

- When calculating a structure factor ($F_{\text{calc}}(\mathbf{H})$) we sum of the contributions of the individual atoms in the unit cell.
- Suppose we have 3 waves with magnitudes of f_1 , f_2 , and f_3 with corresponding phase angles δ_1 , δ_2 , and δ_3 .

The superposition of these waves will give a resultant vector whose x and y components can be written as:

$$x = f_1 \cos \delta_1 + f_2 \cos \delta_2 + f_3 \cos \delta_3 = \sum_j f_j \cos \delta_j$$

$$y = f_1 \sin \delta_1 + f_2 \sin \delta_2 + f_3 \sin \delta_3 = \sum_j f_j \sin \delta_j$$

The magnitude of the resultant vector is

$$|F| = (x^2 + y^2)^{1/2} = \left[\left(\sum_j f_j \cos \delta_j \right)^2 + \left(\sum_j f_j \sin \delta_j \right)^2 \right]^{1/2}$$

Superposition of Waves (Pictorial)

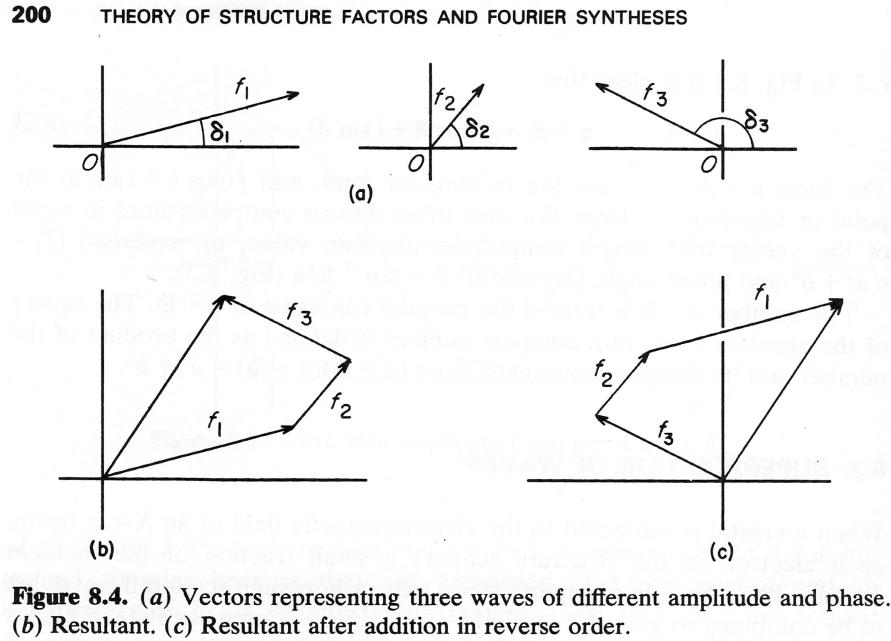
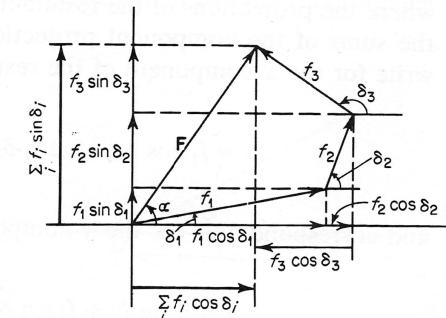


Figure 8.4. (a) Vectors representing three waves of different amplitude and phase.
(b) Resultant. (c) Resultant after addition in reverse order.

Figure 8.5. Components on the coordinate axes of a sum of vectors are equal to the sums of the components of the individual vectors.



Relating the Phase Angle to the Positions of the Atoms

- The phase difference for a unit cell translation will be 2π
- If atom lays along some fraction of that unit cell length, the phase change (relative to the origin) will be that fraction of 2π
- The total phase difference will be the sum for the different unit cell directions
- $\delta = 2\pi(hx + ky + lz)$
- Important take home point: The structural information is primarily in the phases!!

Incorporating Phase Expression into Structure Factor Equation

$$|F_{hkl}| = \left[\sum_j [f_j \cos 2\pi(hx_j + ky_j + lz_j)]^2 + [\sum_j f_j \sin 2\pi(hx_j + ky_j + lz_j)]^2 \right]^{1/2}$$

Crystallographers write this equation more compactly as :

$$|F_{hkl}| = (A_{hkl}^2 + B_{hkl}^2)^{1/2}$$

where :

$$A_{hkl} = \sum_j f_j \cos 2\pi(hx_j + ky_j + lz_j)$$

$$B_{hkl} = \sum_j f_j \sin 2\pi(hx_j + ky_j + lz_j)$$

The vector form , F_{hkl} can then be written as :

$$F_{hkl} = A_{hkl} + i B_{hkl}$$

The phase angle for reflection hkl is then calculated using :

$$\phi_{hkl} = \arctan \left(\frac{B_{hkl}}{A_{hkl}} \right)$$

Structure Factor Equation and Systematic Absences

- Crystal structures in space groups with translational symmetry elements exhibit systematic absences
- The structure factor equation can be used to show that the affected reflections are systematically absent rather than being accidentally zero
- This can be highlighted by factoring the structure factor equation for the affected class of reflections and using the symmetry equivalent positions for the symmetry operator
- We illustrate this with 3 cases:
 - 2_1 screw axis running parallel to [010]
 - n glide plane reflecting across the (010)
 - Body (I) centred Bravais lattice

Systematic absence: 2_1 screw axis parallel to [010]

Equivalent positions for 2_1 screw axis: $x, y, z; -x, y+1/2, -z$

We can drop out the h and l dependent terms because they are 0 for this class of reflection

$$F_{0k0} = f_j e^{2\pi i k y_j} + f_j e^{2\pi i k (y_j + 1/2)}$$

$$F_{0k0} = f_j e^{2\pi i k y_j} + f_j e^{2\pi i k y_j} e^{\pi i k}$$

Factor out common term:

$$F_{0k0} = f_j e^{2\pi i k y_j} (1 + e^{\pi i k})$$

$e^{\pi i k} = +1$ for $k = 2n$ and
 -1 for $k = 2n+1$

Systematic Absence: n glide reflecting across (010)

Equivalent positions for n glide plane: $x, y, z; x+1/2, -y, z+1/2$

We can drop out the k dependent term because $k=0$ for this class of reflections

$$F_{h0l} = f_j e^{2\pi i(hx_j + lz_j)} + f_j e^{2\pi i(hx_j + lz_j + h/2 + l/2)}$$

Factor out common term:

$$F_{h0l} = f_j e^{2\pi i(hx_j + lz_j)} \left(1 + e^{\pi i(h+l)} \right)$$

$e^{\pi i(h+l)} = +1$ for $h+l=2n$ and
 -1 for $h+l=2n+1$

Systematic Absence: Body (I) centred reflections (hkl)

Equivalent positions for body centring: $x, y, z; x+1/2, y+1/2, z+1/2$

$$F_{hkl} = f_j e^{2\pi i(hx_j + ky_j + lz_j)} + f_j e^{2\pi i(hx_j + ky_j + lz_j + h/2 + k/2 + l/2)}$$

Factor out common term:

$$F_{hkl} = f_j e^{2\pi i(hx_j + ky_j + lz_j)} \left(1 + e^{\pi i(h+k+l)} \right)$$

$$e^{\pi i(h+k+l)} = +1 \text{ for } h+k+l=2n \text{ and} \\ -1 \text{ for } h+k+l=2n+1$$

Effect of Atomic Motion on X-ray Scattering

- Atoms in a crystal vibrate
- This “thermal motion” has an effect on the scattering power of the atom
- Thermal motion spreads out the electron density over a larger volume
- Causes the scattering power to fall off more rapidly

For the isotropic case ,the decrease in scattering power is given by the following expression:

$$e^{-B(\sin^2 \theta)/\lambda^2}$$

Where $B=8\pi^2\langle u^2 \rangle$

The effective scattering factor then is the atomic scattering factor , f_o , multiplied by the thermal motion factor :

$$f_{eff} = f_o e^{-B(\sin^2 \theta)/\lambda^2}$$

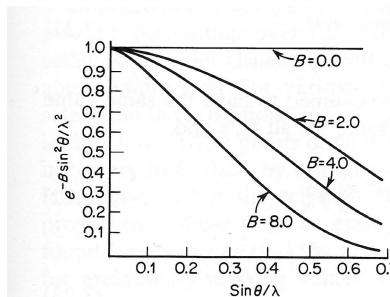
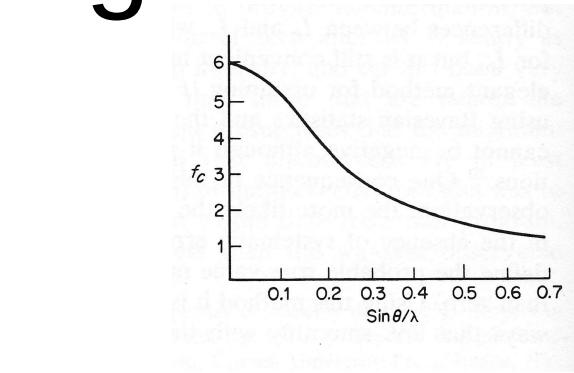


Figure 7.4. Temperature factor $e^{-B(\sin^2 \theta)/\lambda^2}$ as a function of $(\sin \theta)/\lambda$.

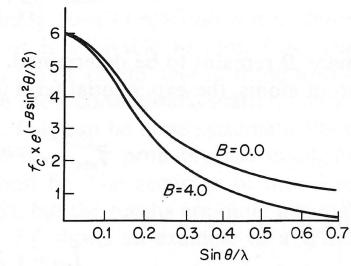


Figure 7.5. The product $f_c e^{-B(\sin^2 \theta)/\lambda^2}$ as a function of $(\sin \theta)/\lambda$.

Anisotropic Displacement Parameters (ADPs)

- In modern crystal structure analysis the instantaneous displacements of the atoms are modeled using “Anisotropic Displacement Parameters” (ADPs)
- This allows the magnitude of the motion of the atom to be different in different directions
- The ADP model postulates atomic motion is:
 - 3 dimensional
 - harmonic
 - rectilinear
- Mathematically, the ADP is a symmetric tensor of rank 2 (looks like a symmetric 3x3 matrix).
- In general, there are 6 independent elements in the ADP tensor. These are designated as u^{11} , u^{22} , u^{33} , u^{12} , u^{13} , and u^{23} and have units of \AA^2
- The number of elements will decrease if the atom resides on a symmetry element

Expression for ADP

$$T = \exp \left[-2\pi^2 (u^{11} h^2 a^{*2} + u^{22} k^2 b^{*2} + u^{33} l^2 c^{*2} + 2u^{12} hk a^* b^* + 2u^{13} hl a^* c^* + 2u^{23} kl b^* c^*) \right]$$

The complete structure factor equation is then :

$$F_{hkl} = \sum_j^N f_j T_j e^{2\pi i (\mathbf{H} \cdot \mathbf{r})}$$

Our story so far ...

- We have concentrated on understanding the intensity distribution of an X-ray diffraction pattern
 - examined several scattering cases
 - developed a structure factor equation
- Using the structure factor equation, we have illustrated how systematic absences arise due to translational symmetry elements
- However, how about going “the other way”? How do we use X-ray diffraction data to recover the electron density distribution in our structure?

Crystal Structure as a Periodic Function

- Crystal structures are periodic. It makes sense to use periodic functions when developing a mathematical model of the structure
- The Fourier series fits this need admirably.
- Example of one dimensional Fourier series:

$$f(x) = a_0 + \sum_{h=1}^n (a_h \cos 2\pi h x + b_h \sin 2\pi h x)$$

Fourier Expression of Electron Density Function

- Skipping a lot of math:
- The coefficients in the Fourier series are the structure factors
- The process of building a particular wave shape by the addition of sine and cosine terms is called a **Fourier Synthesis**
- Fourier synthesis is the inverse Fourier transform of the structure factor equation
- With the structure factor amplitudes $|F_{hkl}|$ and phases we are able to perform a Fourier synthesis to represent the electron density distribution in the crystal

$$\rho(x, y, z) = \frac{1}{V} \sum_h \sum_k \sum_l F_{hkl} e^{-2\pi i(hx+ky+lz)}$$

We remember that F_{hkl} is a vector which can be expressed as $F_{hkl} = |F_{hkl}| e^{i\phi_{hkl}}$

Our equation becomes :

$$\rho(x, y, z) = \frac{1}{V} \sum_h \sum_k \sum_l |F_{hkl}| e^{i\phi_{hkl}} e^{-2\pi i(hx+ky+lz)}$$

The expression can be rewritten as :

$$\rho(x, y, z) = \frac{1}{V} \sum_h \sum_k \sum_l |F_{hkl}| e^{-2\pi i(hx+ky+lz - \phi_{hkl})}$$

Evaluating the Fourier Function

- We have a set of $|F_{hkl}|$ coming from our experiment
- The phase, ϕ_{hkl} is calculated from the known part of the structure
- The function is evaluated at points x,y,z spaced as a regular grid over the asymmetric unit

Other Useful Fourier Coefficients

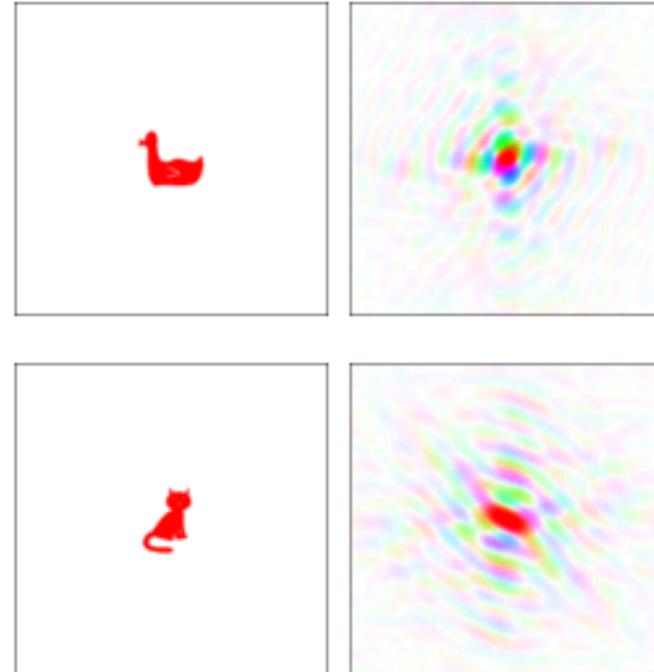
- **Most important:** $(F_o - F_c)$ gives a **difference Fourier map**
- The difference map accentuates the missing parts of the structure
- Other coefficient sometimes used: F_o , F_c , $(2F_o - F_c)$, F_o^2 (Patterson map)
- Double weighting F_o in a difference map can help find missing atoms (e.g. fractionally occupied sites or disordered atoms) or when a significant part of the structure is missing
- Check your crystallographic software documentation for other, more exotic, coefficients. Give them a try in your structure analysis. How much do they help?

Demonstration that Structural Information is the Phases

- Our expression for an atom's contribution to a reflection's phase is:
 $\varphi_{hkl} = 2\pi i(hx_i + ky_i + lz_i)$
- The phase of atom i's wavelet depends on the position of atom in the unit cell
- Although we try to collect as accurate and complete data as possible, it is possible for us to recover a structure with inaccurate intensity data if our phases are relatively accurate
- We will use Kevin Cowtan's "Fourier Animals" to illustrate this point
(see: <http://www.ysbl.york.ac.uk/~cowtan/fourier/magic.html>)

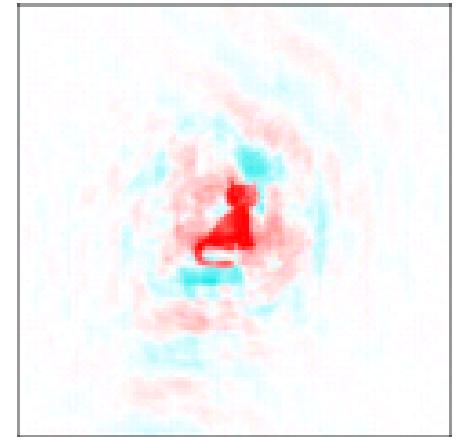
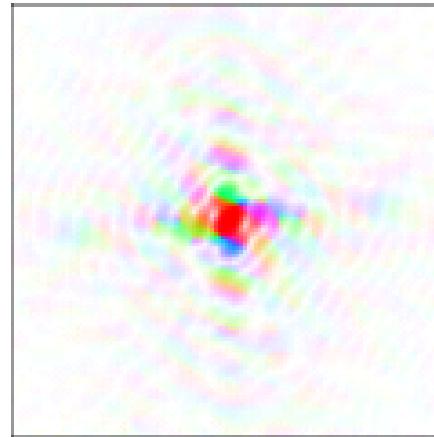
Kevin Cowtan's Fourier Animal Magic

- Images of a duck and cat and their respective Fourier transforms
- When transforming a 2D image, one can obtain both the magnitudes and phases separately
- What happens if we take the duck magnitudes and apply the cat phases and do the inverse transform?
- What will the image look like?



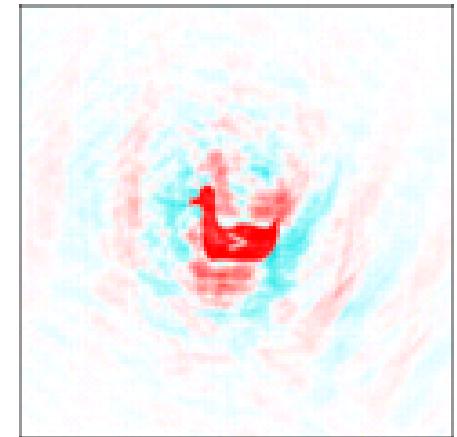
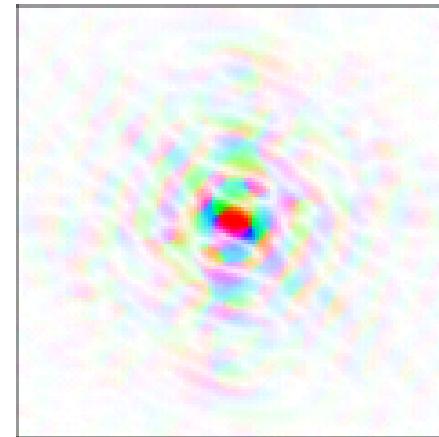
Duck Magnitudes and Cat Phases

- The left image is the Fourier space image using the magnitudes derived from the duck image and the phases derived from the cat image
- The right hand image is the result of doing the inverse transform back into direct space
- This shows that it is phases which carry the structural information when dealing with Fourier transforms



Cat Magnitudes and Duck Phases

- The left image is the Fourier space image derived from the cat magnitudes and the duck phases
- The right hand image is the result of doing the inverse transform back into direct space
- As with duck magnitude and the cat phases, we recover the image of the animal whose phases we used



Summary

- Structure factor theory accounts for the intensity distribution of an X-ray diffraction pattern
- Relatively simple model
 - spherical, neutral atoms
 - 3 dimensional rectilinear harmonic motion
- The structure factor equation and Fourier synthesis equation are the Fourier transforms of one another
- Structural information is stored primarily in the phases