Structure Factors and Fourier Synthesis

\( F_{hk\ell} \): function of reflection indices and atom positions in unit cell:

- all atoms scatter waves in \( h k \ell \) direction
- to develop equations that represent how waves add:

  - wave represented as vector moving with constant angular velocity:

    \[ \mathbf{F} = f \cos \phi \]

  - Superposition of Waves

    - 2 waves of same frequency, but different phase (\( \delta \)), add to give a new wave, with a different amplitude and phase (from either) but the same frequency.

    \[ x_1 = f_1 \cos \phi \quad x_2 = f_2 \cos (\phi + \delta) \]

    - trigometric identity

    \[ F \cos (\phi + \alpha) = f_1 \cos \phi + f_2 \cos (\phi + \delta) \]

    \[ F \cos \alpha \cos \phi - F \sin \alpha \sin \phi = (f_1 + f_2 \cos \delta) \cos \phi - f_2 \sin \delta \sin \phi \]

    \[ x_F = x_1 + x_2 \]

    \[ \phi = 0^\circ \quad F \cos \alpha = f_1 + f_2 \cos \delta \]

    \[ \phi = 90^\circ \quad F \sin \alpha = f_2 \sin \delta \]
Superposition of Waves

\[ F \cos \alpha = x = f_1 + f_2 \cos \delta \quad y = f_2 \sin \delta = F \sin \alpha \]

Superposition of Waves

\[ x = f_1 \cos \delta_1 + f_2 \cos \delta_2 + f_3 \cos \delta_3 = \sum_{j=1}^{N} f_j \cos \delta_j \]
\[ y = f_1 \sin \delta_1 + f_2 \sin \delta_2 + f_3 \sin \delta_3 = \sum_{j=1}^{N} f_j \sin \delta_j \]
\[ |F| = (x^2 + y^2)^{1/2} = \left[ \left( \sum_{j=1}^{N} f_j \cos \delta_j \right)^2 + \left( \sum_{j=1}^{N} f_j \sin \delta_j \right)^2 \right]^{1/2} \]
\[ \alpha = \tan^{-1} \left( \frac{\sum_{j=1}^{N} f_j \sin \delta_j}{\sum_{j=1}^{N} f_j \cos \delta_j} \right) = \tan^{-1} \left( \frac{B}{A} \right) \]

Structure Factors

Obvious (from symbols) that structure factor, \( F_{hk\ell} \), results from \( N \) waves scattered in \((h k \ell)\) direction by \( N \) atoms in unit cell each wave has an amplitude \( \alpha \) to \( f_j \) (scattering factor) and a phase \( \delta_j \) with respect to the origin of unit cell to calculate \( F \)'s, need to know \( \delta \)'s in terms of atomic position and indices of reflection needed

Atom Phases

Consider \((1 0 0)\) Miller planes

\[ \delta = 2\pi h x = 2\pi 1(0.5) \]

Atom at \((0.5, 0, 0)\) is exactly out of phase \((\pi)\) wrt atom at \((0, 0, 0)\)

\(\frac{1}{2}\) cycle

Atom at \((1, 0, 0)\) has a phase difference of \(2\pi\) wrt atom at \((0, 0, 0)\)

\((1\) cycle)
Atom Phases

Consider $(2 0 0)$ Miller planes

atom at $(0.25, 0, 0)$ is exactly out of phase ($\pi$) wrt atom at $(0, 0, 0)$

atom at $(1, 0, 0)$ has a phase difference of $4\pi$ wrt atom at $(0, 0, 0)$

Consider $(2 0 0)$ Miller planes

$\delta = 2\pi hx = 2\pi z(0.25)$

$[\text{expression to calculate structure factors from known } e^{-}\text{density}]$

to solve crystal structure, also need to perform inverse operation:

$e^{-}\text{density}$ is periodic, can be represented by Fourier Series

Jean Baptiste Joseph Fourier

French

(1768 - 1830)
Fourier Transform in Crystallography

structure factors \( F_{hk\ell} \)
electron density \( \rho (x, y, z) \)

Fourier Synthesis

Fourier Analysis

Fourier Synthesis

Fourier Synthesis

general form of 1-D Fourier series

\[
f(x) = \sum_{-\infty}^{\infty} C_n e^{2\pi i n x} = \sum_{-\infty}^{\infty} c_n e^{2\pi i n x}
\]

where \( h \) is an index of the term #

only \( \cos \) terms in box-car function \( \Rightarrow \) centrosymmetric:

\[
f(x) = f(-x)\cos(-x) = \cos(x)\sin(-x) = \cos(x)
\]

\[
f(x) = \sum_{-\infty}^{\infty} C_n \cos 2\pi nx
\]

\[
y = \frac{\pi}{4}
\]

\[
y = -\frac{1}{7} \cos (2\pi) 7x
\]

\[
y = -\frac{1}{9} \cos (2\pi) 9x
\]

\[
y = -\frac{1}{11} \cos (2\pi) 11x
\]

\[
y = \frac{1}{13} \cos (2\pi) 13x
\]
Fourier Synthesis
\[ y = \cos(2\pi x) \]

Fourier Synthesis
\[ y = \frac{-1}{3} \cos(2\pi 3x) \]

Fourier Synthesis
\[ y = \frac{1}{5} \cos(2\pi 5x) \]

Fourier Synthesis
\[ y = \frac{-1}{7} \cos(2\pi 7x) \]

Fourier Synthesis
\[ y = \frac{1}{9} \cos(2\pi 9x) \]

Fourier Synthesis
\[ y = \frac{-1}{11} \cos(2\pi 11x) \]
Fourier Synthesis

\[ y = \frac{1}{13} \cos(2\pi 13x) \]
Fourier Synthesis

3-D periodic density in a crystal could be represented by:

\[ \rho(x, y, z) = \sum_{h'k'\ell'} |F_{hk\ell}| e^{-2\pi i (hx + ky + \ell z - \alpha_{hk\ell})} \]

Finally: expanding exponential into \( \cos \) and \( \sin \) terms and assuming Friedel’s Law (\( \sin \) cancels for Friedel pairs):

\[ \rho(x, y, z) = \frac{1}{V} \sum_{h} \sum_{k} \sum_{\ell} |F_{hk\ell}| \cos 2\pi (hx + ky + \ell z - \alpha_{hk\ell}) \]
Structure Factors: 1-D Example – 2 atoms

\[ a = 10.0 \text{ Å} \]

\[ x_c = 0.185 \quad 0.815 = x_c \]

\[ x_c \] (centrosymmetric)

\[ F_{\text{calc}} = \sum f_j e^{2\pi i h x_j} \]

\[ F_b = \sum f_j e^{2\pi i h x_j} \]

\[ F_x = \frac{\sum f_j e^{2\pi i h x_j}}{\sum f_j e^{2\pi i h x_j}} \]

scattering power (in direction of \( h \))

\[ \cos(-x) = \cos(x) \]

\[ \sin(-x) = -\sin(x) \]

\[ \alpha = \tan^{-1}\left(\frac{\sum f_j \sin x_j}{\sum f_j \cos x_j}\right) \]

\[ \alpha = 0 \text{ or } \pi \]

sign of \( \pm \) or on \( F_b \)

\[ F_b = 2f_c \cos 2\pi x_c \]

\[ x_c = 0.185 \]

Electron Density: 1-D Example – 2 atoms

a Fourier synthesis on \( F_b \) should give the structure:

\[ \rho(x) = \frac{1}{L} \sum_{h} F_h e^{-2\pi i h x} \]

\[ \rho(x) = \frac{1}{L} \sum_{h} F_h \cos 2\pi hx - i \sin 2\pi hx \]

since \( F_b = F_{\text{even}} \)

\[ \rho(x) = \frac{1}{L} \sum_{h} F_h \cos 2\pi hx - i \sin 2\pi hx \]

Friedel’s Law

\[ \rho(x) = \frac{1}{L} \sum_{h} F_h \cos 2\pi hx + F_{-h} + \sum_{h} F_h \cos 2\pi hx - i \sin 2\pi hx \]

Scattering Factor: \( f_c \)

\[ \sin \theta/\lambda = 1/2d = h/2a \]

\[ h = \pm 1 \]

\[ d = 10.0 \text{ Å} \]

\[ \sin \theta/\lambda = 0.050 \]

\[ h = \pm 2 \]

\[ d = 5.00 \text{ Å} \]

\[ \sin \theta/\lambda = 0.100 \]

\[ h = \pm 3 \]

\[ d = 3.33 \text{ Å} \]

\[ \sin \theta/\lambda = 0.150 \]
Electron Density: 1-D Example – 2 atoms

\[ \rho(x) = \frac{1}{L} \sum_{h} \left[ F_{h} \cos(2\pi hx - i \sin(2\pi hx)) + F_{0} + \sum_{h} F_{h} \cos(2\pi hx - i \sin(2\pi hx)) \right] \]

since: \[ \cos(-x) = \cos(x) \]
\[ \sin(-x) = -\sin(x) \]

\[ \rho(x) = \frac{1}{L} \left( F_{0} + 2 \sum_{h} F_{h} \cos(2\pi hx) \right) \]
\[ F_{0} = \text{total e}^{-} \text{ in unit cell} \]
$F_1 \cos 2\pi hx$

$F_2 \cos 2\pi hx$

$F_3 \cos 2\pi hx$

$F_4 \cos 2\pi hx$

$F_5 \cos 2\pi hx$

$F_6 \cos 2\pi hx$

$F_7 \cos 2\pi hx$

$F_8 \cos 2\pi hx$

$F_9 \cos 2\pi hx$

$F_{10} \cos 2\pi hx$

$F_{11} \cos 2\pi hx$

$F_{12} \cos 2\pi hx$
\[ F_{12} \cos 2\pi hx \]

\[ (2\sum F_h \cos 2\pi hx) / 10 \text{ for } h = 1 - 2 \]

fractional coordinate - x

\[ (2\sum F_h \cos 2\pi hx) / 10 \text{ for } h = 1 - 3 \]

fractional coordinate - x

\[ (2\sum F_h \cos 2\pi hx) / 10 \text{ for } h = 1 - 4 \]

fractional coordinate - x

\[ (2\sum F_h \cos 2\pi hx) / 10 \text{ for } h = 1 - 5 \]

fractional coordinate - x

\[ (2\sum F_h \cos 2\pi hx) / 10 \text{ for } h = 1 - 6 \]

fractional coordinate - x
**3-D Structure**

The 3-D calculation of $p(x, y, z)$ is called:

- Fourier synthesis
- Fourier map
- e$^{-}$ density map

**3-D Electron Density**

Note ripples around the atom (Au) because of finite data

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**Systematic Absences**

$$F_{\text{abs}} = \sum f_{j} e^{2\pi i (hj + kj + lj)}$$

$$F_{\text{abs}} = \sum f_{m} \sum \left[ e^{2\pi i (hx + ky + lx + 0m)} \right]$$  
$m = \# \text{ asym units}$  
$n = \text{ atoms in asym unit}$

$$G_{\text{abs}} = e^{2\pi i (hx + ky + lx)}$$

Example: consider 2 atoms related by 2-fold screw axis along b:

- $x, y, z$  
- $x, y + \frac{1}{2}, z$

$$G_{\text{abs}} = e^{2\pi i (hx + ky + lj + \frac{1}{2}l)} + e^{2\pi i (hx - ky - \frac{1}{2}l)}$$

$$G_{\text{abs}} = e^{2\pi i (hx + ky + lj + \frac{1}{2}l)} + e^{2\pi i (hx - ky - \frac{1}{2}l)} + e^{2\pi i (hx + ky + \frac{1}{2}l)} + e^{2\pi i (hx - ky - \frac{1}{2}l)}$$

Looking at 0 $k$ 0 reflections:

- $G_{\text{abs}} = e^{2\pi i (1 + e^{2\pi i})}$
- $G_{\text{abs}} = 2 e^{2\pi i 0}$ for $k = 2n$ (even)
- $G_{\text{abs}} = 0$ for $k = 2n + 1$ (odd)