The Fourier Transform, the Wave Equation and Crystals

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X RAYS
AND
CRYSTAL STRUCTURE

BY

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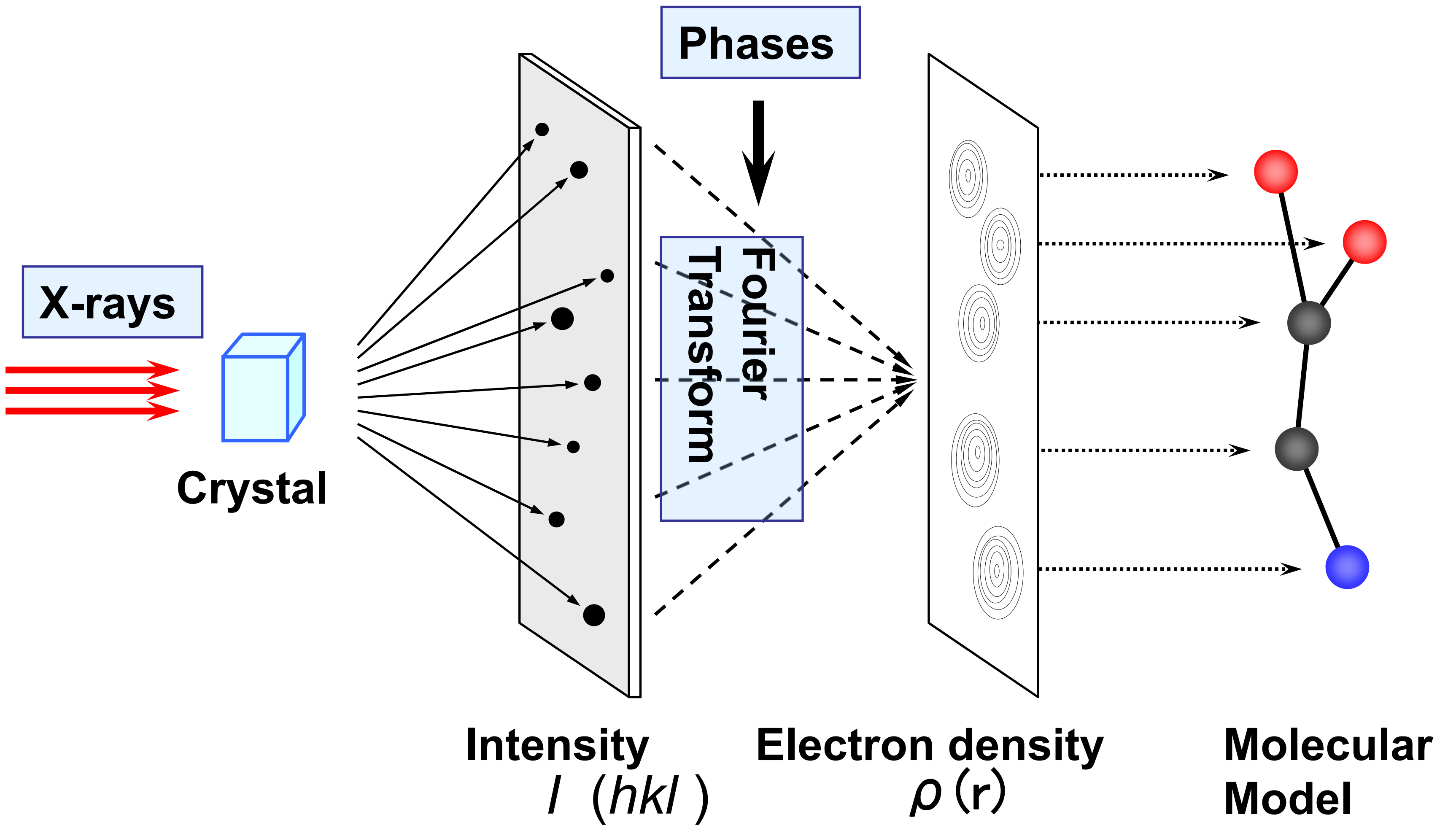
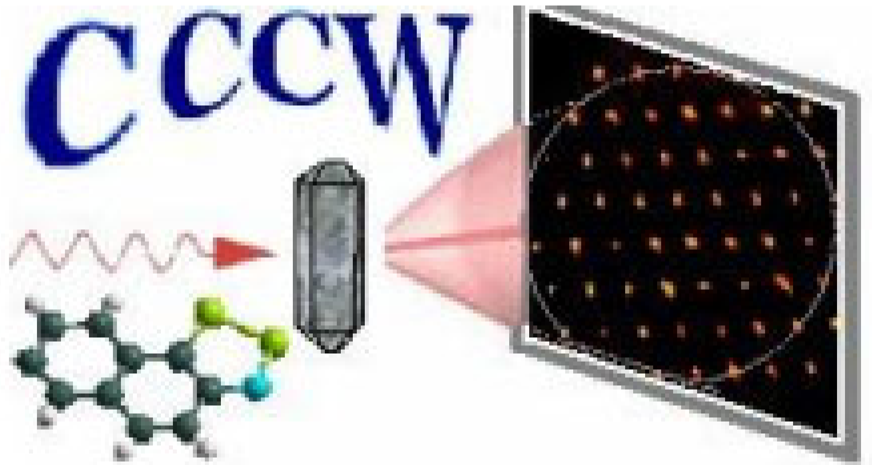
35000 ft view of X-ray Structure Analysis

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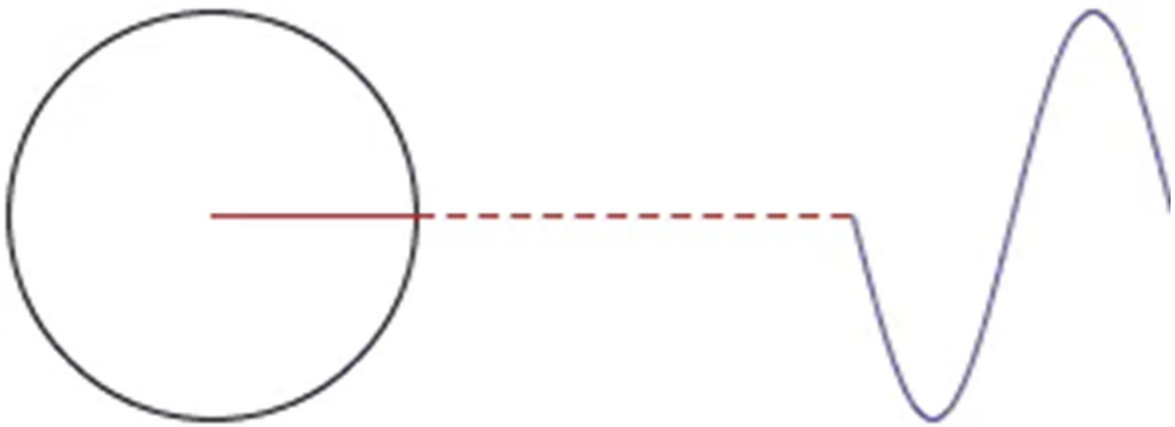
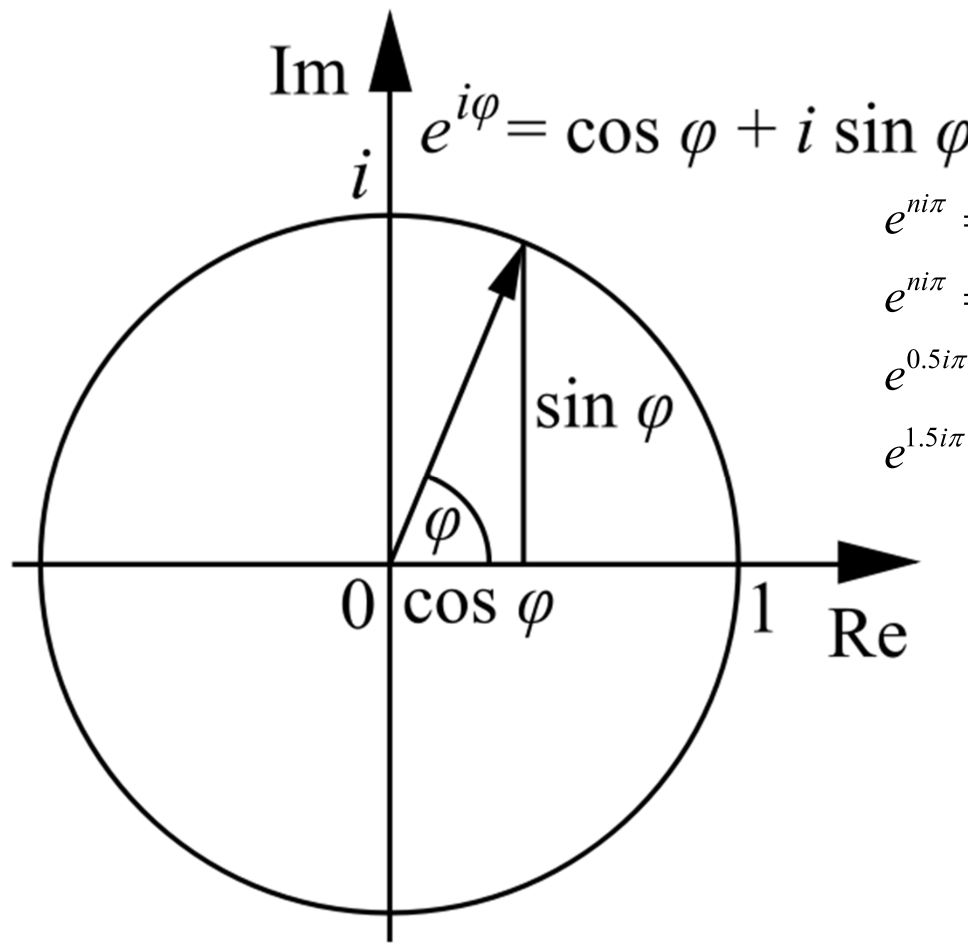
Fourier Theory

- Originally proposed by Jean-Bapiste Joseph Fourier in 1822 in *The Analytical Theory of Heat*
- Described discrete functions as the infinite sum of sines



What is a circle?



$$e^{ni\pi} = e^{-ni\pi} = -1 \text{ for } n \text{ odd}$$

$$e^{ni\pi} = e^{-ni\pi} = 1 \text{ for } n \text{ even}$$

$$e^{0.5i\pi} = i$$

$$e^{1.5i\pi} = -i$$

http://en.wikipedia.org/wiki/Euler's_formula

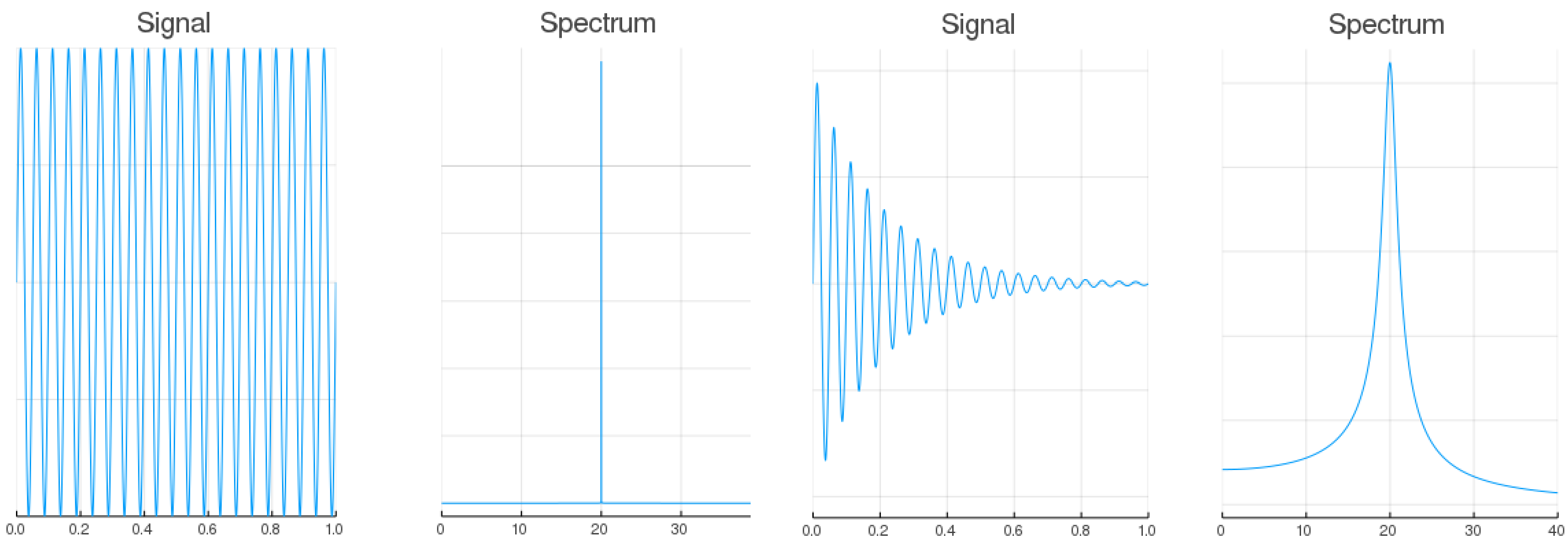
The Fourier Transform

$$F(k) = \int_{-\infty}^{\infty} f(x) e^{ikx} dx$$

$$F(k) = Tf(x)$$

In three dimensions this is generalized to:

$$F(\mathbf{k}) = \int_{\mathbf{r}} f(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r} = Tf(\mathbf{r})$$



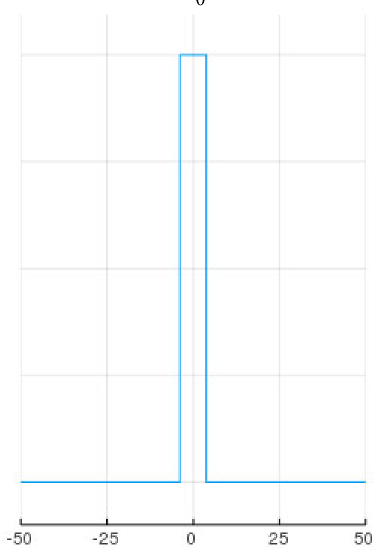
The Fourier Transform

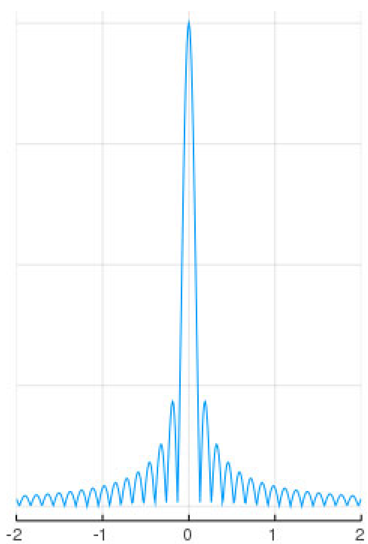
Let's look at an example:

$$-\infty < x < -X_0, \quad f(x) = 0$$
$$-X_0 \le x \le X_0, \quad f(x) = h$$
$$X_0 < x < \infty, \quad f(x) = 0$$

$$F(k) = \int_{-\infty}^{\infty} f(x) e^{ikx} dx$$

$$F(k) = h \int_{-X_0}^{X_0} e^{ikx} dx$$





$$F(k) = h \left[\frac{e^{ikx}}{ik} \right]_{-X_0}^{X_0} = h \frac{e^{ikX_0} - e^{ik(-X_0)}}{ik}$$

$$\sin\theta = \frac{e^{i\theta} - e^{-i\theta}}{2i}, \qquad \theta = kX_0$$

$$F(k) = 2h \frac{\sin kX_0}{k} = 2X_0 h \frac{\sin kX_0}{kX_0}$$

$$\sin kX_0 = 0$$

$$kX_0 = \pm\pi$$

$$k = \pm \frac{\pi}{X_0}$$

The Fourier Transform

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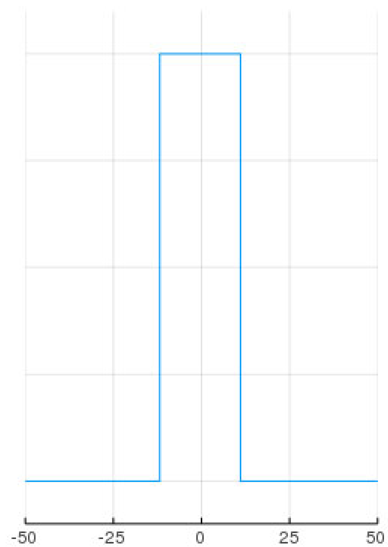

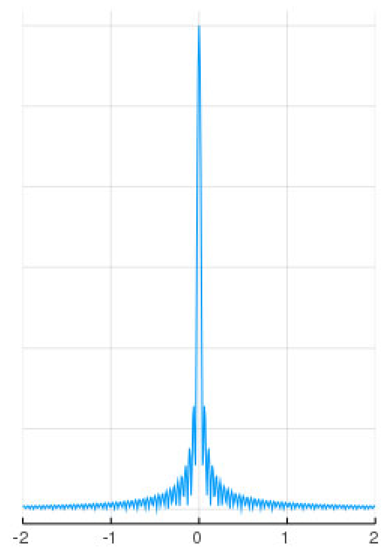

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$$\sin kX_0 = 0$$

$$kX_0 = \pm\pi$$

$$k = \pm \frac{\pi}{X_0}$$

The Dirac δ function

$$\delta\left(x-x_0\right)\begin{cases}+\infty, & \left(x-x_0\right)=0\\ 0, & \left(x-x_0\right)\neq 0\end{cases}$$

$$\int_{-\infty}^{\infty}\delta\left(x-x_0\right)dx=1$$

A 3D lattice may be decribed as a three dimensional array of delta functions.

$$\mathbf{r} = p\mathbf{a}+q\mathbf{b}+r\mathbf{c}$$

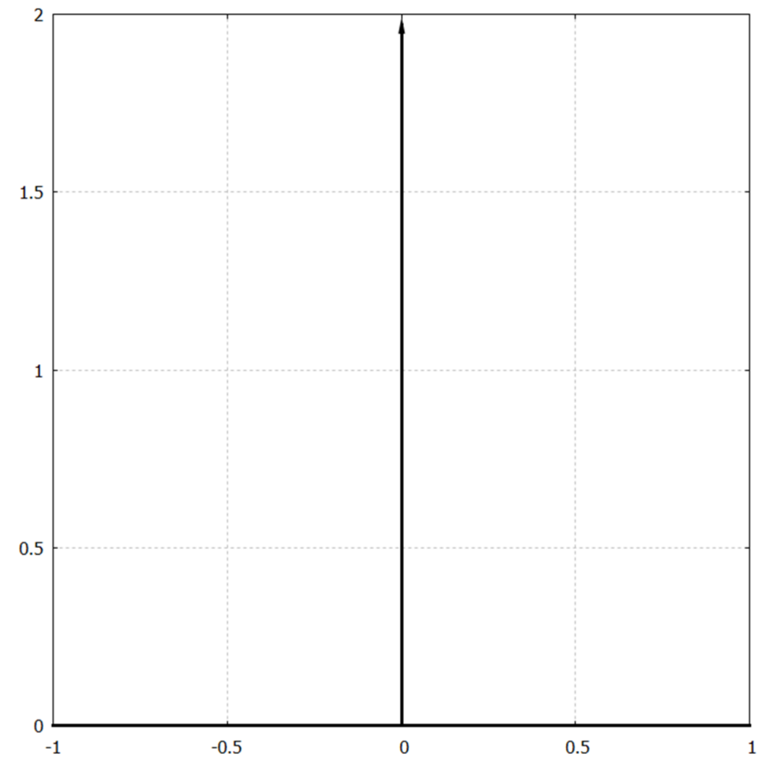
$$l(\mathbf{r}) = \sum_{\text{all p, q, r}} \delta(\mathbf{r}-[p\mathbf{a}+q\mathbf{b}+r\mathbf{c}])$$

An important property of the δ function is that acts as a sift:

$$\int_{-\infty}^{\infty} f(x)\delta(x-x_0)dx = f(x_0)\int_{-\infty}^{\infty}\delta(x-x_0)dx = f(x_0)$$

In three dimensions:

$$\int_{-\infty}^{\infty} f(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}_0)d\mathbf{r} = f(\mathbf{r}_0)$$

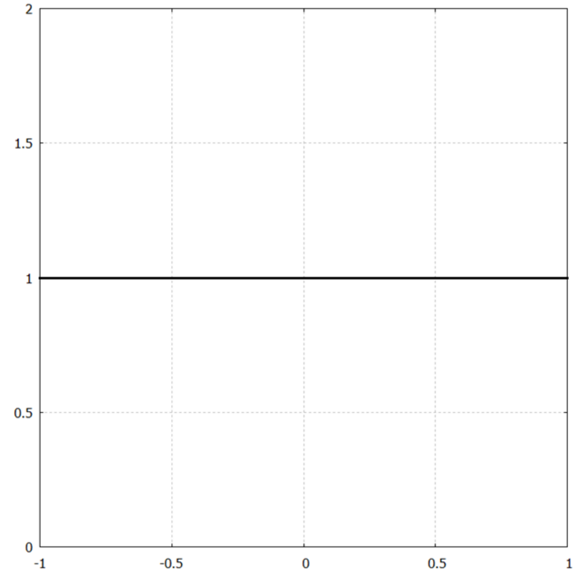


Fourier transforms and δ functions

One δ function:

$$F(k)=\int_{-\infty}^{\infty} f(x)e^{ikx}dx$$

$$=\int_{-\infty}^{\infty} \delta(x)e^{ikx}dx=\left[e^{ikx}\right]_{x=0}=e^{0}=1$$



Two δ functions:

$$f(x)=\delta(x+x_0)+\delta(x-x_0)$$

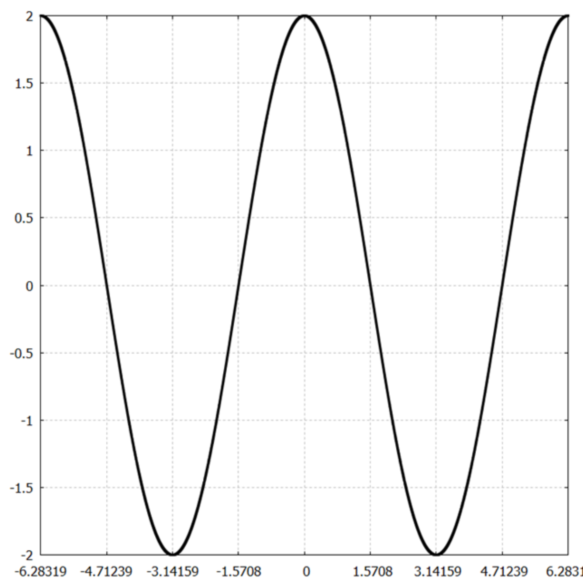
$$F(k)=\int_{-\infty}^{\infty} f(x)e^{ikx}dx$$

$$=\int_{-\infty}^{\infty} \delta(x+x_0)e^{ikx}dx+\int_{-\infty}^{\infty} \delta(x-x_0)e^{ikx}dx$$

$$=e^{-ikx_0}+e^{ikx_0}$$

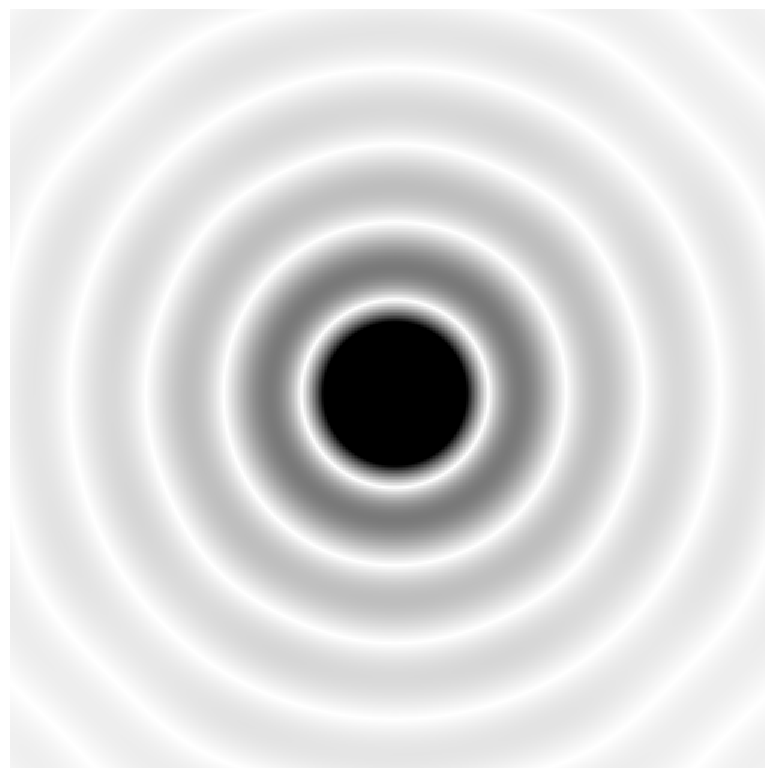
$$\cos\theta=\frac{e^{i\theta}+e^{-i\theta}}{2}, \qquad \theta=\mathrm{kx}_0$$

$$F(k)=2\cos kx_0$$



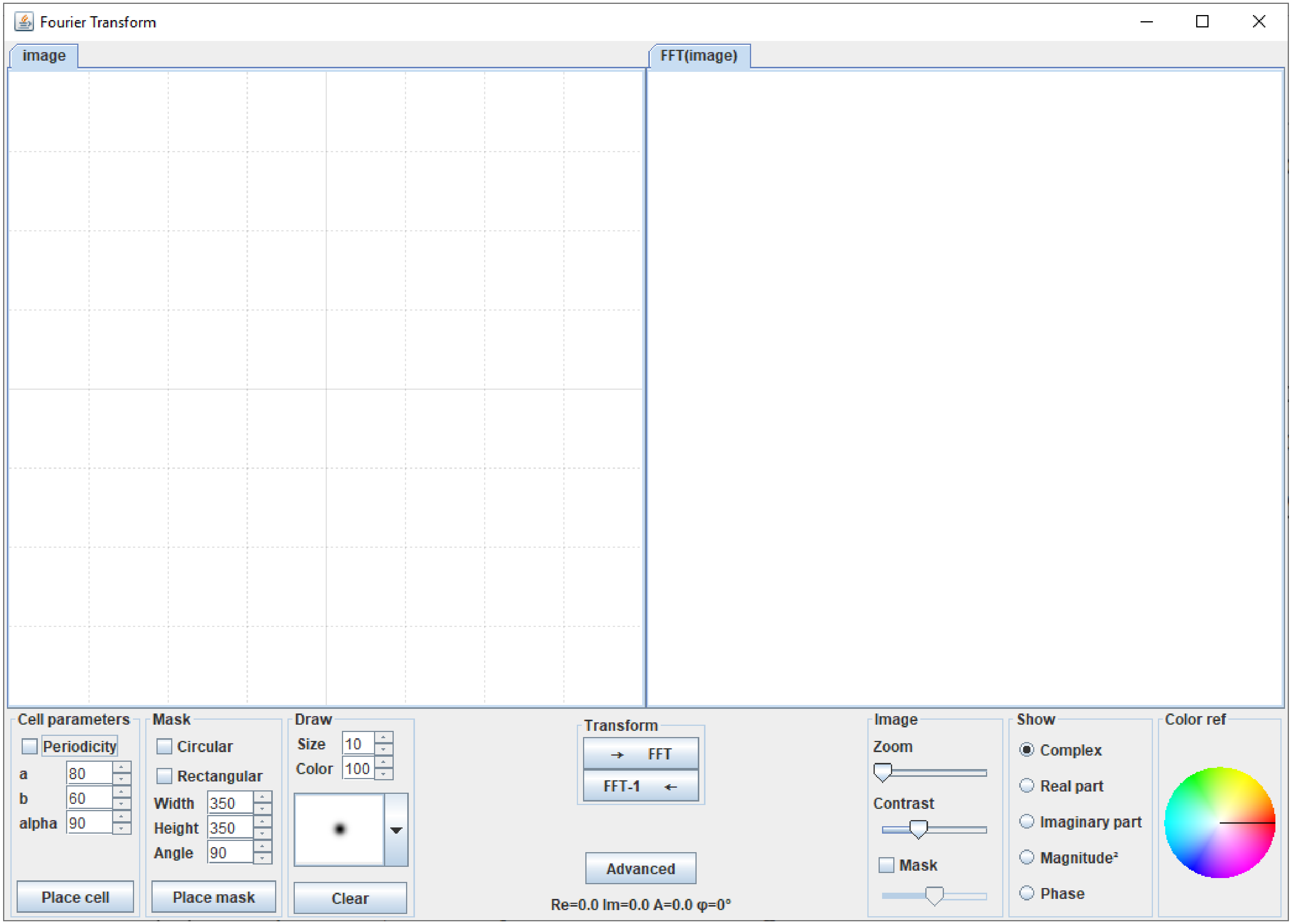
The Fourier Transform

$$F(\mathbf{k}) = \int_{\text{all } \mathbf{r}} f(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}} \, d\mathbf{r} = Tf(\mathbf{r})$$



The Fourier Transform

$$F(\mathbf{k}) = \int_{\text{all } \mathbf{r}} f(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}}\, d\mathbf{r} = Tf(\mathbf{r})$$



Fourier Transform
image
FFT(image)
Cell parameters
Periodicity
a 80
b 60
alpha 90
Place cell
Mask
Circular
Rectangular
Width 350
Height 350
Angle 90
Place mask
Draw
Size 10
Color 100
Clear
Transform
→ FFT
FFT-1 ←
Advanced
Re=0.0 Im=0.0 A=0.0 φ=0°
Image
Zoom
Contrast
Mask
Show
Complex
Real part
Imaginary part
Magnitude²
Phase
Color ref

Convolutions

$$c(\mathbf{u}) = \int_{\text{all } \mathbf{r}} f(\mathbf{r}) g(\mathbf{u}-\mathbf{r})\, d\mathbf{r}$$

$$c(\mathbf{u}) = f(\mathbf{r}) * g(\mathbf{r}) = \int_{\text{all } \mathbf{r}} f(\mathbf{r}) g(\mathbf{u}-\mathbf{r})\, d\mathbf{r}$$

$$f(\mathbf{r}) * g(\mathbf{r}) = \int_{\text{all } \mathbf{r}} f(\mathbf{r}) g(\mathbf{u}-\mathbf{r})\, d\mathbf{r} = \int_{\text{all } \mathbf{r}} f(\mathbf{u}-\mathbf{r}) g(\mathbf{r})\, d\mathbf{r}$$

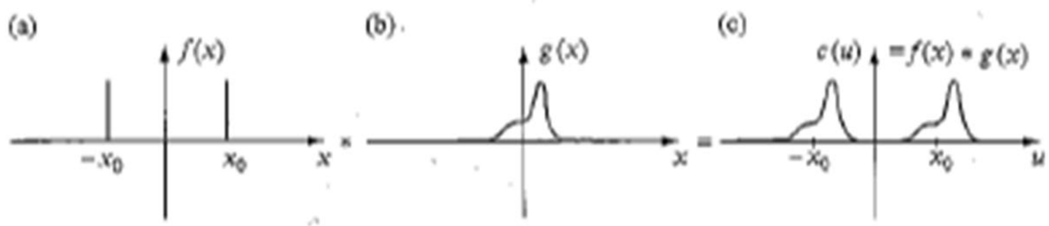


Fig. 5.17 *The convolution integral* $c(u) = \int_{-\infty}^{\infty} f(x) g(u-x)\, dx$. If we choose $f(x)$ to be two δ functions at $x = \pm x_0$, then the operation of convoluting the array with an arbitrary function $g(x)$ results in centring $g(x)$ over each function. The steps by which we achieve this are shown in Fig. 5.18.

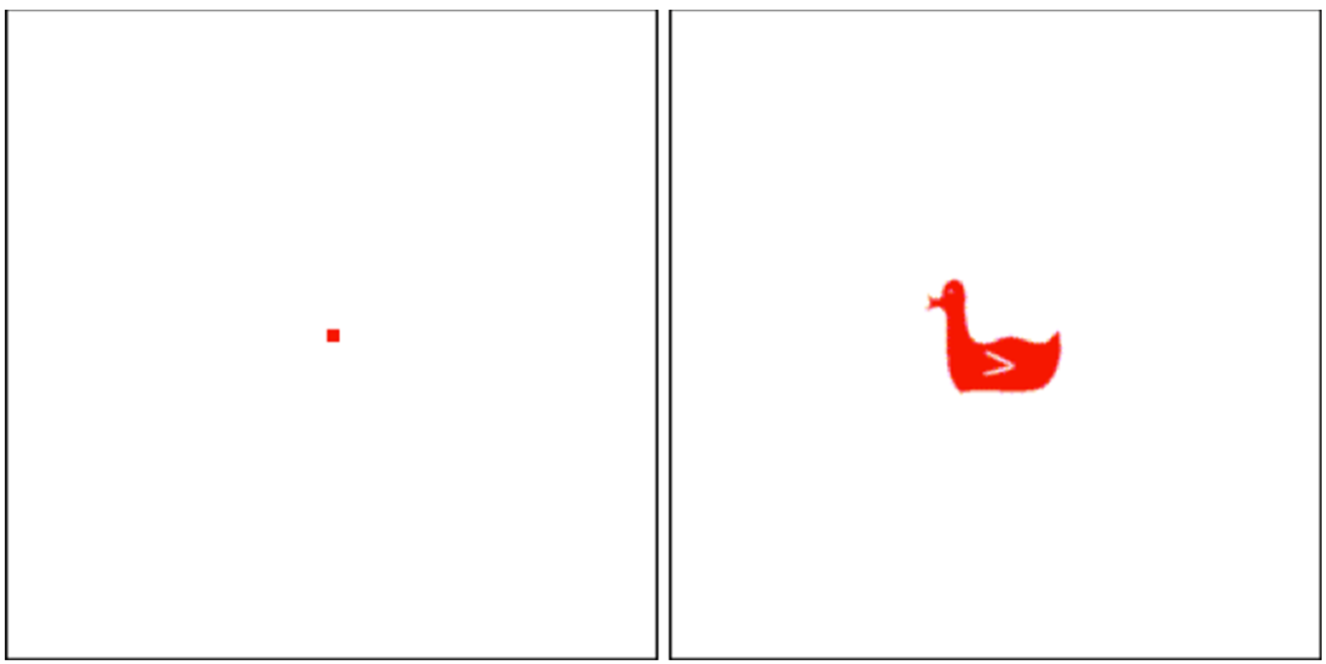
Sherwood and Cooper, pg 169

Convolutions

$$c(\mathbf{u}) = \int_{\text{all } \mathbf{r}} f(\mathbf{r}) g(\mathbf{u}-\mathbf{r})\, d\mathbf{r}$$

$$c(\mathbf{u}) = f(\mathbf{r}) * g(\mathbf{r}) = \int_{\text{all } \mathbf{r}} f(\mathbf{r}) g(\mathbf{u}-\mathbf{r})\, d\mathbf{r}$$

$$f(\mathbf{r}) * g(\mathbf{r}) = \int_{\text{all } \mathbf{r}} f(\mathbf{r}) g(\mathbf{u}-\mathbf{r})\, d\mathbf{r} = \int_{\text{all } \mathbf{r}} f(\mathbf{u}-\mathbf{r}) g(\mathbf{r})\, d\mathbf{r}$$



Convolutions

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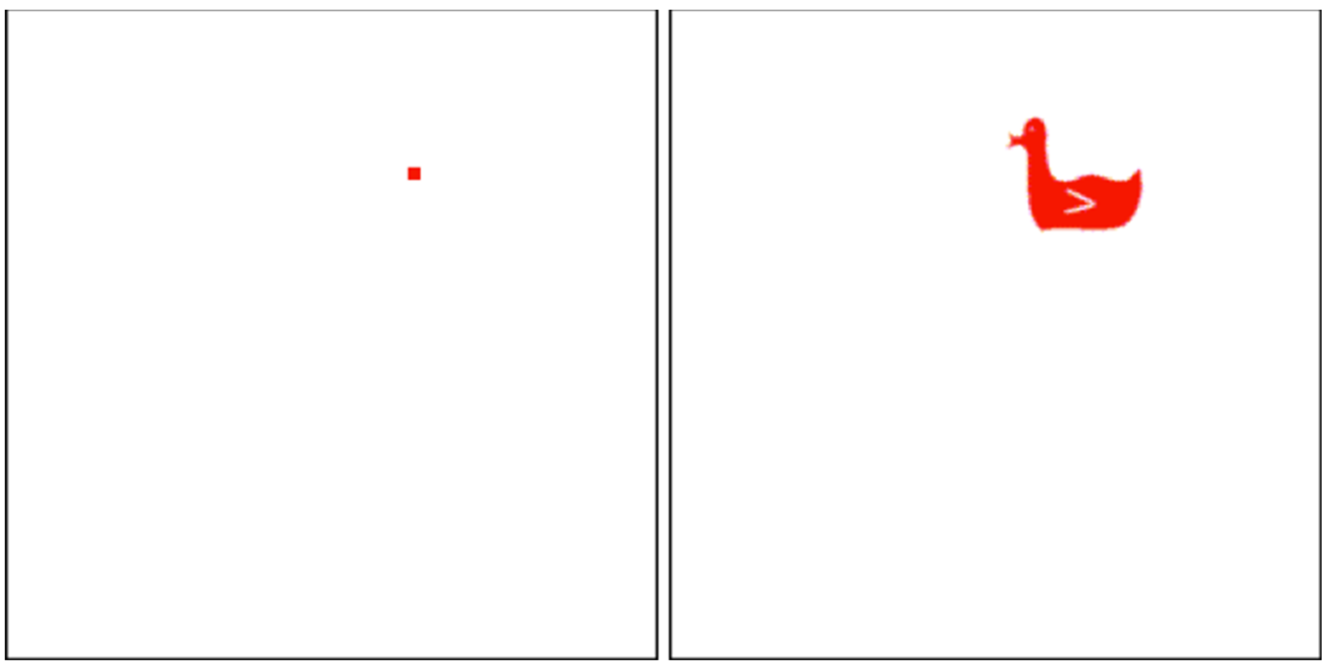

Convolutions

$$c(\mathbf{u}) = \int_{\text{all } \mathbf{r}} f(\mathbf{r}) g(\mathbf{u}-\mathbf{r})\, d\mathbf{r}$$

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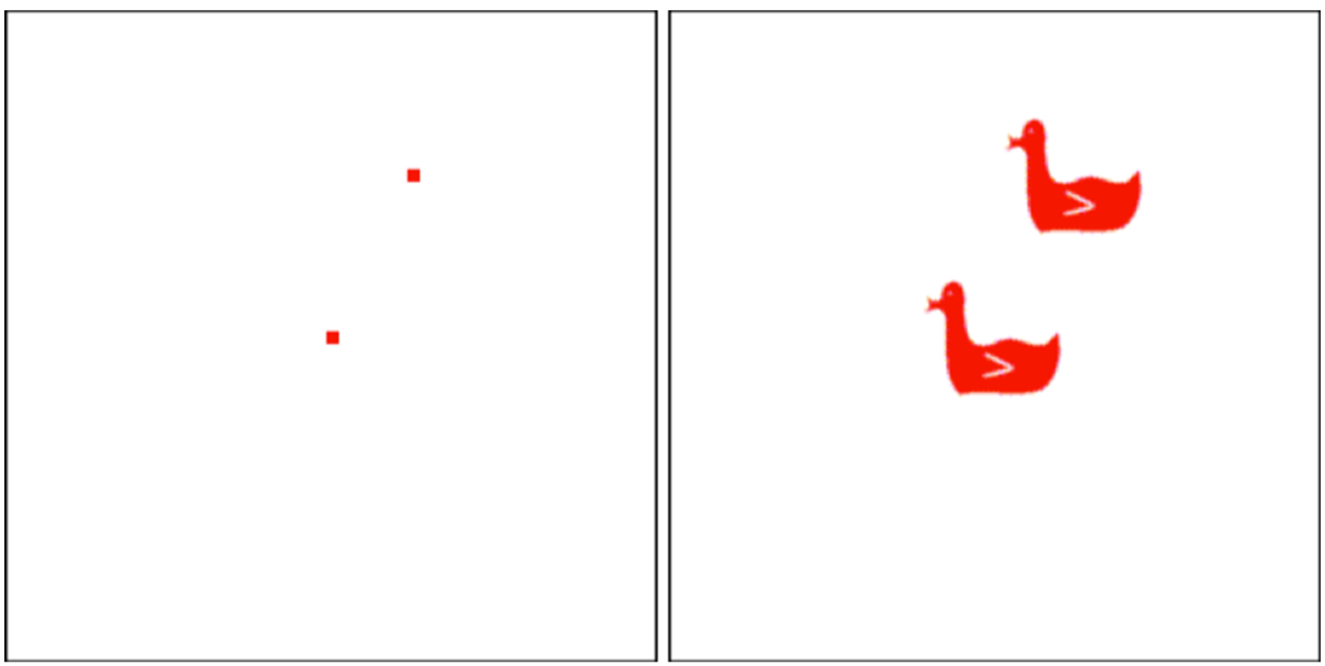
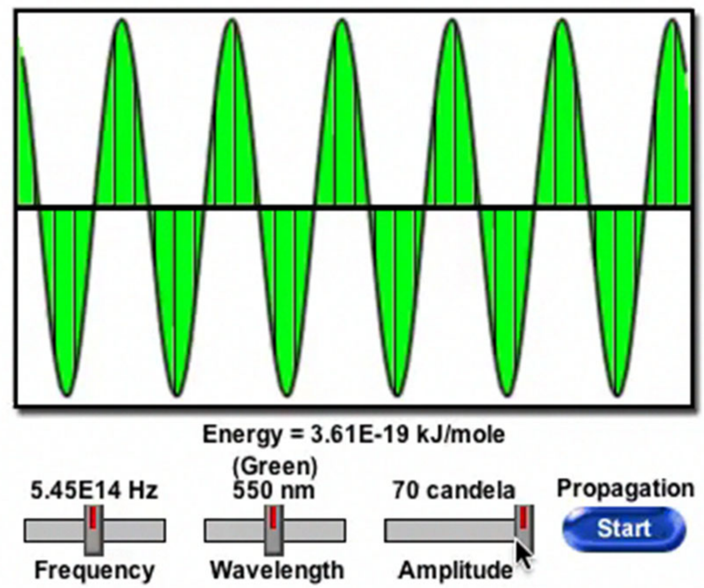


Fourier Transform of a Convolution

$$F(\mathbf{k}) = T[f(\mathbf{r}) * g(\mathbf{r})]$$
$$T[f(\mathbf{r}) * g(\mathbf{r})] = T[f(\mathbf{r})] \cdot T[g(\mathbf{r})]$$
$$T[f(\mathbf{r}) \cdot g(\mathbf{r})] = T[f(\mathbf{r})] * T[g(\mathbf{r})]$$

Waves and Electromagnetic Radiation

- What is a wave?
  - Direction of propagation
  - Amplitude
    - Wave crest
    - Wave trough
  - Wavelength
    - Period
    - Frequency



http://www.olympusmicro.com/primer/java/wavebasics/index.html

Waves and Electromagnetic Radiation

- What is a wave?
  - Direction of propagation
  - Amplitude
    - Wave crest
    - Wave trough
  - Wavelength
    - Period
    - Frequency

$$\psi(x,0) = \psi_0 \cos 2\pi \frac{x}{\lambda}$$

$$\psi(0,t) = \psi_0 \cos 2\pi \frac{t}{\tau}$$

$$\psi(x,t) = \psi_0 \cos\left(2\pi \frac{x}{\lambda} - 2\pi \frac{t}{\tau}\right)$$

$$k = \frac{2\pi}{\lambda}$$

$$\omega = \frac{2\pi}{\tau}$$

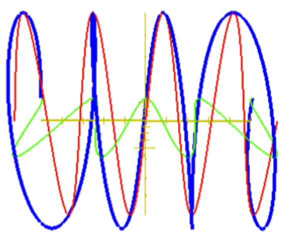
$$\psi(x,t) = \psi_0 \cos\left(kx - \omega t\right)$$

$$\frac{\Delta x}{\Delta t} = \frac{k}{\omega} = \mathrm{v}$$

$$\frac{\partial^2\psi(x,y,z,t)}{\partial x^2}+\frac{\partial^2\psi(x,y,z,t)}{\partial y^2}+\frac{\partial^2\psi(x,y,z,t)}{\partial z^2}=\frac{1}{v^2}\frac{\partial^2\psi(x,y,z,t)}{\partial t^2}$$

$$\psi(x,y,z,t)=\psi_0\cos(k_x x+k_y y+k_z z-\omega t)$$

$$k_x^2+k_y^2+k_z^2=\frac{\omega^2}{v^2}$$



$$\mathbf{r}=(x,y,z)$$

$$\mathbf{k}=(k_x,k_y,k_z)$$

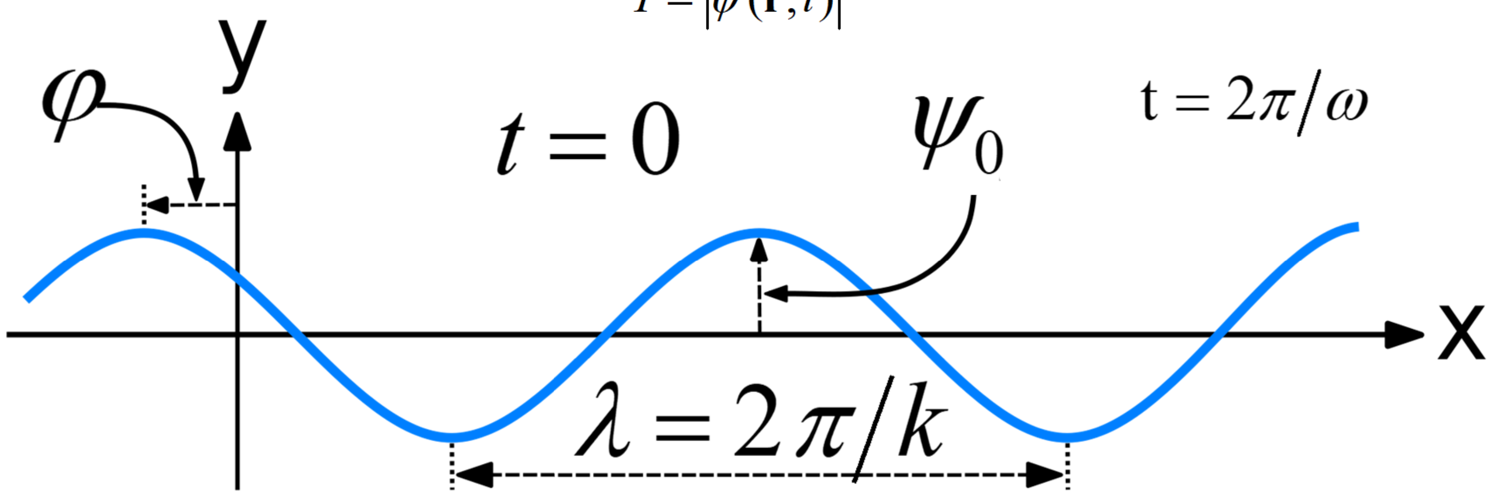
$$\mathbf{k}\cdot\mathbf{r}=(k_x x+k_y y+k_z z)$$

$$\psi(\mathbf{r},t)=\psi_0\cos(\mathbf{k}\cdot\mathbf{r}-\omega t)$$

$$\psi(\mathbf{r},t)=\psi_0\cos(\mathbf{k}\cdot\mathbf{r}-\omega t+\phi)$$

$$\psi(\mathbf{r},t)=\psi_0 e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t+\phi)}$$

$$I=\left|\psi(\mathbf{r},t)\right|^2$$



Diffraction

- Diffraction by one dimensional objects
- Diffraction by two dimensional objects
- Diffraction by three dimensional objects

Diffraction by a one dimensional object

$$\mathbf{k} = (k_x, 0, k_z)$$

$$\mathbf{k} \cdot \mathbf{r} = (k_x, 0, k_z) \cdot (x, 0, 0)$$

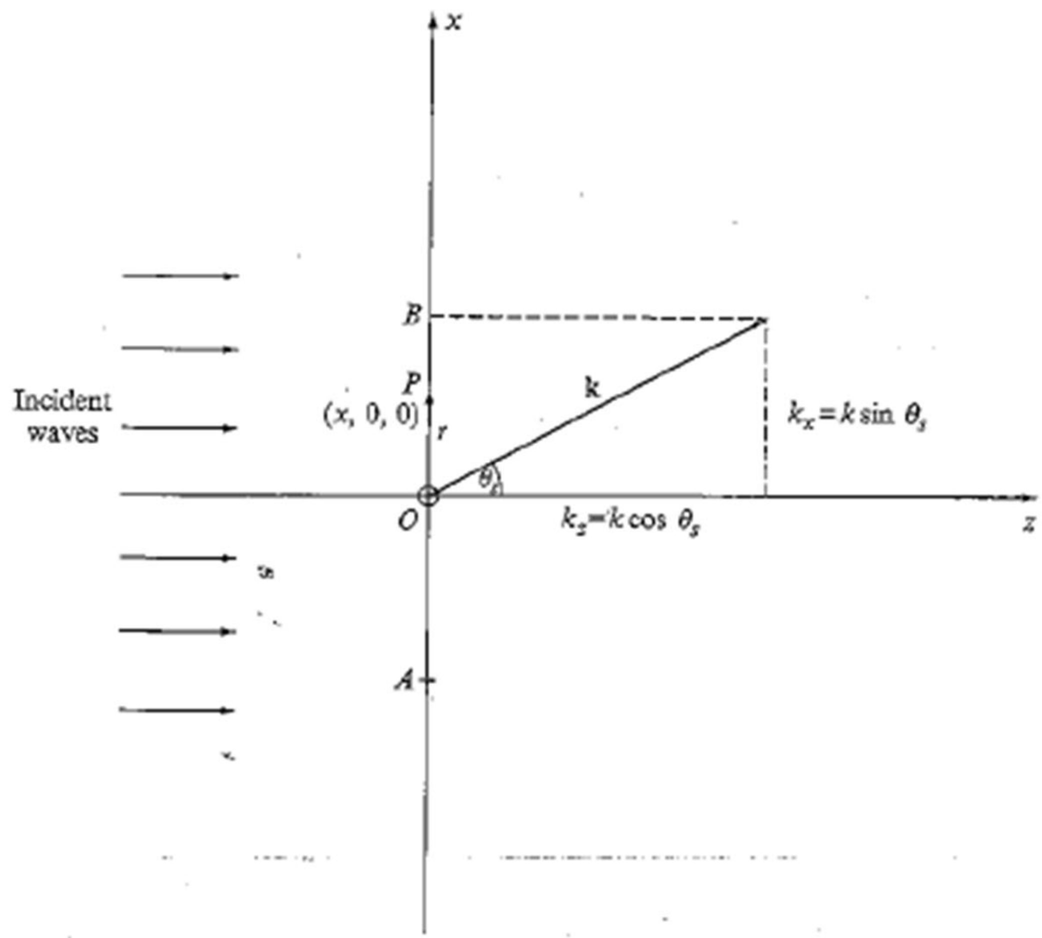
$$\mathbf{k} \cdot \mathbf{r} = k_x x$$

$$k_x = k \sin\theta_s$$

$$\mathbf{k} \cdot \mathbf{r} = kx \sin\theta_s$$

$$F(\mathbf{k}) = \int_{-\infty}^{\infty} f(x) e^{ikx\sin\theta_s}\, dx$$

$$F(\sin\theta_s) = \int_{-\infty}^{\infty} f(x) e^{ikx\sin\theta_s}\, dx$$



Diffraction by one narrow slit

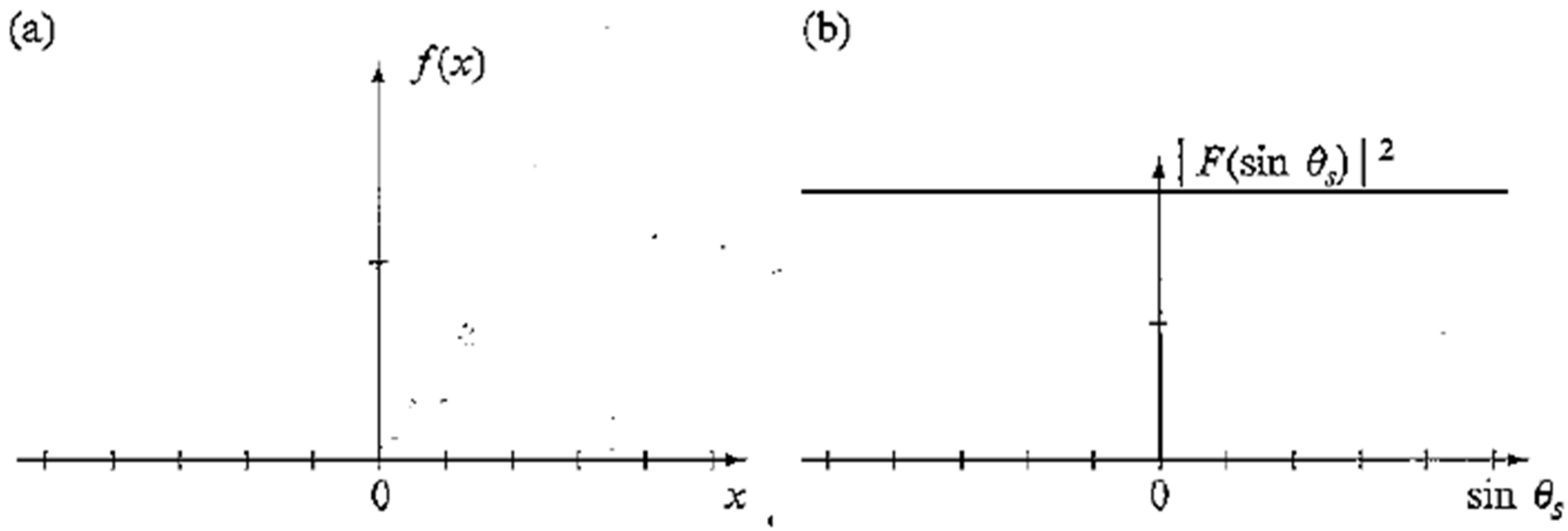
A narrow slit is defined by:

$$f(x) = \delta(x) \text{ and } \delta(0) = +\infty$$

$$F(\sin\theta_s) = \int_{-\infty}^{\infty} \delta(x) e^{ikx\sin\theta_s} dx = \int_{-\infty}^{\infty} \delta(x) dx = 1$$

$$F(\sin\theta_s) = 1$$

$$\left|F(\sin\theta_s)\right|^2 = 1$$

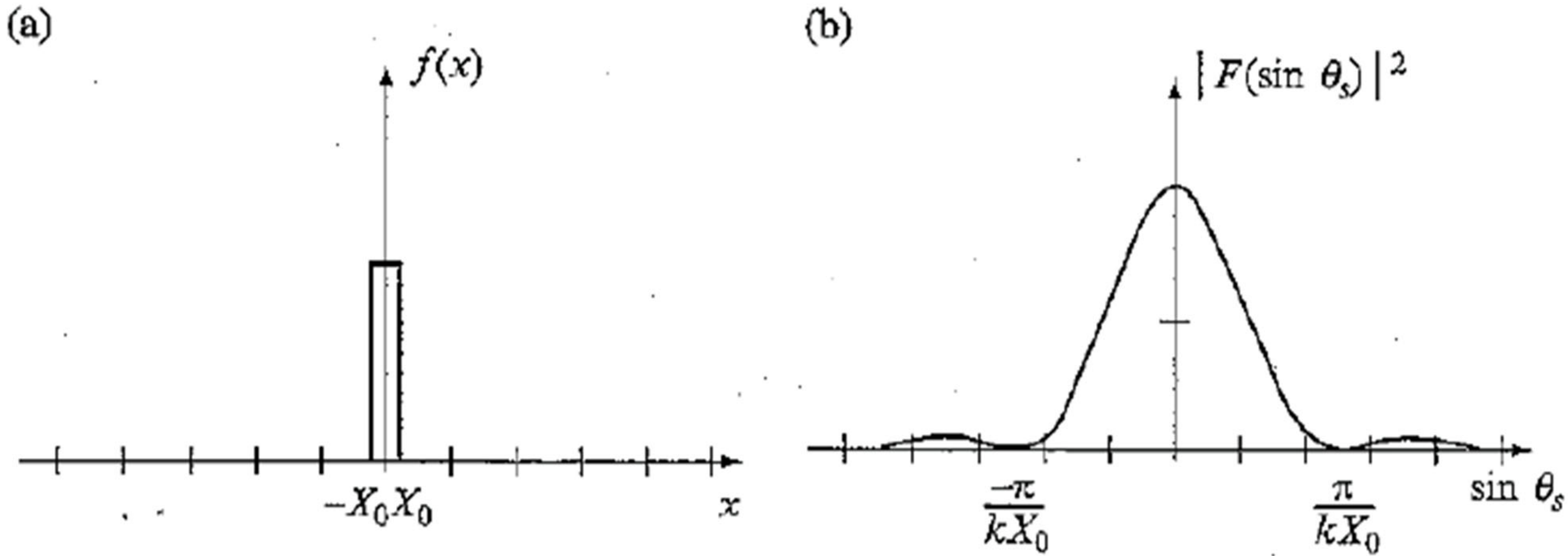


Diffraction by one wide slit

$$f(x) = 0 \text{ if } -\infty < x < -X_0$$
$$f(x) = 1 \text{ if } -X_0 < x < X_0$$
$$f(x) = 0 \text{ if } \quad X_0 < x < \infty$$

$$F(\sin\theta_s) = \int_{-\infty}^{\infty} f(x) e^{ikx\sin\theta_s}\,dx = \int_{-X_0}^{X_0} e^{ikx\sin\theta_s}\,dx = \left[\frac{e^{ikx\sin\theta_s}}{ikx\sin\theta_s}\right]_{-X_0}^{X_0} = \frac{e^{ikX_0\sin\theta_s} - e^{-ikX_0\sin\theta_s}}{ikX_0\sin\theta_s} = 2X_0\frac{\sin(kX_0\sin\theta_s)}{kX_0\sin\theta_s}$$

$$\left|F(\sin\theta_s)\right|^2 = 4X_0^2\frac{\sin^2(kX_0\sin\theta_s)}{\left(kX_0\sin\theta_s\right)^2}$$



Diffraction by two narrow slits

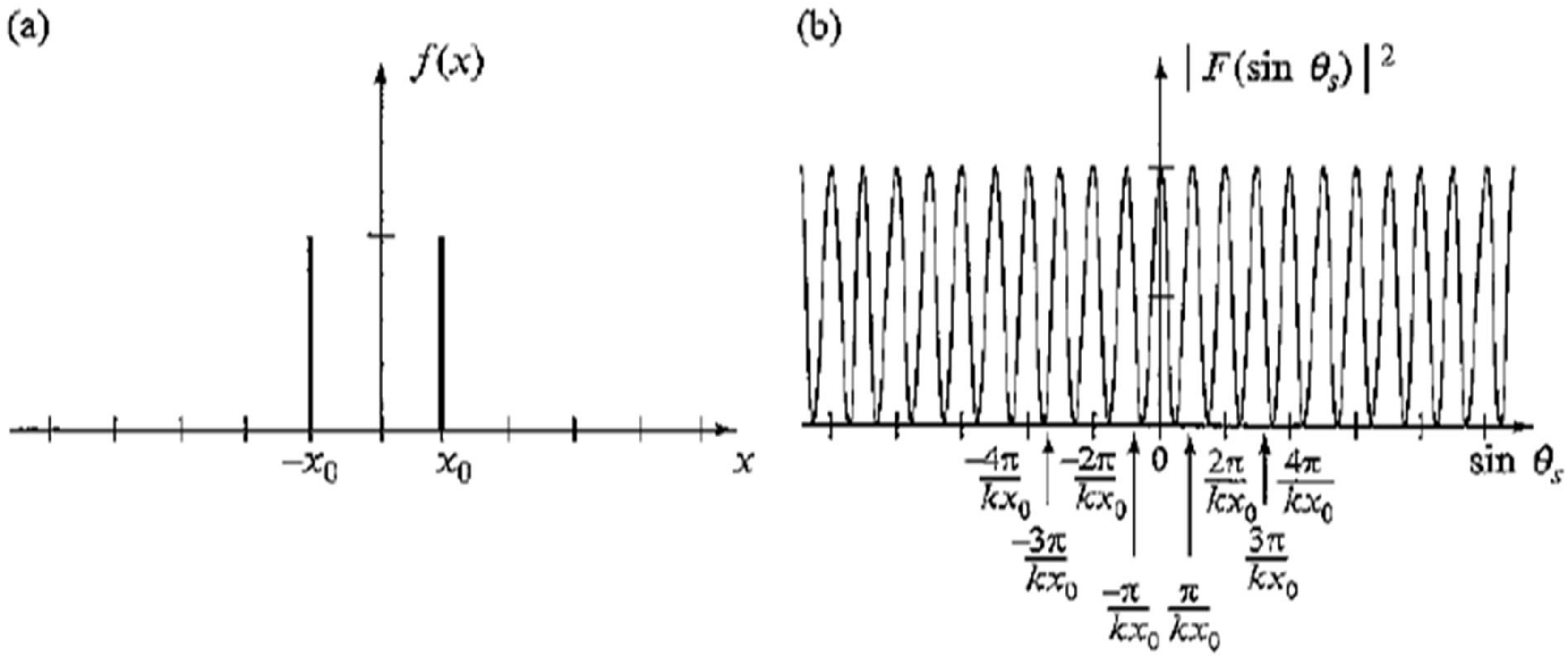
Two narrow slits are defined by:

$$f(x) = \delta(x + x_0) + \delta(x - x_0) \text{ and } \delta(x_0) = +\infty \text{ and } \delta(-x_0) = +\infty$$

$$F(\sin\theta_s) = \int_{-\infty}^{\infty} f(x) e^{ikx\sin\theta_s} dx = 2\cos(kx_0 \sin\theta_s)$$

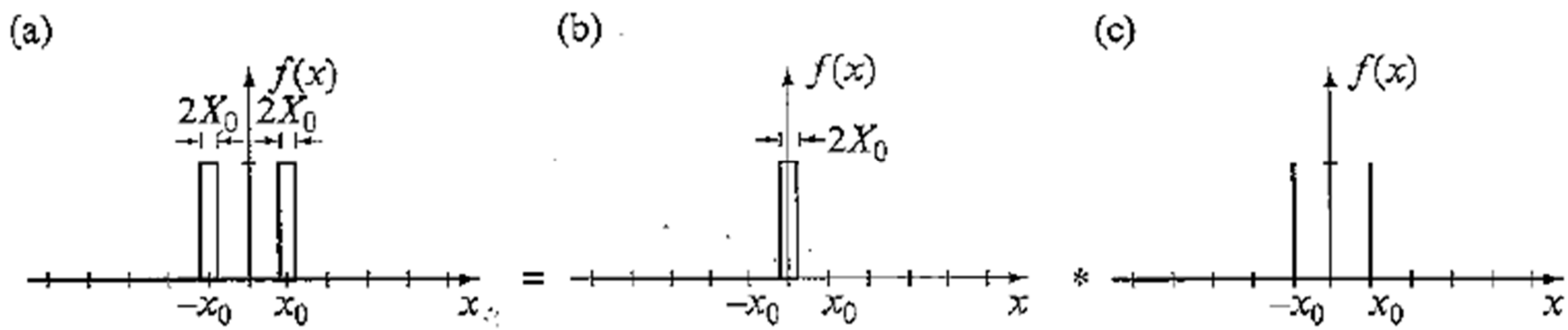
$$F(\sin\theta_s) = 2\cos(kx_0 \sin\theta_s)$$

$$\left|F(\sin\theta_s)\right|^2 = 4\cos^2(kx_0 \sin\theta_s)$$

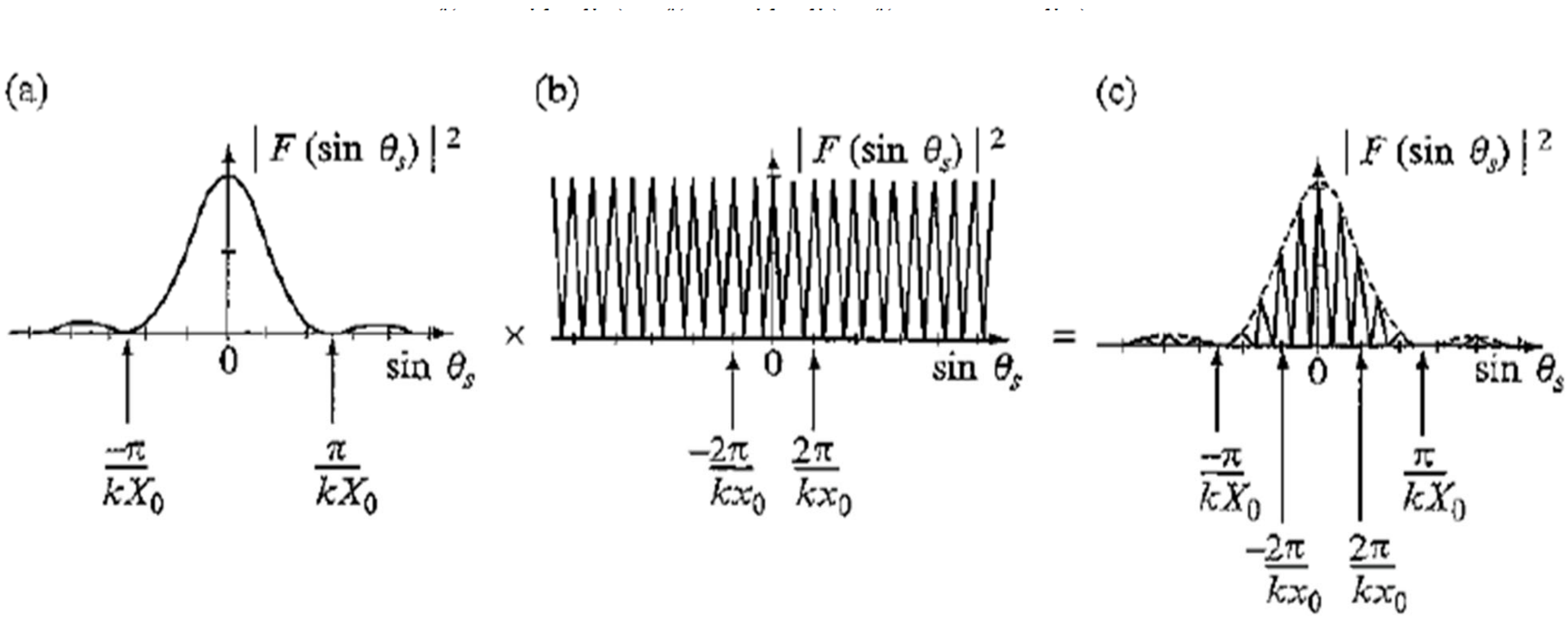


Diffraction by Two Wide Slits

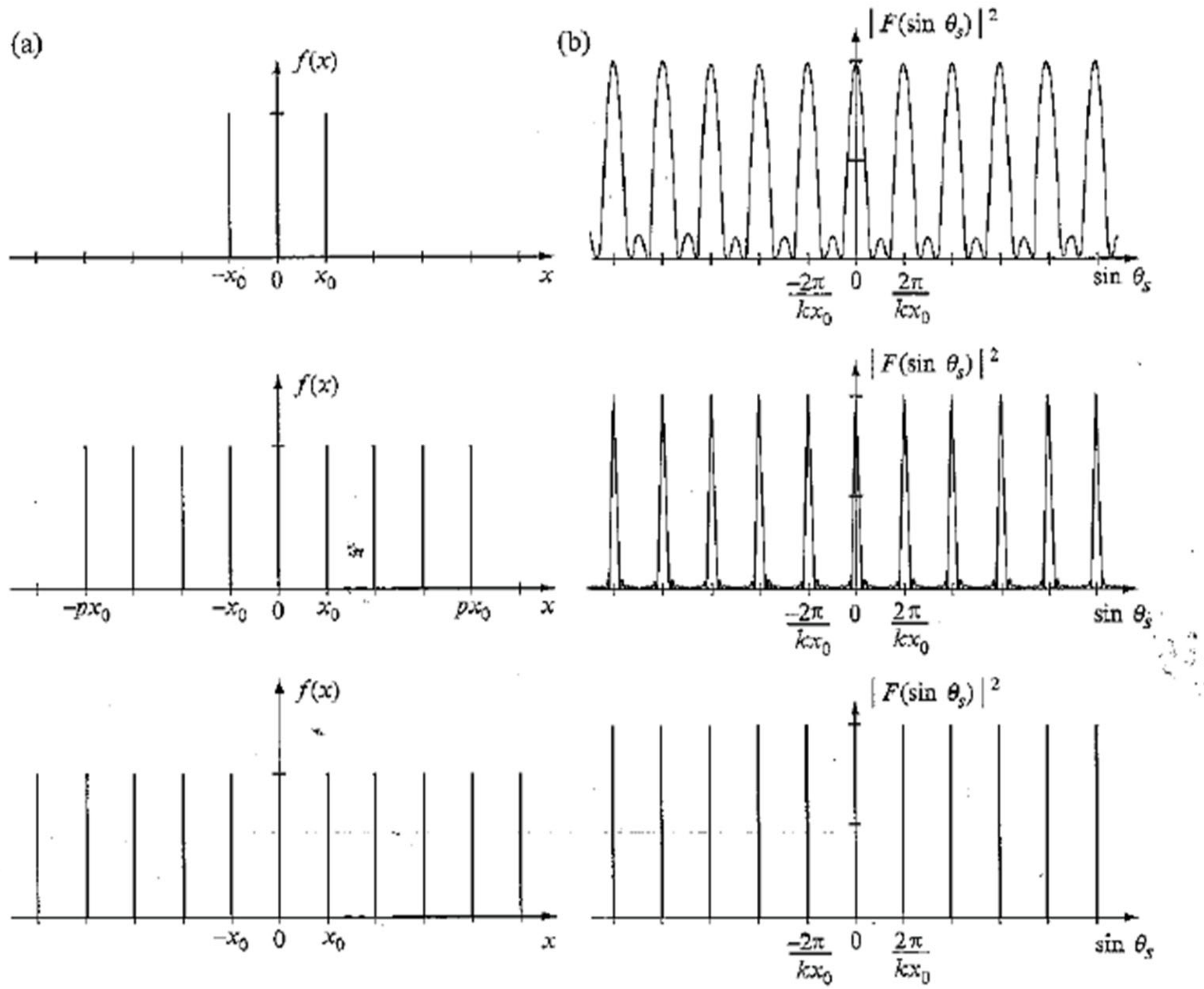
$$f(x) = 0 \text{ if } -\infty < x < -(x_0 + X_0)$$
$$f(x) = 1 \text{ if } -(x_0 + X_0) \le x \le -(x_0 - X_0)$$
$$f(x) = 0 \text{ if } -(x_0 - X_0) < x < (x_0 - X_0)$$
$$f(x) = 1 \text{ if } (x_0 - X_0) \le x \le (x_0 + X_0)$$
$$f(x) = 0 \text{ if } (x_0 + X_0) < x < \infty$$
$$f(\text{two wide slits}) = f(\text{one wide slit}) * f(\text{two narrow slits})$$



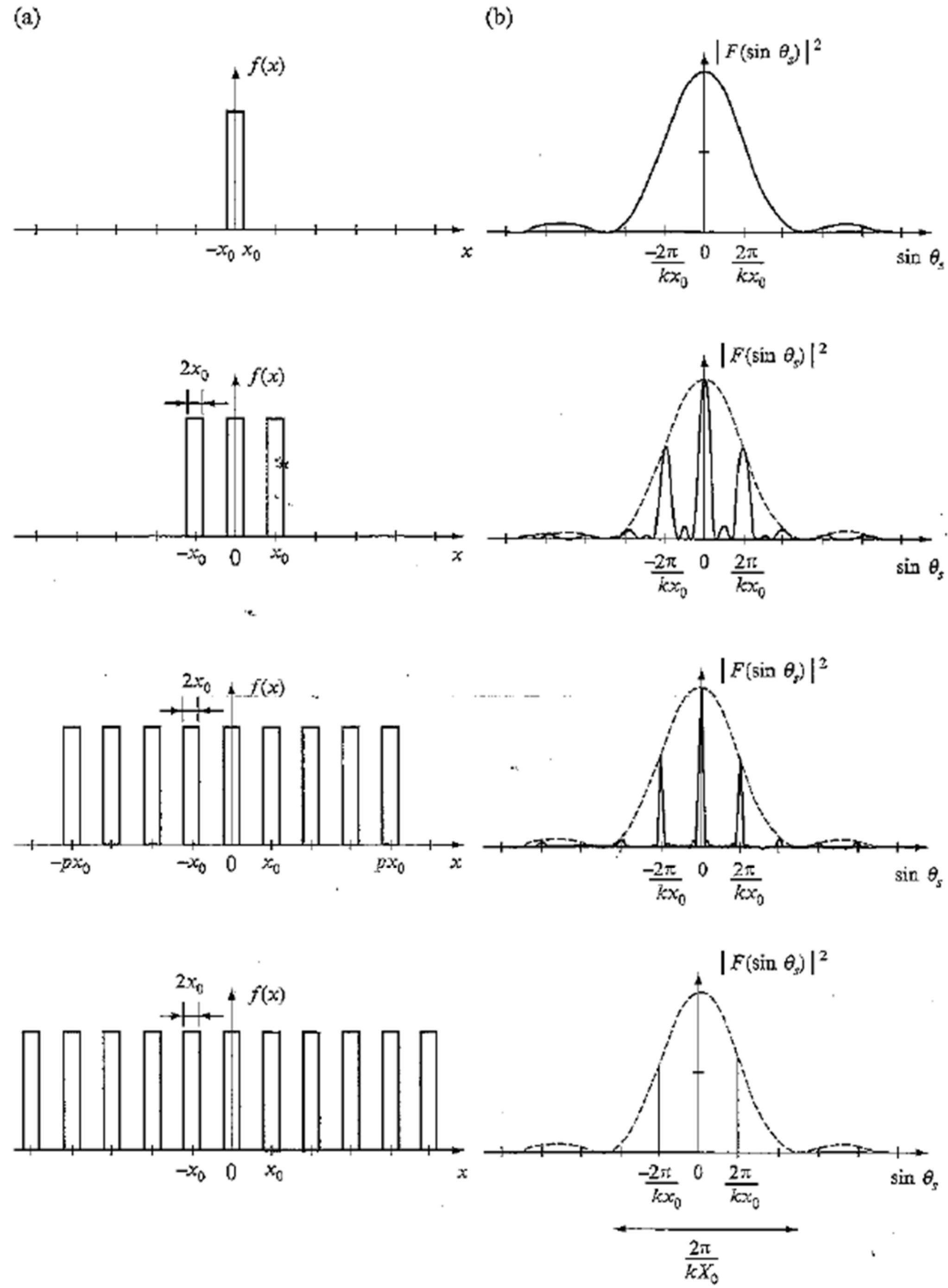
Diffraction by Two Wide Slits



Diffraction by N Narrow Slits



- The position of the main peaks in a diffraction pattern is determined solely by the lattice spacing of the object
- The shape of each main peak is determined by the overall shape of the object.
- The effect of the object (motif) is to alter the intensity of each main peak, but the positions of the main peaks remain unchanged.



(a)
(b)
$f(x)$
$-x_0$ x_0
x
$|F(\sin\theta_s)|^2$
$\frac{-2\pi}{kx_0}$ 0 $\frac{2\pi}{kx_0}$
$\sin\theta_s$
$2x_0$
$-x_0$ 0 x_0
$-px_0$ px_0
$\frac{2\pi}{kX_0}$

- The positions of the main peaks give information about the lattice
- The shape of each main peak gives information on the overall object shape.
- The set of intensities of the main peaks gives information on the structure of the motif.

Diffraction by a 3D Lattice

$$\mathbf{r} = p\mathbf{a} + q\mathbf{b} + r\mathbf{c}$$

$$f(\mathbf{r}) = \sum_{\text{all } p,q,r} \delta(\mathbf{r} - [p\mathbf{a} + q\mathbf{b} + r\mathbf{c}])$$

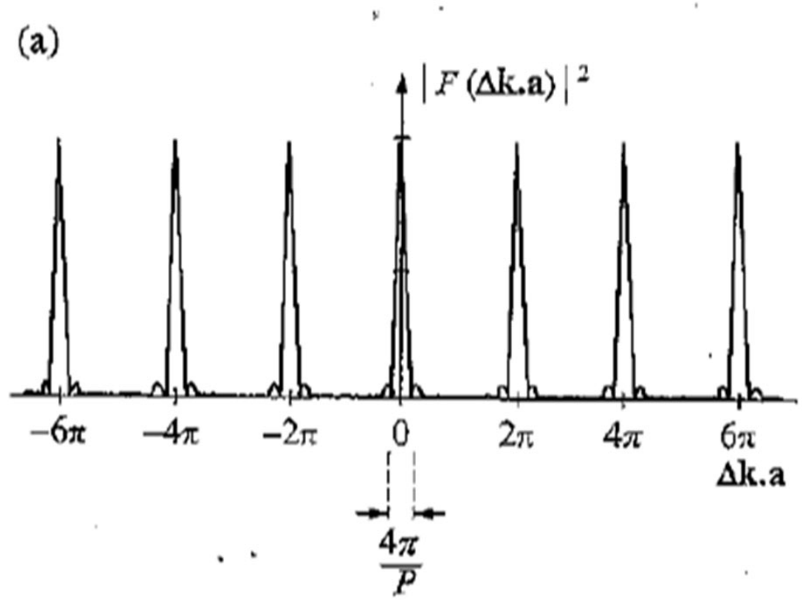
$$F(\Delta\mathbf{k}) = \int_{\text{all } \mathbf{r}} f(\mathbf{r}) e^{i\Delta\mathbf{k}\cdot\mathbf{r}} d\mathbf{r}$$

$$F(\Delta\mathbf{k}) = \int_{\text{all } \mathbf{r}} \sum_{\text{all } p,q,r} \delta(\mathbf{r} - [p\mathbf{a} + q\mathbf{b} + r\mathbf{c}]) e^{i\Delta\mathbf{k}\cdot\mathbf{r}} d\mathbf{r}$$

$$F(\Delta\mathbf{k}) = \sum_{\text{all } p,q,r} e^{i\Delta\mathbf{k}\cdot(p\mathbf{a}+q\mathbf{b}+r\mathbf{c})} = \sum_{\text{all } p,q,r} e^{ip\Delta\mathbf{k}\cdot\mathbf{a}} \cdot e^{iq\Delta\mathbf{k}\cdot\mathbf{b}} \cdot e^{ir\Delta\mathbf{k}\cdot r}$$

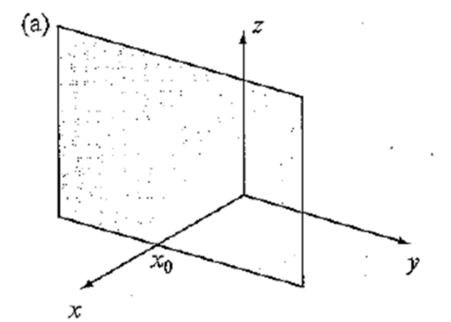
$$F(\Delta\mathbf{k}) = \sum_{\text{all } p} e^{ip\Delta\mathbf{k}\cdot\mathbf{a}} \cdot \sum_{\text{all } q} e^{iq\Delta\mathbf{k}\cdot\mathbf{b}} \cdot \sum_{\text{all } r} e^{ir\Delta\mathbf{k}\cdot r}$$

$$\left|F(\Delta\mathbf{k})\right|^2 = \frac{\sin^2 \frac{P\Delta\mathbf{k}\cdot\mathbf{a}}{2}}{\sin^2 \frac{\Delta\mathbf{k}\cdot\mathbf{a}}{2}} \cdot \frac{\sin^2 \frac{Q\Delta\mathbf{k}\cdot\mathbf{b}}{2}}{\sin^2 \frac{\Delta\mathbf{k}\cdot\mathbf{b}}{2}} \cdot \frac{\sin^2 \frac{R\Delta\mathbf{k}\cdot\mathbf{c}}{2}}{\sin^2 \frac{\Delta\mathbf{k}\cdot\mathbf{c}}{2}}$$



Maxima are seen at $\Delta\mathbf{k}\cdot\mathbf{a} = 2h\pi$ where h is a positive or negative integer

$$|F(\Delta\mathbf{k})|^2 = \frac{\sin^2 \frac{P\Delta\mathbf{k}\cdot\mathbf{a}}{2}}{\sin^2 \frac{\Delta\mathbf{k}\cdot\mathbf{a}}{2}} \cdot \frac{\sin^2 \frac{Q\Delta\mathbf{k}\cdot\mathbf{b}}{2}}{\sin^2 \frac{\Delta\mathbf{k}\cdot\mathbf{b}}{2}} \cdot \frac{\sin^2 \frac{R\Delta\mathbf{k}\cdot\mathbf{c}}{2}}{\sin^2 \frac{\Delta\mathbf{k}\cdot\mathbf{c}}{2}}$$



We see maxima when

$\Delta\mathbf{k}\cdot\mathbf{a} = 2h\pi$ where h is a positive or negative integer

The first zero occurs at:

$P\dfrac{\Delta\mathbf{k}\cdot\mathbf{a}}{2} = \pm\pi$ and the peak width is $\Delta(\Delta\mathbf{k}\cdot\mathbf{a}) = \dfrac{4\pi}{P}$

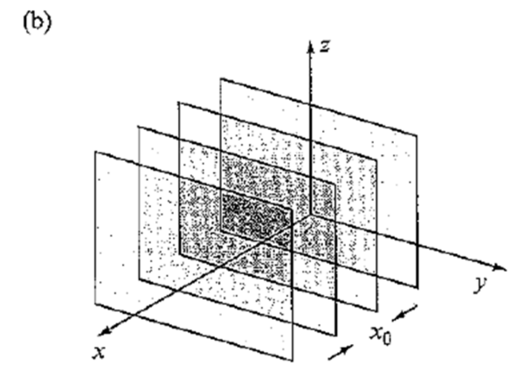
As P, Q and R tend to infinity the functions become δ functions:

$$|F(\Delta\mathbf{k})|^2 = \left[\sum_{\text{all } h}\delta(\Delta\mathbf{k}\cdot\mathbf{a}-2h\pi)\right]^2 \cdot \left[\sum_{\text{all } k}\delta(\Delta\mathbf{k}\cdot\mathbf{b}-2k\pi)\right]^2 \cdot \left[\sum_{\text{all } l}\delta(\Delta\mathbf{k}\cdot\mathbf{c}-2l\pi)\right]^2$$

Each term $\delta(\Delta\mathbf{k}\cdot\mathbf{a}-2h\pi)$ represents a plane and each summation represents a series of planes.

All three summations thus represents three sets of parallel planes with each intersection of three planes representing a lattice point.

$$|F(\Delta\mathbf{k})|^2 = \frac{\sin^2\dfrac{P\Delta\mathbf{k}\cdot\mathbf{a}}{2}}{\sin^2\dfrac{\Delta\mathbf{k}\cdot\mathbf{a}}{2}}\cdot\frac{\sin^2\dfrac{Q\Delta\mathbf{k}\cdot\mathbf{b}}{2}}{\sin^2\dfrac{\Delta\mathbf{k}\cdot\mathbf{b}}{2}}\cdot\frac{\sin^2\dfrac{R\Delta\mathbf{k}\cdot\mathbf{c}}{2}}{\sin^2\dfrac{\Delta\mathbf{k}\cdot\mathbf{c}}{2}}$$



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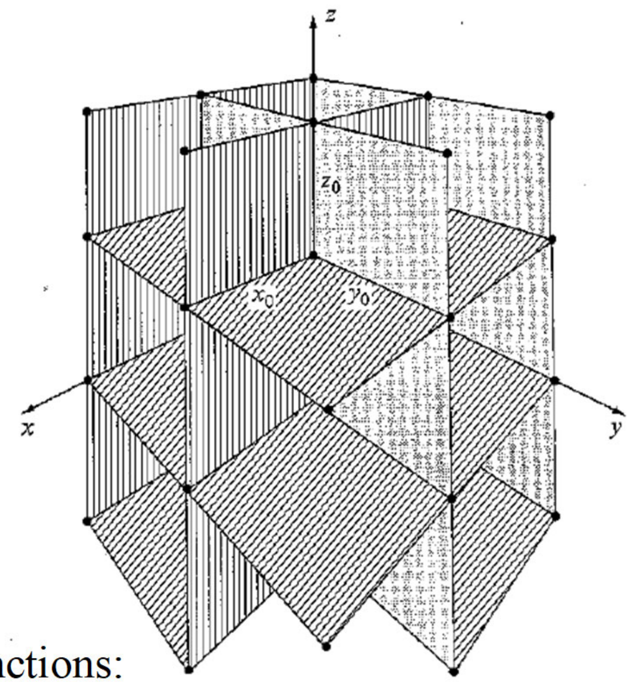

We see maxima when

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The first zero occurs at:

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As P, Q and R tend to infinity the functions become δ functions:

$$|F(\Delta\mathbf{k})|^2 = \left[\sum_{\text{all } h} \delta(\Delta\mathbf{k}\cdot\mathbf{a} - 2h\pi)\right]^2 \cdot \left[\sum_{\text{all } k} \delta(\Delta\mathbf{k}\cdot\mathbf{b} - 2k\pi)\right]^2 \cdot \left[\sum_{\text{all } l} \delta(\Delta\mathbf{k}\cdot\mathbf{c} - 2l\pi)\right]^2$$

Each term $\delta(\Delta\mathbf{k}\cdot\mathbf{a} - 2h\pi)$ represents a plane and each summation represents a series of planes.

All three summations thus represents three sets of parallel planes with each intersection of three planes representing a lattice point.

The Reciprocal Lattice

$$\mathbf{a}^* \cdot \mathbf{a} = 1,\ \mathbf{b}^* \cdot \mathbf{a} = 0,\ \mathbf{c}^* \cdot \mathbf{a} = 0$$

$$\mathbf{a}^* \cdot \mathbf{b} = 0,\ \mathbf{b}^* \cdot \mathbf{b} = 1,\ \mathbf{c}^* \cdot \mathbf{b} = 0$$

$$\mathbf{a}^* \cdot \mathbf{c} = 0,\ \mathbf{b}^* \cdot \mathbf{c} = 0,\ \mathbf{c}^* \cdot \mathbf{c} = 1$$

Since $\mathbf{b}^* \cdot \mathbf{a} = 0$ and $\mathbf{c}^* \cdot \mathbf{a} = 0$, $\mathbf{a}^*$ must be perpendicular to $\mathbf{b}$ and $\mathbf{c}$.

$$\mathbf{a}^* = \alpha(\mathbf{b} \wedge \mathbf{c})$$

and

$$\mathbf{a}^* \cdot \mathbf{a} = 1$$

so

$$\mathbf{a} \cdot \alpha(\mathbf{b} \wedge \mathbf{c}) = 1 \text{ and } \mathbf{a} \cdot (\mathbf{b} \wedge \mathbf{c}) = V,$$

so

$$\alpha = \frac{1}{V}$$

$$\mathbf{a}^* = \frac{\mathbf{b} \wedge \mathbf{c}}{\mathbf{a} \cdot (\mathbf{b} \wedge \mathbf{c})} = \frac{\mathbf{b} \wedge \mathbf{c}}{V},\ \mathbf{b}^* = \frac{\mathbf{c} \wedge \mathbf{a}}{\mathbf{a} \cdot (\mathbf{b} \wedge \mathbf{c})} = \frac{\mathbf{c} \wedge \mathbf{a}}{V},\ \mathbf{c}^* = \frac{\mathbf{a} \wedge \mathbf{b}}{\mathbf{a} \cdot (\mathbf{b} \wedge \mathbf{c})} = \frac{\mathbf{a} \wedge \mathbf{b}}{V}$$

Diffraction

- In this section we will:
  - Learn scattering (diffraction) by a single electron
  - Learn scattering by a group of electrons
  - Define the electron density function
  - Define the structure factor
  - Define the atomic scattering factor
  - Apply a correction for thermal motion
  - Define Friedel’s Law and when it fails
  - What the effect of translational symmetry has on the diffraction pattern

Thomson Scattering by a Single Electron

http://www.xtal.iqfr.csic.es/Cristalografia/parte_05-en.html

$$\mathbf{a} = \frac{e}{m}\mathbf{E}_{in}$$

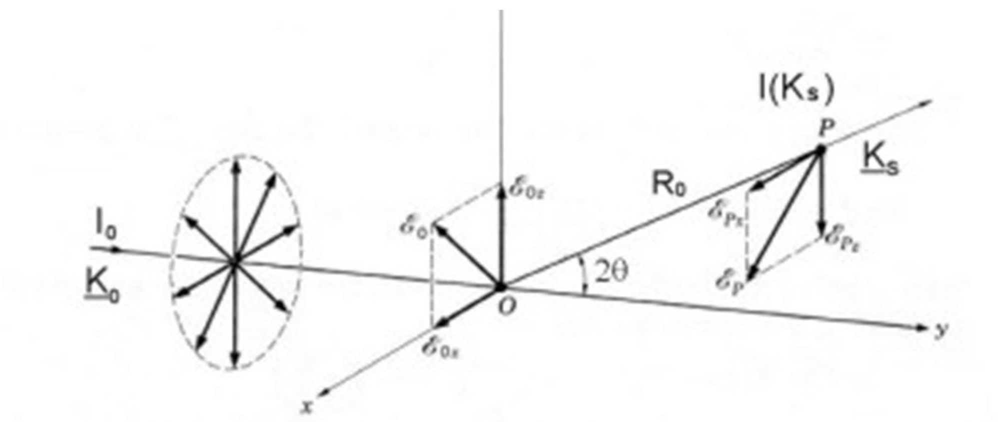
$$\frac{E_{scat}}{E_{in}} = \frac{e^2}{4\pi\varepsilon_0 rmc^2}\sqrt{\frac{1+\cos^2 2\theta}{2}}$$

$$\varepsilon_0 = 8.854\times10^{-12}\ \mathrm{F\cdot m^{-1}}$$

$c =$ speed of light

$r =$ radius of interaction

$\theta =$ Bragg angle



Thomson Scattering by a Group of Electrons (I)

$$\frac{E_{scat}}{E_{in}} = \frac{e^2}{4\pi\varepsilon_0 rmc^2}\sqrt{\frac{1+\cos^2 2\theta}{2}}$$

$$f_e = \frac{e^2}{4\pi\varepsilon_0 rmc^2}$$

$$\frac{E_{scat}}{E_{in}} = f_e\sqrt{\frac{1+\cos^2 2\theta}{2}}$$

but if the beam is polarized we can write:

$$\frac{E_{scat}}{E_{in}} = f_e p(2\theta)$$

where $p(2\theta)$ is the polarization factor.

For now let's ignore $p(2\theta)$.

Thomson Scattering by a Group of Electrons (II)

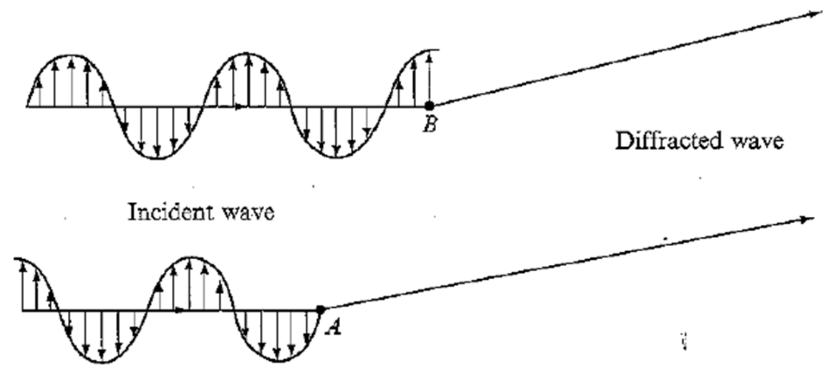
$$\left(E_{scat}\right)_A = f_e E_{in}$$

$$\left(E_{scat}\right)_B = f_e E_{in} e^{i\phi}$$

$$\left(E_{scat}\right)_{tot} = \left(E_{scat}\right)_A + \left(E_{scat}\right)_B$$

$$\frac{\left(E_{scat}\right)_{tot}}{E_{in}} = f_e + f_e e^{i\phi}$$

$$\frac{\left(E_{scat}\right)_{tot}}{E_{in}} = \sum_n f_e e^{i\phi_n}$$



Remember

$$\boxed{F(\Delta\mathbf{k}) = \int_{\text{all } r} f(\mathbf{r}) e^{i\Delta\mathbf{k}\cdot\mathbf{r}}\, d\mathbf{r}}$$

The amplitude function of a group of electrons is

$$f_e \rho(\mathbf{r})$$

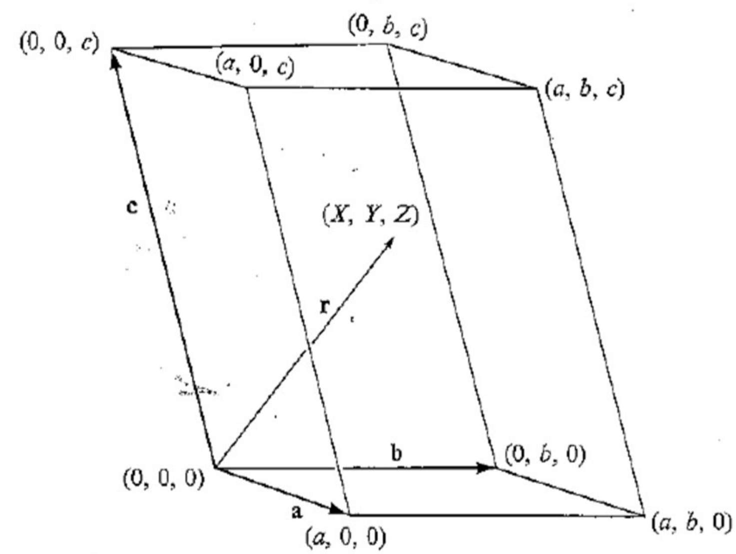
Substituting into $F(\Delta\mathbf{k})$ gives

$$F(\Delta\mathbf{k}) = \int_{\text{all } r} f_e \rho(\mathbf{r}) e^{i\Delta\mathbf{k}\cdot\mathbf{r}}\, d\mathbf{r}$$

Thomson Scattering by a Group of Electrons (III)

$$F(\Delta\mathbf{k}) = \int_{\text{all } r} f_e \rho(\mathbf{r}) e^{i\Delta\mathbf{k}\cdot\mathbf{r}}\, d\mathbf{r}$$

$$F(\Delta\mathbf{k}) = f_e \int_{\text{unit cell}} \rho(\mathbf{r}) e^{i\Delta\mathbf{k}\cdot\mathbf{r}}\, d\mathbf{r} \text{ or } F_{rel}(\Delta\mathbf{k}) = \int_{\text{unit cell}} \rho(\mathbf{r}) e^{i\Delta\mathbf{k}\cdot\mathbf{r}}\, d\mathbf{r}$$



Let's define coordinates of the unit cell as follows:

$$0 \le X \le a,\ 0 \le Y \le b,\ 0 \le Z \le c$$

$$x = \frac{X}{a},\ \mathrm{y} = \frac{Y}{b},\ \mathrm{z} = \frac{Z}{c} \text{ and } 0 \le x \le 1,\ 0 \le y \le 1,\ 0 \le z \le 1$$

X, Y and Z represent absolute coordinates and

x, y and z represent fractional coordinates.

$$\mathbf{r} = x\mathbf{a} + y\mathbf{b} + z\mathbf{c}$$

$$d\mathbf{r} = dx\ dy\ dz\ \mathbf{a}\cdot\mathbf{b}\wedge\mathbf{c} = V\ dx\ dy\ dz$$

$\rho(\mathbf{r})$ becomes $\rho(x, y, z)$

Thomson Scattering by a Group of Electrons (IV)

$$F_{rel}(\Delta\mathbf{k}) = V\int_{x=0}^{x=1}\int_{y=0}^{y=1}\int_{z=0}^{z=1}\rho(x,y,z)e^{i\Delta\mathbf{k}\cdot(x\mathbf{a}+y\mathbf{b}+z\mathbf{c})}dx\ dy\ dz$$

$$\Delta\mathbf{k} = 2\pi\mathbf{S}_{hkl}$$

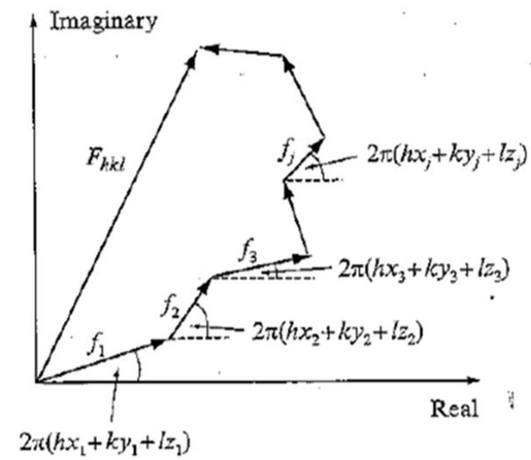
$$\mathbf{S}_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$$

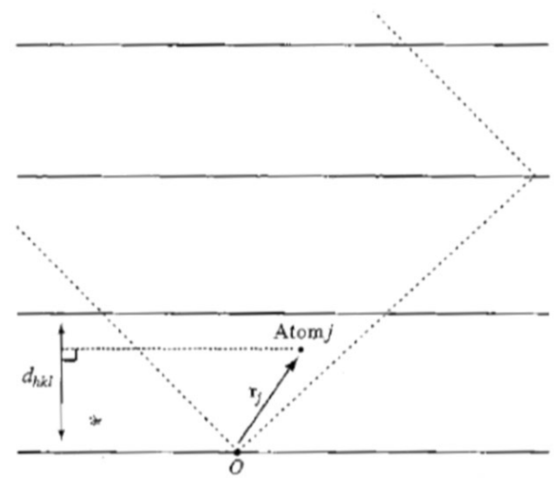
$$\Delta\mathbf{k}\cdot\mathbf{r} = 2\pi(h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*)\cdot(x\mathbf{a}+y\mathbf{b}+z\mathbf{c})$$
$$= 2\pi(hx+ky+lz)$$

$$F_{rel}(\Delta\mathbf{k}) = F_{hkl} = V\int_0^1\int_0^1\int_0^1\rho(x,y,z)e^{2\pi i(hx+ky+lz)}dx\ dy\ dz$$

$$F_{hkl} = \left|F_{hkl}\right|e^{i\phi_{hkl}}$$

$$I_{hkl} \propto |F_{hkl}|^2$$





The Electron Density Function

$$F_{rel}(\Delta\mathbf{k}) = F_{hkl} = V \int_{x=0}^{x=1} \int_{y=0}^{y=1} \int_{z=0}^{z=1} \rho(x,y,z) e^{i\Delta\mathbf{k}\cdot(x\mathbf{a}+y\mathbf{b}+z\mathbf{c})} dx\ dy\ dz$$

F_{hkl} is the Fourier transform of $\rho(x,y,z)$

$$\rho(x,y,z) = \frac{1}{V} \int_{\text{all }\Delta\mathbf{k}} F_{rel}(\Delta\mathbf{k}) e^{-i\Delta\mathbf{k}\cdot(x\mathbf{a}+y\mathbf{b}+z\mathbf{c})} d(\Delta\mathbf{k})$$

$$\rho(x,y,z) = \frac{1}{V} \int_{\text{all }\Delta\mathbf{k}} F_{rel}(\Delta\mathbf{k}) e^{-2\pi i(hx+ky+lz)} d(\Delta\mathbf{k})$$

But the hkl values are discrete so we can rewrite this as

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

The Structure Factor (I)

$$F_{hkl} = V \int_{x=0}^{x=1} \int_{y=0}^{y=1} \int_{z=0}^{z=1} \rho(x,y,z) e^{i\Delta\mathbf{k}\cdot(x\mathbf{a}+y\mathbf{b}+z\mathbf{c})} dx\ dy\ dz$$

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

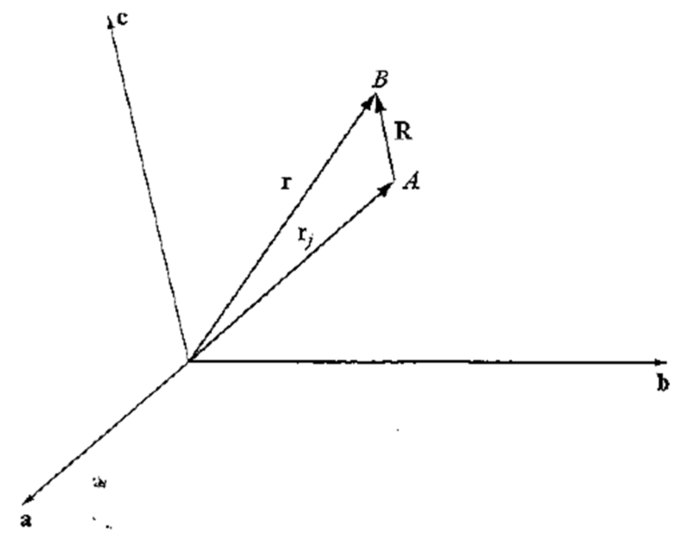
$$\mathbf{r} = x\mathbf{a} + y\mathbf{b} + z\mathbf{c}$$

$$F_{hkl} = \int_{\text{unit cell}}^{x=1} \rho(\mathbf{r}) e^{2\pi i \mathbf{S}_{hkl}\cdot\mathbf{r}} d\mathbf{r}$$

$$\mathbf{r} = \mathbf{r}_j + \mathbf{R}$$

$$\rho(\mathbf{r}) = \sum_j \rho_j(\mathbf{r} - \mathbf{r}_j)$$

$$F_{hkl} = \int_{\text{unit cell}}^{x=1} \sum_j \rho_j(\mathbf{r} - \mathbf{r}_j) e^{2\pi i \mathbf{S}_{hkl}\cdot\mathbf{r}} d\mathbf{r}$$



The Structure Factor (II)

$$F_{hkl} = \int_{\text{unit cell}}^{x=1} \sum_j \rho_j\left(\mathbf{r}-\mathbf{r}_j\right) e^{2\pi i \mathbf{S}_{hkl}\cdot\mathbf{r}}\, d\mathbf{r}$$

Assume the positions of the atoms, $\mathbf{r}_j$, are constant, then $d\mathbf{r} = d\mathbf{R}$

$$F_{hkl} = \int_{\text{unit cell}}^{x=1} \sum_j \rho_j(\mathbf{R})\, e^{2\pi i \mathbf{S}_{hkl}\cdot(\mathbf{r}_j+\mathbf{R})} d\mathbf{R}$$

$$F_{hkl} = \sum_j e^{2\pi i \mathbf{S}_{hkl}\cdot\mathbf{r}_j} \int_{\text{atom}} \rho_j(\mathbf{R}) e^{2\pi i \mathbf{S}_{hkl}\cdot\mathbf{R}}\, d\mathbf{R}$$

Let us define the atomic scattering factor, f_j

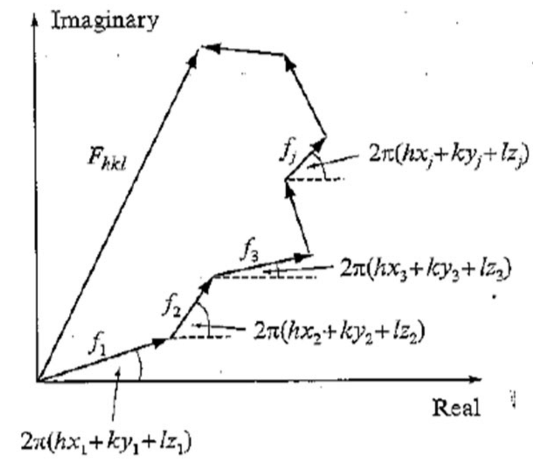
$$f_j = \int_{\text{atom}} \rho_j(\mathbf{R}) e^{2\pi i \mathbf{S}_{hkl}\cdot\mathbf{R}}\, d\mathbf{R}$$

$$F_{hkl} = \sum_j f_j e^{2\pi i \mathbf{S}_{hkl}\cdot\mathbf{r}_j}$$

$$\mathbf{r}_j = x_j\mathbf{a} + y_j\mathbf{b} + z_j\mathbf{c}$$

$$\mathbf{S}_{hkl}\cdot\mathbf{r}_j = \left(h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*\right)\cdot\left(x_j\mathbf{a} + y_j\mathbf{b} + z_j\mathbf{c}\right) = hx_j + ky_j + lz_j$$

$$F_{hkl} = \sum_j f_j e^{2\pi i (hx_j + ky_j + lz_j)}$$



The Structure Factor

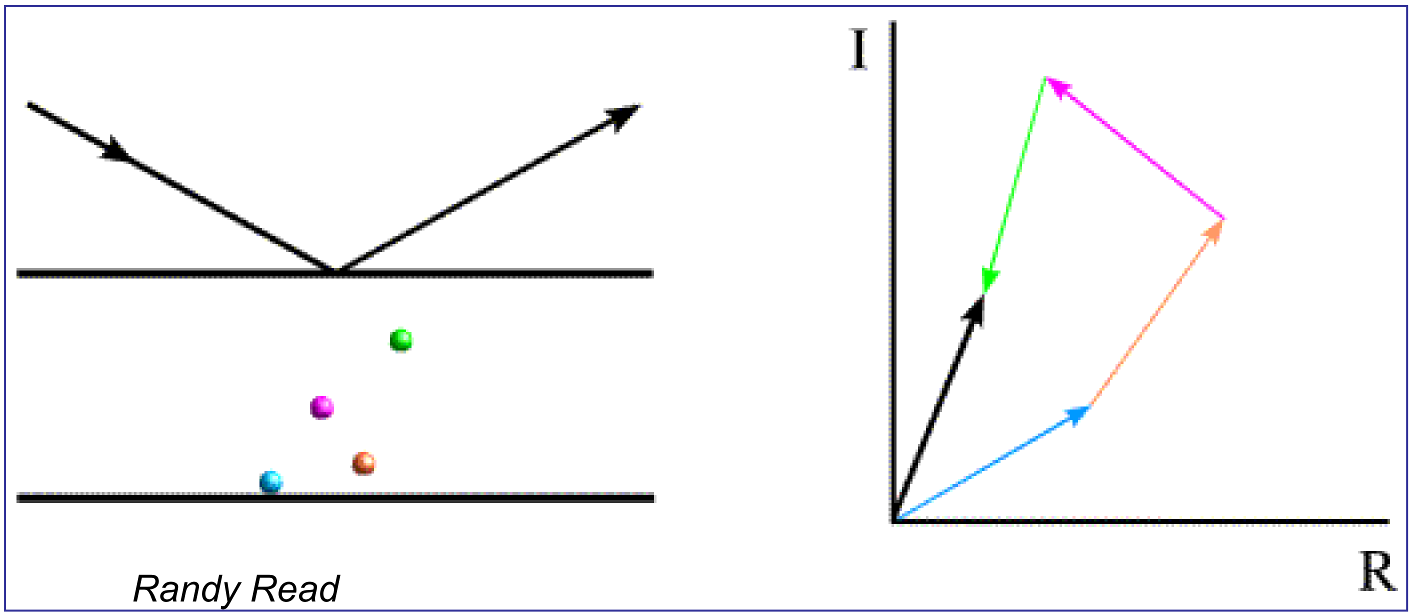
$$F_{hkl} = V \int_{x=0}^{x=1} \int_{y=0}^{y=1} \int_{z=0}^{z=1} \rho(x,y,z) e^{i\Delta\mathbf{k}\cdot(x\mathbf{a}+y\mathbf{b}+z\mathbf{c})}\, dx\ \ dy\ \ dz$$

$$F_{hkl} = \sum_j f_j e^{2\pi i(hx_j+ky_j+lz_j)}$$

- In the first equation the coordinates (x, y, z) refer to any position within the unit cell, whereas (x_j, y_j, z_j) in the second equation define the position of the atoms.
- $\rho(x, y, z)$ is a continuous function describing the overall electron density, f_j, is a property of each atom.
- The first equation requires an integration over the entire unit cell, but the second equation requires a summation over the positions of the atoms within the unit cell.

What does $F_{hkl} = \sum_j f_j e^{2\pi i(hx+ky+lz)} = |F_{hkl}| e^{i\varphi}$ mean?

• The amplitude of scattering depends on the number of electrons in each atom.
• The phase depends on the fractional distance it lies from the lattice plane.

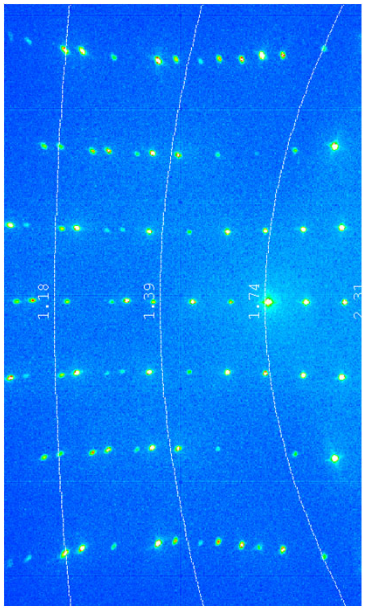


Scattering from lattice planes

Atomic structure factors add as **complex numbers**, or **vectors**.

How Important is the Phase?

Structure Factor and Intensity



$$F_{hkl} = \sum_j f_j \, e^{2\pi i \left(hx_j + ky_j + lz_j\right)}$$

$$I_{hkl} = \frac{I_0}{\omega} K L_{hkl} p_{hkl} A_{hkl} e_{hkl} \left|(F_{hkl})_T\right|^2 V$$

$$K = \left(\frac{q^2}{4\pi\epsilon_0 m_e c^2}\right)^2 N^2 \lambda^3 \qquad L_{hkl} = \frac{1}{\sqrt{(\sin 2\theta)^2 - \xi^2}}$$

$$p_{hkl} = \frac{\left((\cos\epsilon)^2 + (\sin\epsilon)^2(\cos 2\theta)^2\right) + (\sin\epsilon)^2 + (\cos\epsilon)^2}{2}$$

$$\epsilon = \cos^{-1}(\xi \csc 2\theta)$$

$$A_{hkl} = \frac{I_{hkl}}{I_0} = e^{-\mu t}$$

The Atomic Scattering Factor

$$d\mathbf{R} = R^2 \sin\phi \; dR \; d\phi \; d\psi \text{ and } \mathbf{S}_{hkl} \cdot \mathbf{R} = S_{hkl} R \cos\phi$$

$$f_j = \int_{\text{atom}} \rho_j(\mathbf{R}) e^{2\pi i \mathbf{S}_{hkl} \cdot \mathbf{R}} \, d\mathbf{R} = \int_{\text{atom}} \rho_j(R) e^{2\pi i S_{hkl} R \cos\phi} R^2 \sin\phi \; dR \; d\phi \; d\psi$$

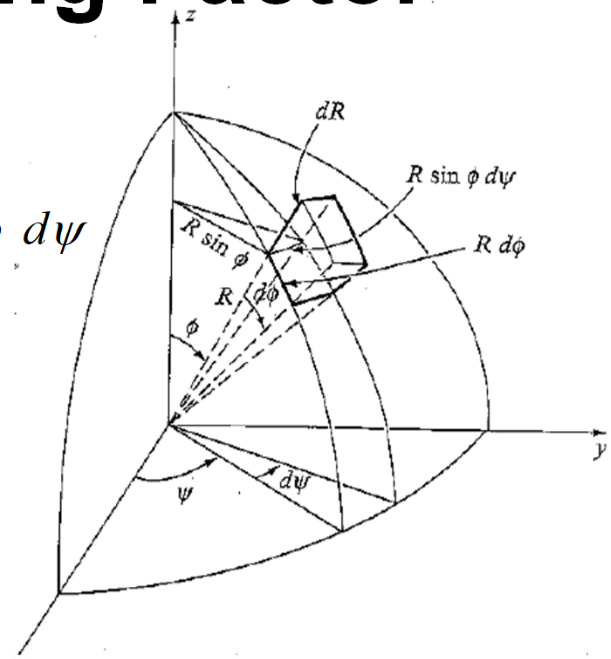
$$f_j = \int_{\psi=0}^{\psi=2\pi} \int_{\phi=0}^{\phi=\pi} \int_{R=0}^{R=\infty} \rho_j(R) e^{2\pi i S_{hkl} R \cos\phi} R^2 \sin\phi \; dR \; d\phi \; d\psi$$

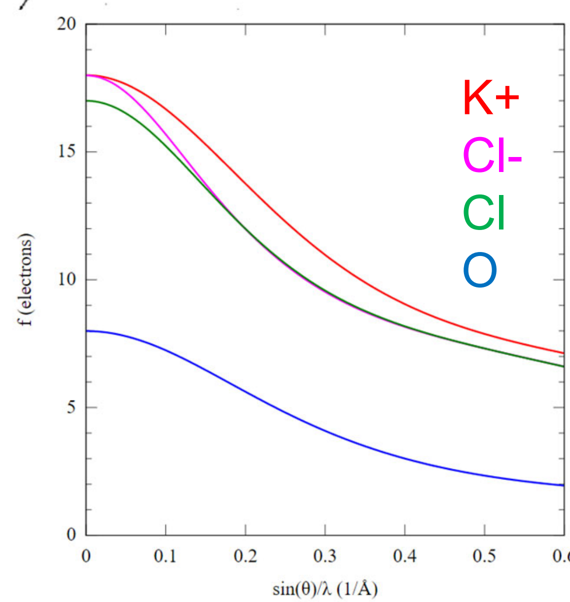
$$f_j = 2\pi \int_0^\infty R^2 \rho_j(R) \left(\frac{e^{2\pi S_{hkl} R} - e^{-2\pi S_{hkl} R}}{2\pi S_{hkl} R} \right) dR$$

$$f_j = 4\pi \int_0^\infty R^2 \rho_j(R) \left(\frac{\sin 2\pi S_{hkl} R}{2\pi S_{hkl} R} \right) dR$$

$$S_{hkl} = \frac{2\sin\theta}{\lambda}$$

$$f_j = 4\pi \int_0^\infty R^2 \rho_j(R) \left(\frac{\sin\left(\frac{4\pi \sin\theta}{\lambda} R \right)}{\frac{4\pi\sin\theta}{\lambda} R} \right) dR$$





Correction for Thermal Motion (I)

$$F_{hkl} = \sum_j f_j e^{2\pi i(hx_j + ky_j + lz_j)}$$

$$F_{hkl} = \sum_j f_j e^{2\pi i \mathbf{S}_{hkl} \cdot \mathbf{r}_j}$$

Consider a small random displacement about $\mathbf{r}_j$

$$F_{hkl} = \sum_j f_j e^{2\pi i \mathbf{S}_{hkl} \cdot (\mathbf{r}_j + \mathbf{u}_j)}$$

$$F_{hkl} = \sum_j f_j e^{2\pi i \mathbf{S}_{hkl} \cdot \mathbf{r}_j} e^{2\pi i \mathbf{S}_{hkl} \cdot \mathbf{u}_j}$$

Let us define $\mathbf{u}_j$ as motion in the direction of $\mathbf{S}_{hkl}$ that is perpendicular to the plane *hkl*:

$\mathbf{S}_{hkl} \cdot \mathbf{u}_j$ becomes $S_{hkl} u_j$ and

$$F_{hkl} = \sum_j f_j e^{2\pi i \mathbf{S}_{hkl} \cdot \mathbf{r}_j} e^{2\pi i S_{hkl} u_j}$$

F_{hkl} is measured over a long time

$$F_{hkl} = \sum_j f_j e^{2\pi i \mathbf{S}_{hkl} \cdot \mathbf{r}_j} \overline{e^{2\pi i S_{hkl} u_j}}$$

$$\overline{e^{2\pi i S_{hkl} u_j}} \approx 1 + 2\pi i \overline{S_{hkl} u_j} - 2\pi^2 \overline{\left(S_{hkl} u_j\right)^2}$$

$$\overline{e^{2\pi i S_{hkl} u_j}} \approx 1 + 2\pi i S_{hkl} \overline{u_j} - 2\pi^2 S_{hkl}^2 \overline{u_j^2}$$

$$\overline{e^{2\pi i S_{hkl} u_j}} \approx 1 - 2\pi^2 S_{hkl}^2 \overline{u_j^2}$$

$$\overline{e^{2\pi i S_{hkl} u_j}} \approx e^{2\pi^2 S_{hkl}^2 \overline{u_j^2}}$$

Correction for Thermal Motion (II)

$$-2\pi^2 S_{hkl}^2 \overline{u_j^2} = -2\pi^2 \left(\frac{2\sin\theta}{\lambda}\right)^2 \overline{u_j^2}$$

$$-2\pi^2 S_{hkl}^2 \overline{u_j^2} = -8\pi^2 \left(\frac{\sin\theta}{\lambda}\right)^2 \overline{u_j^2}$$

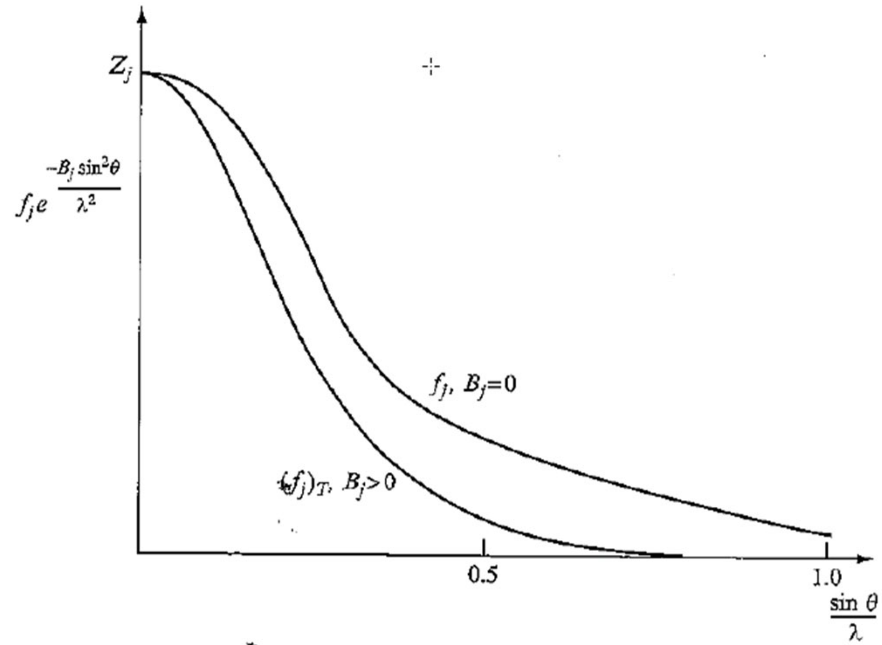
Let us define $B_j = 8\pi^2 \overline{u_j^2}$

$$\overline{e^{2\pi i S_{hkl} u_j}} \approx e^{-B_j (2\sin\theta/\lambda)^2}$$

$$\left(f_j\right)_T = f_j e^{-B_j (2\sin\theta/\lambda)^2}$$

$$\left(F_{hkl}\right)_T = \sum_j \left(f_j\right)_T e^{2\pi i (hx_j + ky_j + lz_j)}$$

$$\left(F_{hkl}\right)_T = \sum_j f_j e^{-B_j (2\sin\theta/\lambda)^2} e^{2\pi i (hx_j + ky_j + lz_j)}$$



Freidel's Law

Let's consider two centrosymmetrically disposed reflections:

$$F_{hkl} = \sum_j f_j e^{2\pi i(hx_j + ky_j + lz_j)}$$

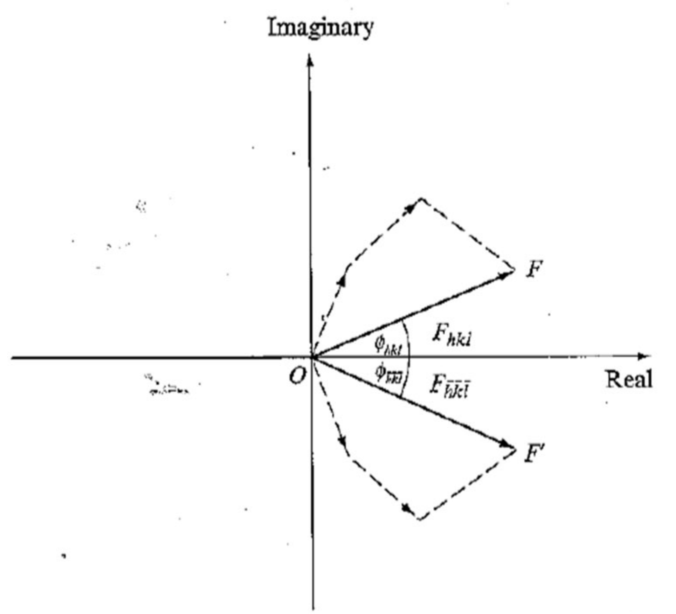
$$F_{\overline{hkl}} = \sum_j f_j e^{2\pi i(\bar{h}x_j + \bar{k}y_j + \bar{l}z_j)} = \sum_j f_j e^{-2\pi i(hx_j + ky_j + lz_j)}$$

$F^*_{hkl} = F_{\overline{hkl}}$ and thus $\left|F_{hkl}\right| = \left|F^*_{hkl}\right| = \left|F_{\overline{hkl}}\right|$

$$I_{hkl} = I_{\overline{hkl}} = \left|F_{hkl}\right|^2 = \left|F_{\overline{hkl}}\right|^2$$

Furthermore:

$$\phi_{\overline{hkl}} = -\phi_{hkl}$$



Dispersion

- Scattering is the result of an interaction of electromagnetic radiation with an electron.
  - Rayleigh or elastic scattering
  - Compton or inelastic scattering
- Dispersion occurs when electromagnetic radiation interacting with a an electron in a shell has nearly the same frequency as the oscillator, ie resonates

$$\frac{d^2\bar{x}_j}{dt^2} + \kappa_j \frac{d\bar{x}_j}{dt} + \omega_j \bar{x}_j = -\frac{\mathrm{e}}{m}\bar{E}_0 e^{i\omega_0 t - i2\pi\bar{k}_0\cdot\bar{r}_j}$$

$$\bar{x}_j = \frac{\mathrm{e}}{m\omega_0^2}\frac{1}{1-\frac{\omega_j^2}{\omega_0^2} - i\frac{\kappa_j}{\omega_0}}\bar{E}_0 e^{i\omega_0 t - i2\pi\bar{k}_0\cdot\bar{r}_j}$$

$$f = \sum_j \frac{\varphi_j}{1-\frac{\omega_j^2}{\omega_0^2} - i\frac{\kappa_j}{\omega_0}} = \sum_j \varphi_j \int_{\omega_j}^{\infty} \frac{w_j\, d\omega}{1-\frac{\omega_j^2}{\omega_0^2} - i\frac{\kappa_j}{\omega_0}} = f^0 + \sum_j \varphi_j(\xi_j + i\eta_j) = f^0 + f' + if''$$

Breakdown of Freidel's Law

$$F_{hkl} = \sum_j f_j e^{2\pi i(hx_j + ky_j + lz_j)}$$

$$F_{hkl} = \sum_{j \neq A} f_j e^{2\pi i(hx_j + ky_j + lz_j)} + \left[\left(f_A^0 + f' + if'' \right) e^{2\pi i(hx_A + ky_A + lz_A)} \right]$$

$$F_{\overline{hkl}} = \sum_j f_j e^{2\pi i(\bar{h}x_j + \bar{k}y_j + \bar{l}z_j)} + \left[\left(f_A^0 + f' + if'' \right) e^{2\pi i(\bar{h}x_A + \bar{k}y_A + \bar{l}z_A)} \right]$$

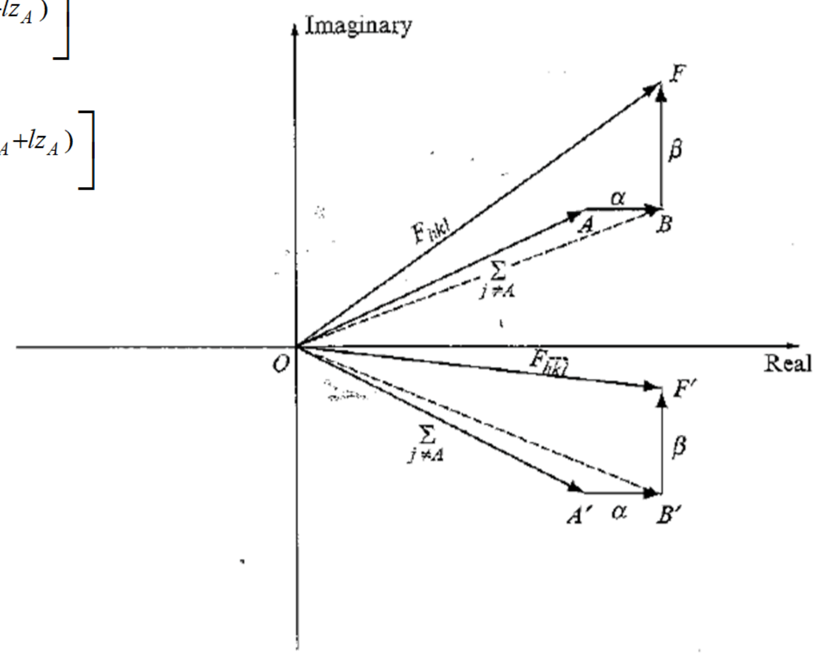
$$F_{\overline{hkl}} = \sum_j f_j e^{-2\pi i(hx_j + ky_j + lz_j)} + \left[\left(f_A^0 + f' + if'' \right) e^{-2\pi i(hx_A + ky_A + lz_A)} \right]$$

$F_{hkl}^* \neq F_{\overline{hkl}}$ and thus $|F_{hkl}| = |F_{hkl}^*| \neq |F_{\overline{hkl}}|$

$I_{hkl} \neq I_{\overline{hkl}}$ and $|F_{hkl}|^2 \neq |F_{\overline{hkl}}|^2$

Furthrmore:

$\phi_{\overline{hkl}} \neq -\phi_{hkl}$



Absorption

- Absorption is another resonance effect and is related to dispersion by the equation

$$\mu_0 = \frac{4\pi N e^2}{m\omega c} f''$$

Systematic Absences (I)

Consider a body centered lattice. For a given atom at coordinates (x, y, z) there will be a second atom at $(x+1/2, y+1/2, z+1/2)$ and F_{hkl} becomes

$$F_{hkl} = \sum_{j}^{j=N/2} \left(f_j e^{2\pi i(hx_j+ky_j+lz_j)} + f_j e^{2\pi i[h(x_j+1/2)+k(y_j+1/2)+l(z_j+1/2)]} \right)$$

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

If $h+k+l$ is even: $e^{\pi i(h+k+l)} = 1$ but

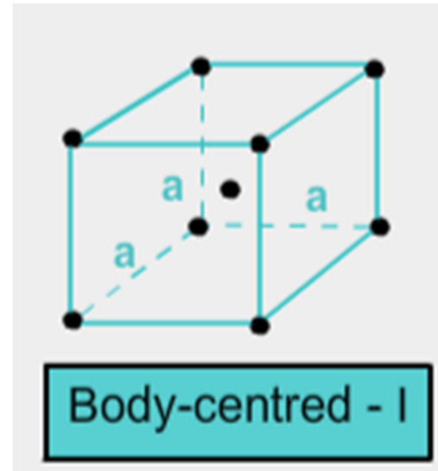
if $h+k+l$ is odd: $e^{\pi i(h+k+l)} = -1$

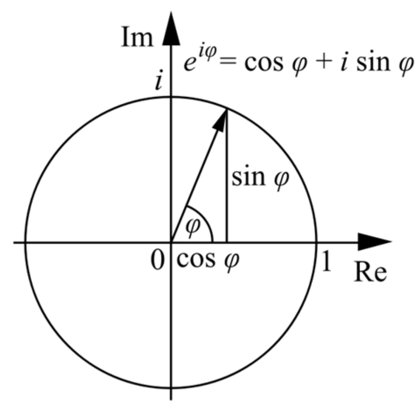
For $h+k+l = 2n$:

$$F_{hkl} = \sum_{j}^{j=N/2} f_j e^{2\pi i(hx_j+ky_j+lz_j)} (1+1) = 2\sum_{j}^{j=N/2} f_j e^{2\pi i(hx_j+ky_j+lz_j)}$$

For $h+k+l = 2n+1$:

$$F_{hkl} = \sum_{j}^{j=N/2} f_j e^{2\pi i(hx_j+ky_j lz_j)} (1+(-1)) = 0$$





Systematic Absences (II)

Let's consider a 2_1 screw axis. For a given atom at coordinates (x, y, z) there will be a second atom at $(-x, y+1/2, -z)$ and F_{hkl} becomes

$$F_{hkl} = \sum_{j}^{j=N/2} \left(f_j e^{2\pi i(hx_j+ky_j+lz_j)} + f_j e^{2\pi i[h(-x_j)+k(y_j+1/2)+l(-z_j)]} \right)$$

For $h=0$ and $l=0$

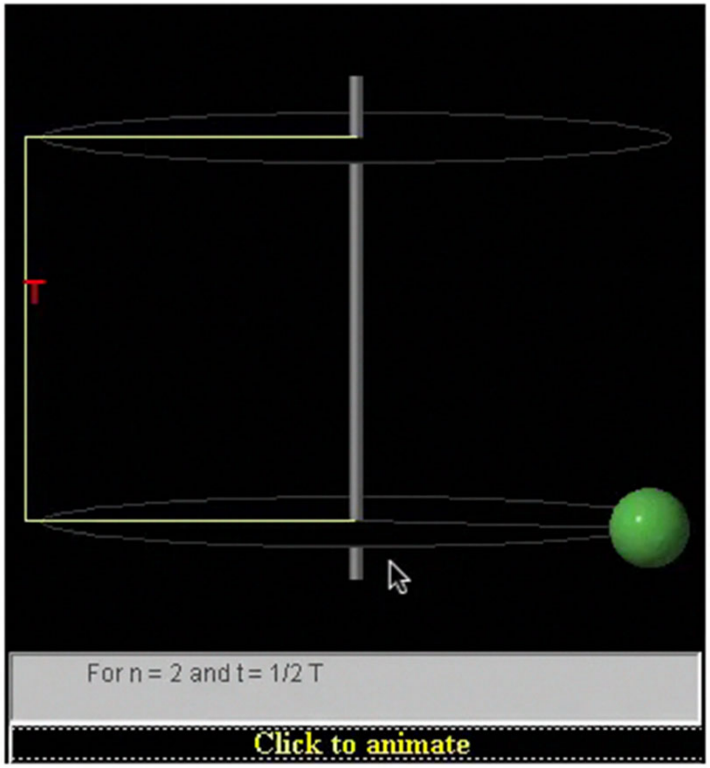
$$F_{hkl} = \sum_{j}^{j=N/2} f_j e^{2\pi i(hx_j+ky_j+lz_j)} \left(1+e^{\pi ik}\right)$$

When k is even $e^{\pi ik}=1$, thus:

$$F_{hkl} = \sum_{j}^{j=N/2} f_j e^{2\pi i(hx_j+ky_jl+z_j)} \left(1+1\right) = 2\sum_{j}^{j=N/2} f_j e^{2\pi i(hx_j+ky_j+lz_j)}$$

For $h=0$ and $l=0$, when k is odd: $e^{\pi ik}=-1$, thus

$$F_{hkl} = \sum_{j}^{j=N/2} f_j e^{2\pi i(hx_j+ky_j+lz_j)} \left(1+(-1)\right) = 0$$



http://wwwba.ic.cnr.it/sites/default/files/abc/abc/symmetry/restr2.htm

Systematic Absences (III)

Let's consider a glide plane. For a given atom at coordinates (x, y, z) there will be a second atom at $(x, -y, z+½)$ and F_{hkl} becomes

$$F_{hkl} = \sum_{j}^{j=N/2} \left(f_j e^{2\pi i(hx_j+ky_j+lz_j)} + f_j e^{2\pi i[h(x_j)+k(-y_j)+l(z_j+1/2)]} \right)$$

For $k = 0$ and

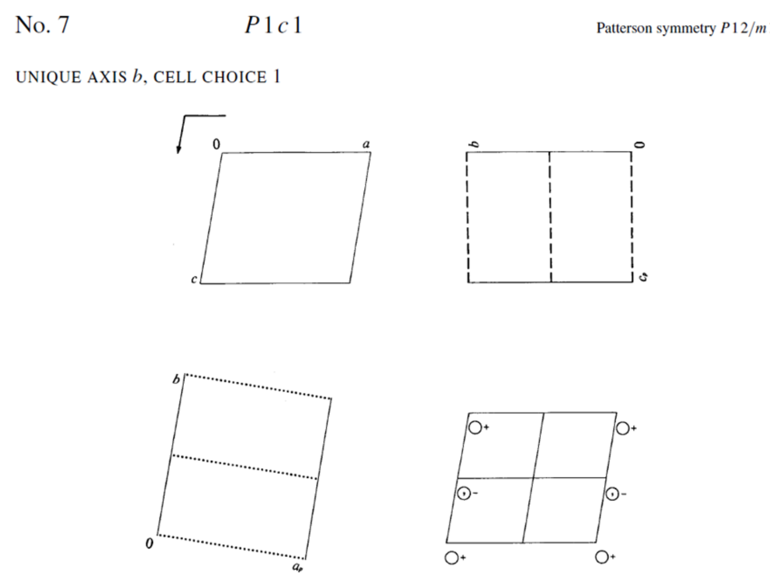
$$F_{hkl} = \sum_{j}^{j=N/2} f_j e^{2\pi i(hx_j+ky_j+lz_j)} \left(1+e^{\pi ik}\right)$$

When k is even $e^{\pi ik} = 1,$ thus:

$$F_{hkl} = \sum_{j}^{j=N/2} f_j e^{2\pi i(hx_j+ky_jl+z_j)} \left(1+1\right) = 2\sum_{j}^{j=N/2} f_j e^{2\pi i(hx_j+ky_j+lz_j)}$$

For $h = 0$ and $l = 0,$ when k is odd: $e^{\pi ik} = -1,$ thus

$$F_{hkl} = \sum_{j}^{j=N/2} f_j e^{2\pi i(hx_j+ky_j+lz_j)} \left(1+(-1)\right) = 0$$



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