The Fourier Transform, the Wave Equation and Crystals

Joe Ferrara, Ph. D.
CSO, Rigaku Americas Corp
VP XRL, Rigaku Corp
Past President, ACA
Secretary-Treasurer USNC/Cr

AMERICAN CRYSTALLOGRAPHIC ASSOCIATION

- The American Crystallographic Association (ACA) advances, promotes and preserves *crystallography, structural science, and allied disciplines* for the benefit of humankind. The ACA provides students, young scientists and experienced crystallographers with opportunities to exhibit their achievements in research, creative and scholarly activities, and leadership. The ACA contributes to the intellectual, economic and scientific advancement of the communities and individuals it serves though conferences, publications and public outreach.
- The American Crystallographic Association represents both Canada and the US to the International Union of Crystallography (IUCr).There is a Canadian division of the ACA and a Canadian representative (voting) on the ACA Council.

ACA 2020

American Crystallographic Association

August 2 - 7, 2020 • San Diego, CA

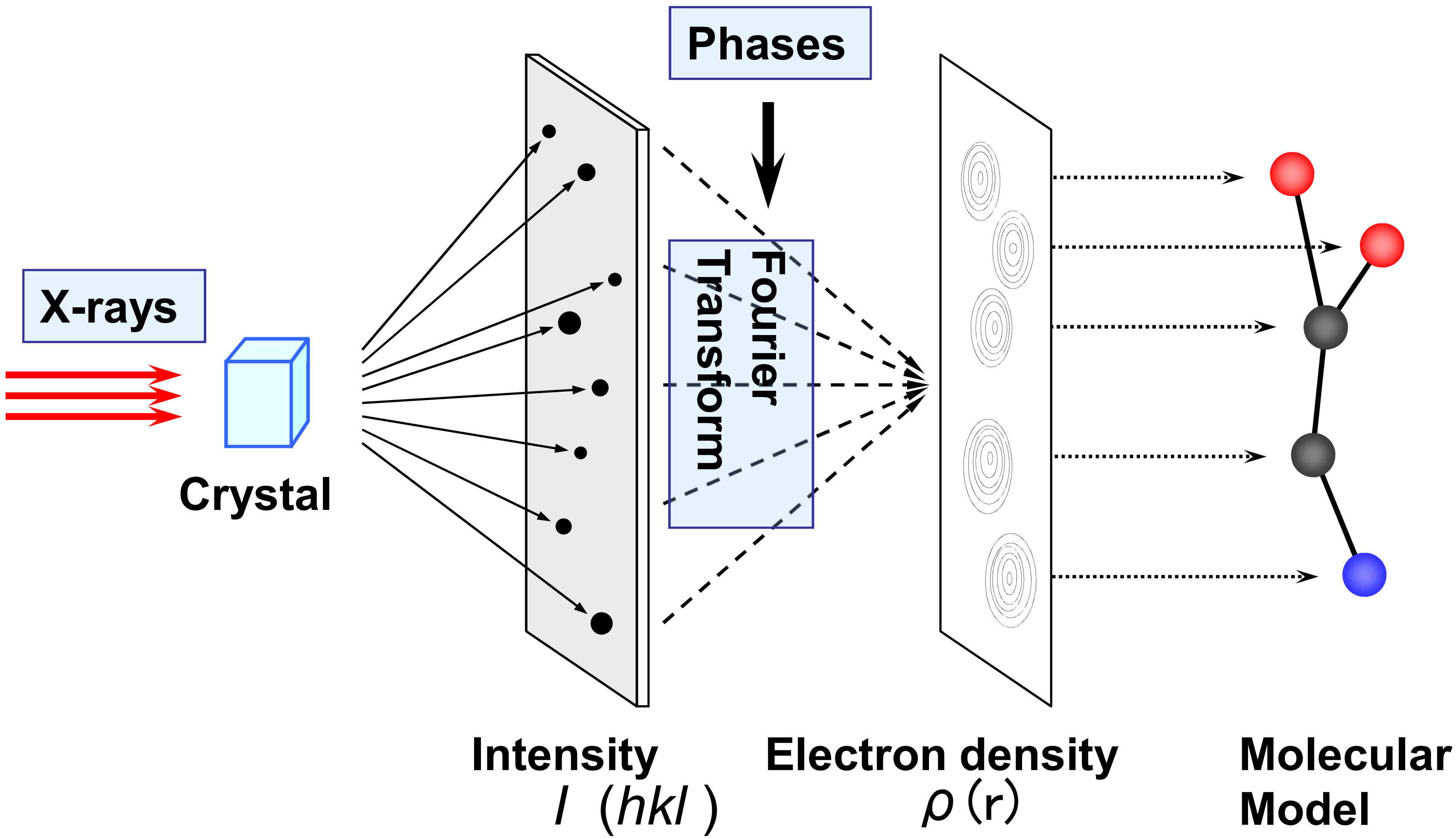
TRAINING THE NEXT GENERATION

- Program Chairs
  - Carla Slebodnick
  - Nozomi Ando
  - Stephan Ginell
  - Brandon Mercado
- Poster Chairs
  - Louise Dawe
  - Tiffany Kinnibrugh

- Virtual
  - Sessions
  - Workshops
  - Poster sessions
  - Award Ceremonies

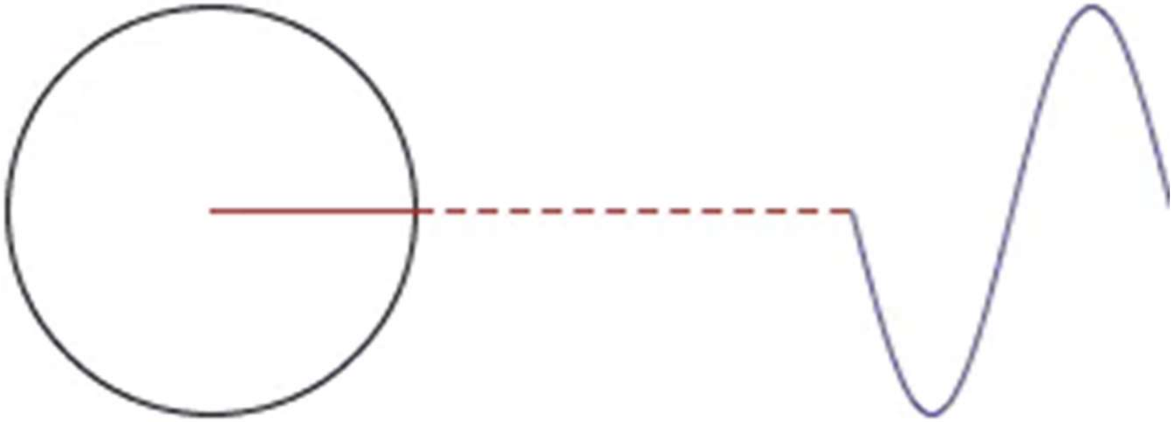
https://www.acameeting.com/

35000 ft view of X-ray Structure Analysis

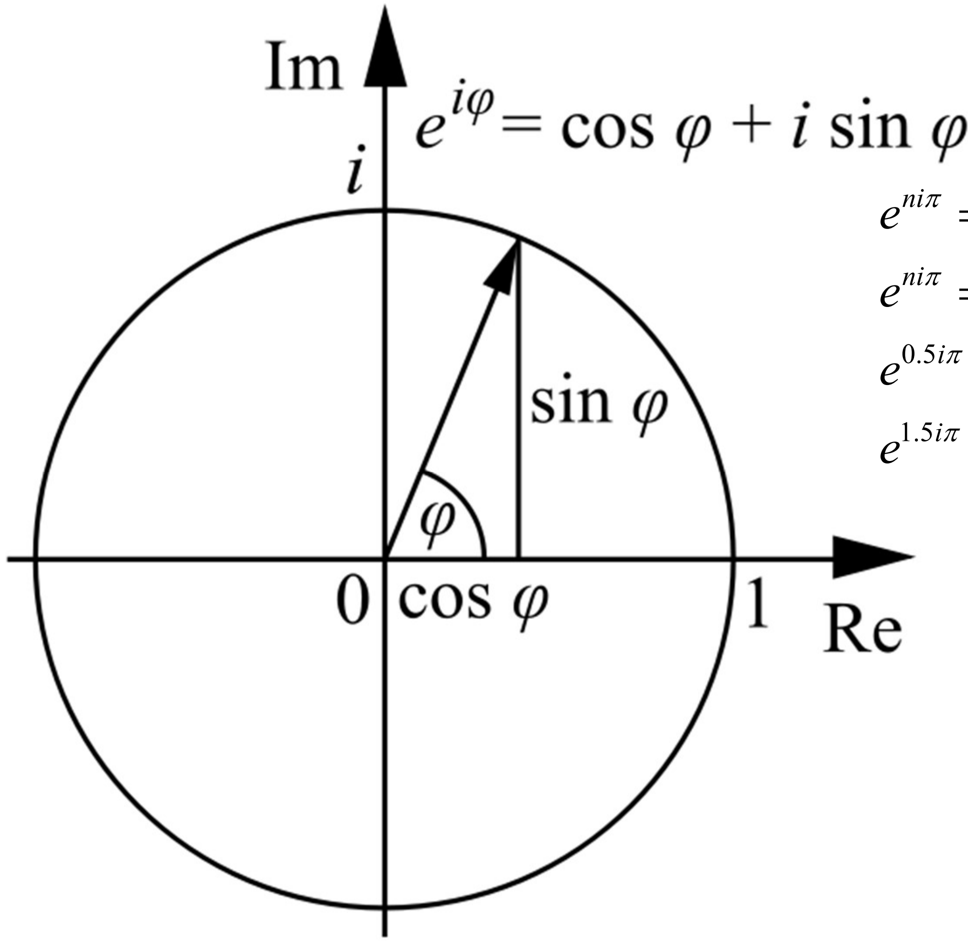


Fourier Theory

- 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

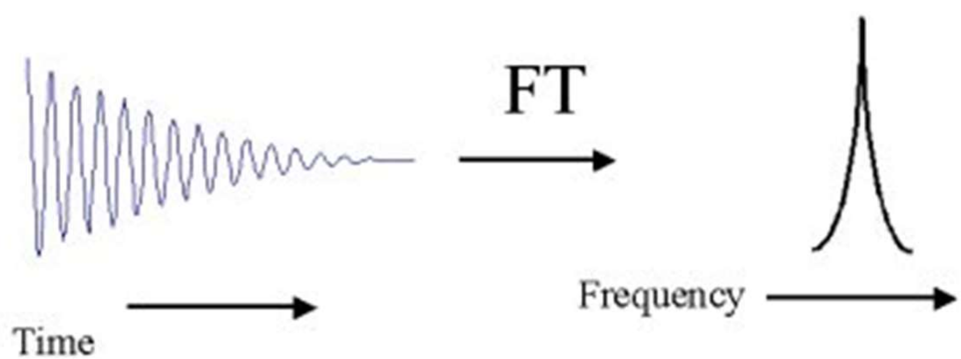
The Fourier Transform

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

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

In the 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 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.

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

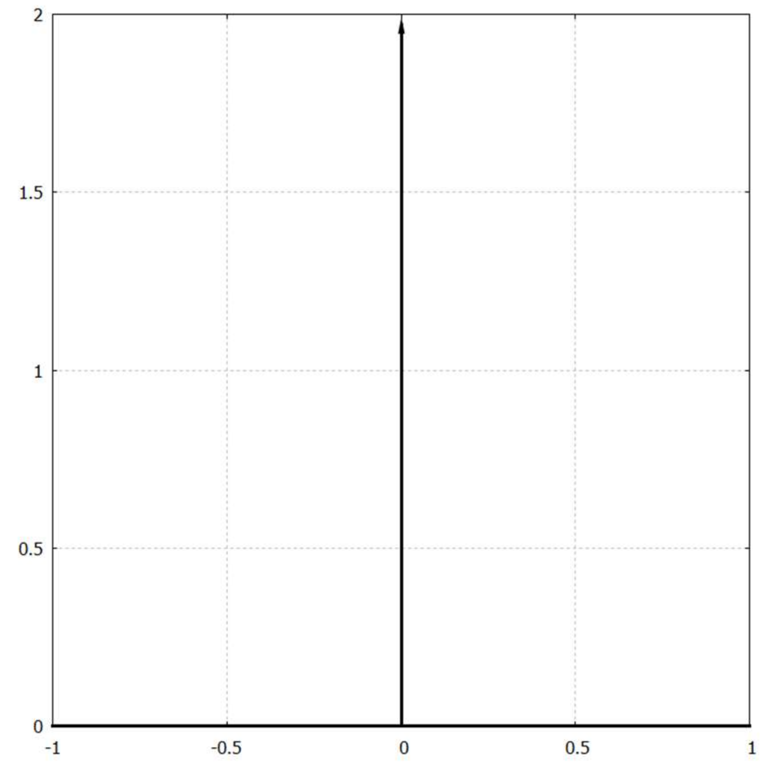
$$l(\mathbf{r}) = \sum_{\text{all p, q, r}} \delta(\mathbf{r}-[p\mathbf{a}+q\mathbf{b}+r\mathbf{c}])$$

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:

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

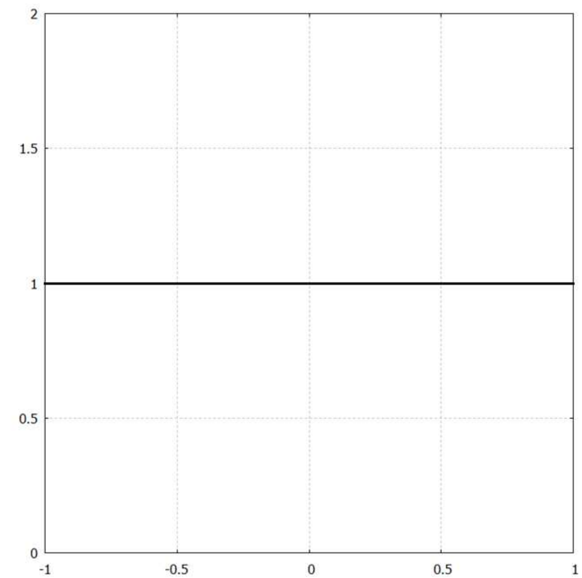


Fourier transforms and δ functions

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:

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

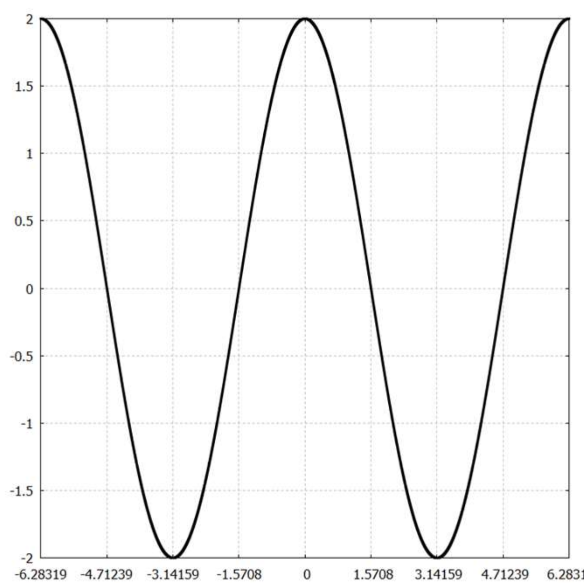
$$F(k) = \int_{-\infty}^{\infty} f(x) e^{ikx} dx$$

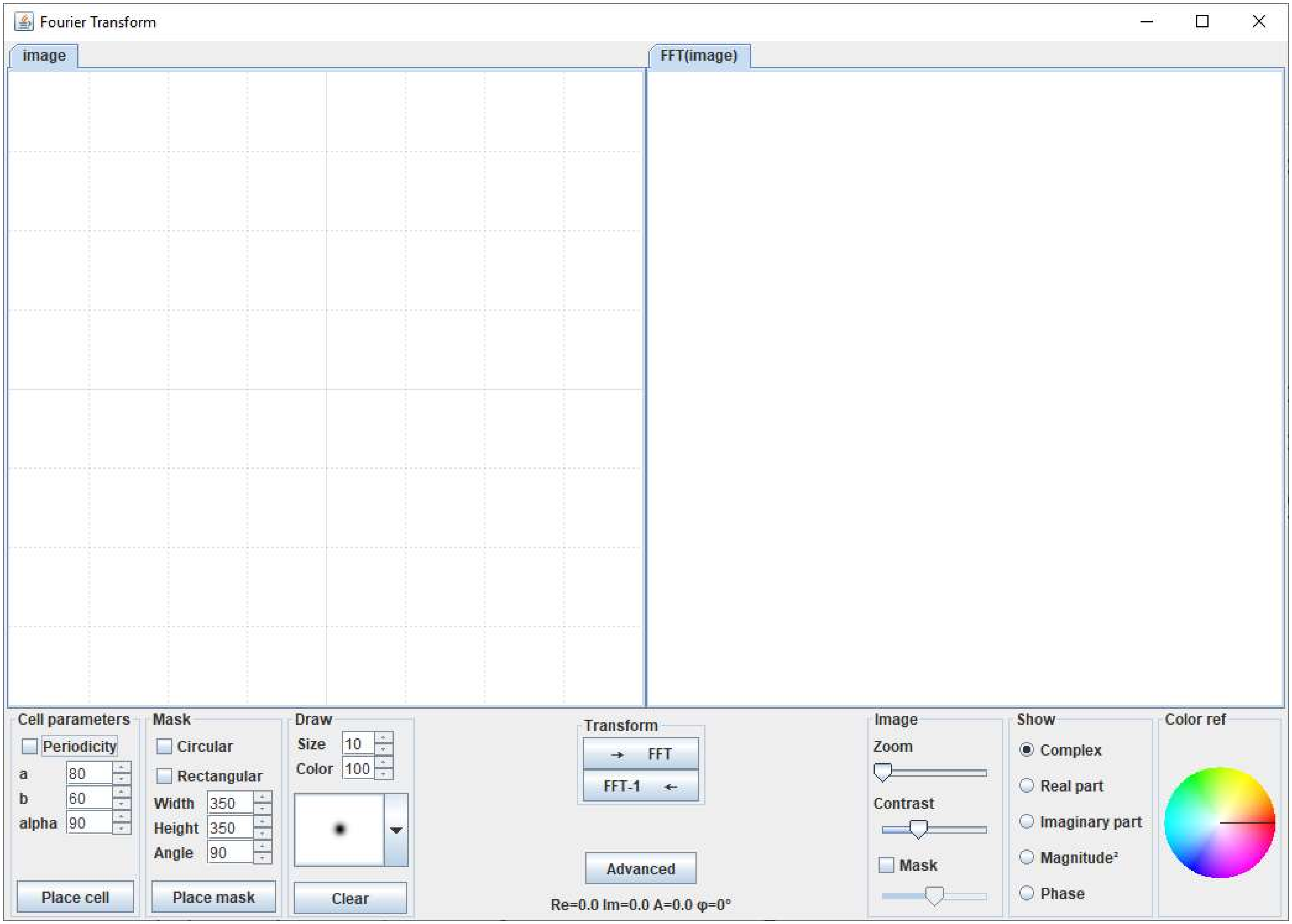
$$= \int_{-\infty}^{\infty} \delta(x + x_0) e^{ikx} dx + \int_{-\infty}^{\infty} \delta(x - x_0) e^{ikx} dx$$

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

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

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

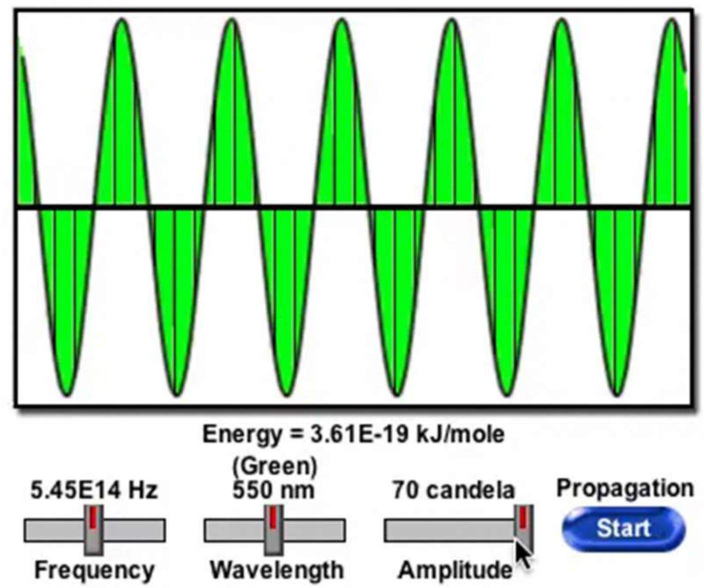




Fourier Transform
image
FFT(image)
Cell parameters
Periodicity
a 80
b 60
alpha 90
Place cell
Mask
Circular
Rectangular
Width 350
Height 350
Angle 90
Place mask
Draw
Size 10
Color 100
Clear
Transform
→ FFT
FFT-1 ←
Advanced
Re=0.0 Im=0.0 A=0.0 φ=0°
Image
Zoom
Contrast
Mask
Show
Complex
Real part
Imaginary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

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

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

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

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

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

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

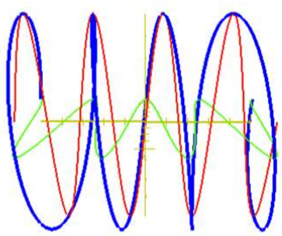
$$\psi(x,t) = \psi_0 \cos\left(kx - \omega t\right)$$

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

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

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

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



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

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

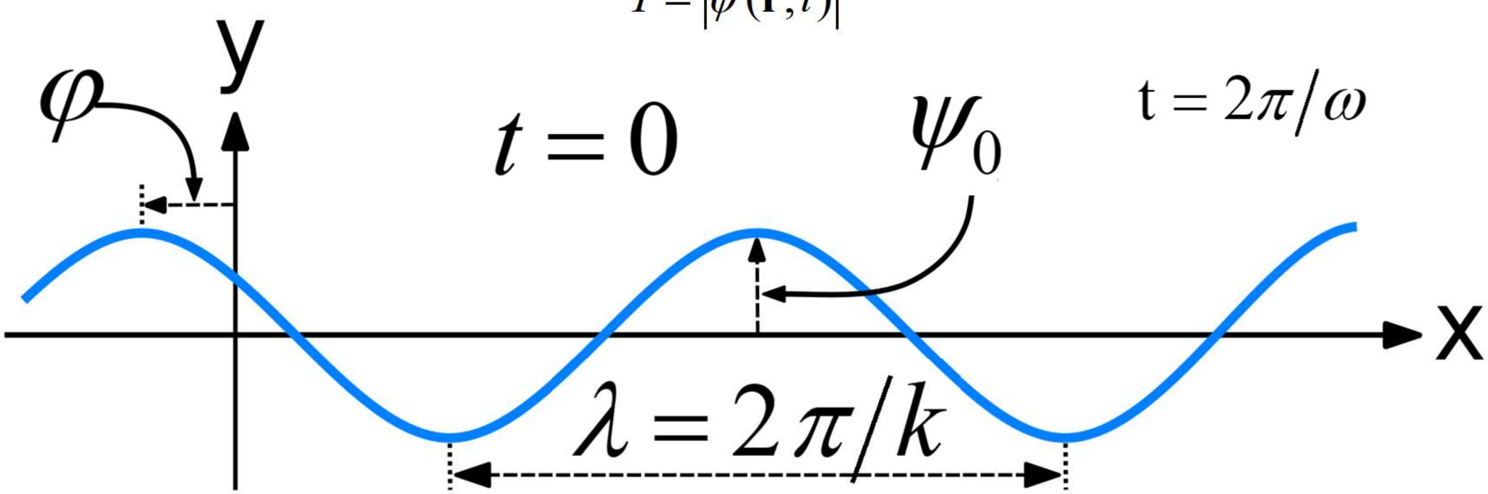
$$\mathbf{k}\cdot\mathbf{r}=(k_x x+k_y y+k_z z)$$

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

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

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

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



Diffraction

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

Diffraction by a one dimensional object

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

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

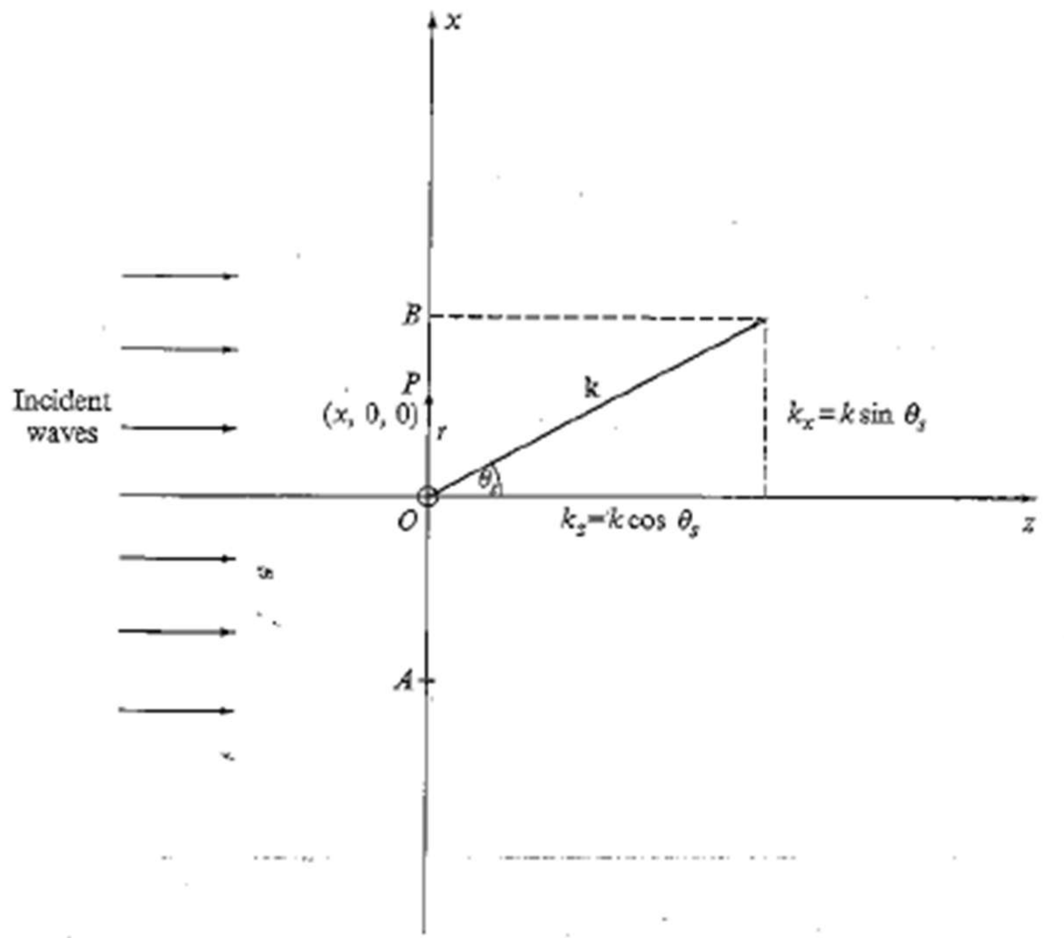
$$\mathbf{k} \cdot \mathbf{r} = k_x x$$

$$k_x = k \sin\theta_s$$

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

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

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



Diffraction by one narrow slit

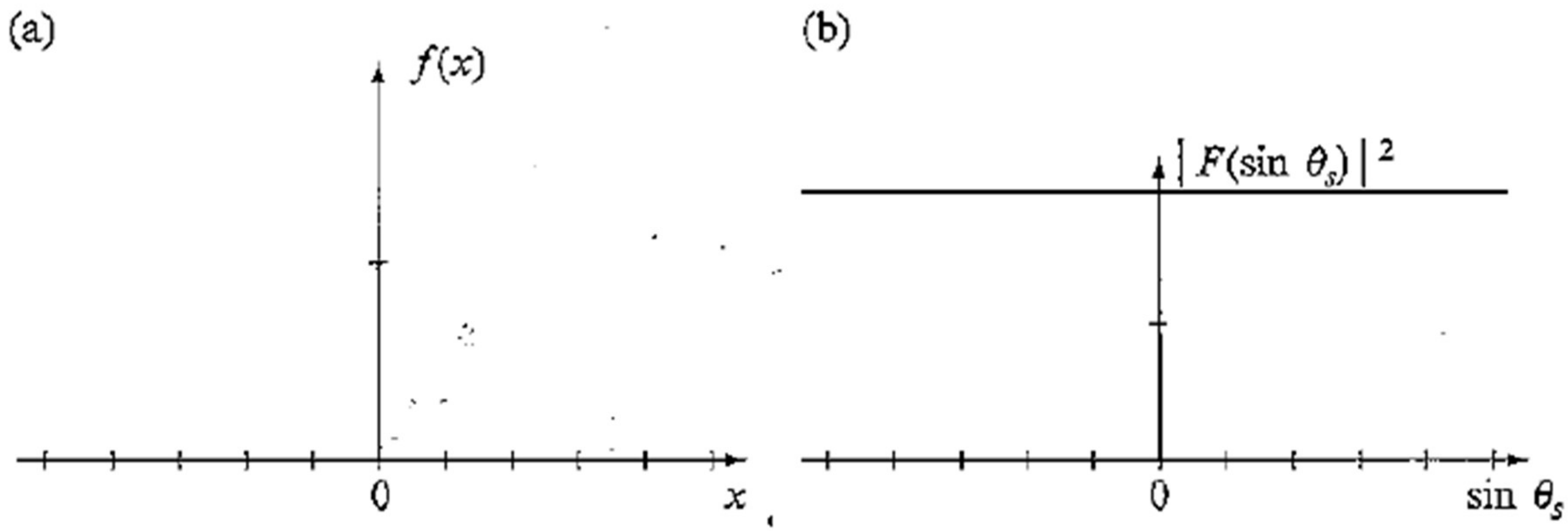
A narrow slit is defined by:

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

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

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

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

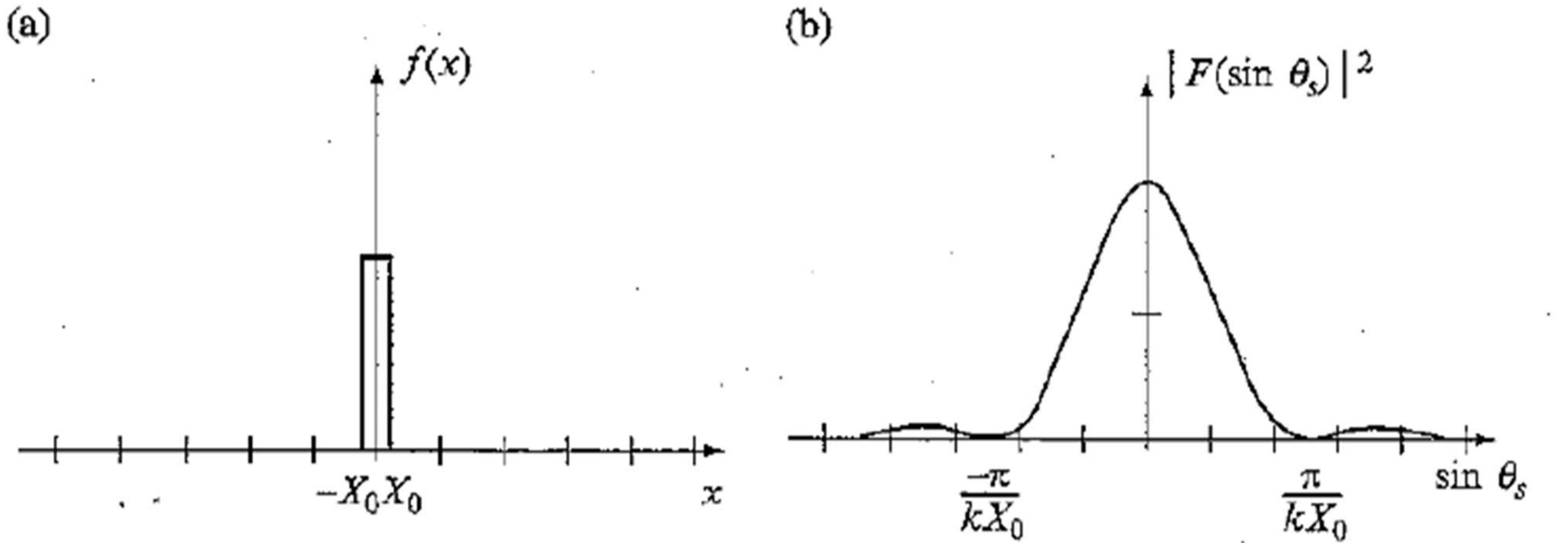


Diffraction by one wide slit

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

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

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



Diffraction by two narrow slits

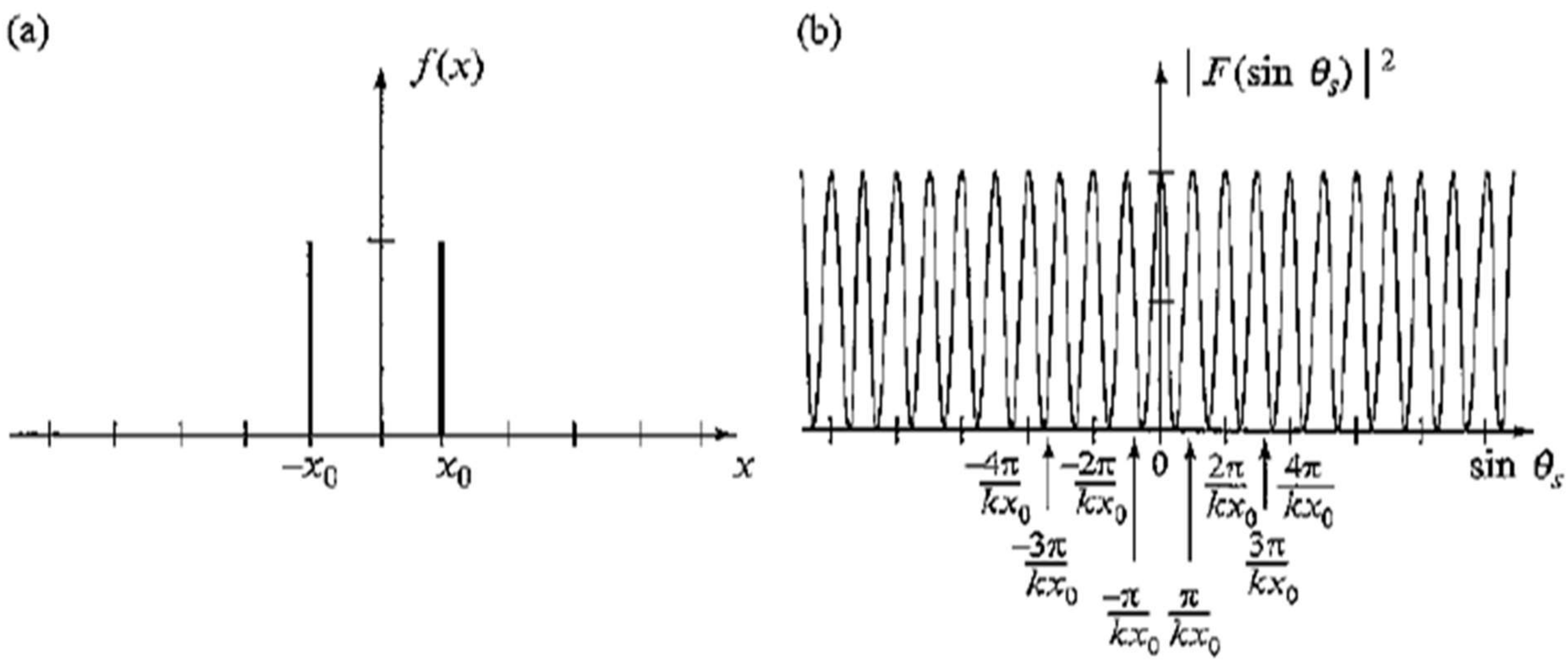
Two narrow slits are defined by:

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

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

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

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



Diffraction by Two Wide Slits

$$f(x) = 0 \text{ if } -\infty < x < -(x_0 + X_0)$$

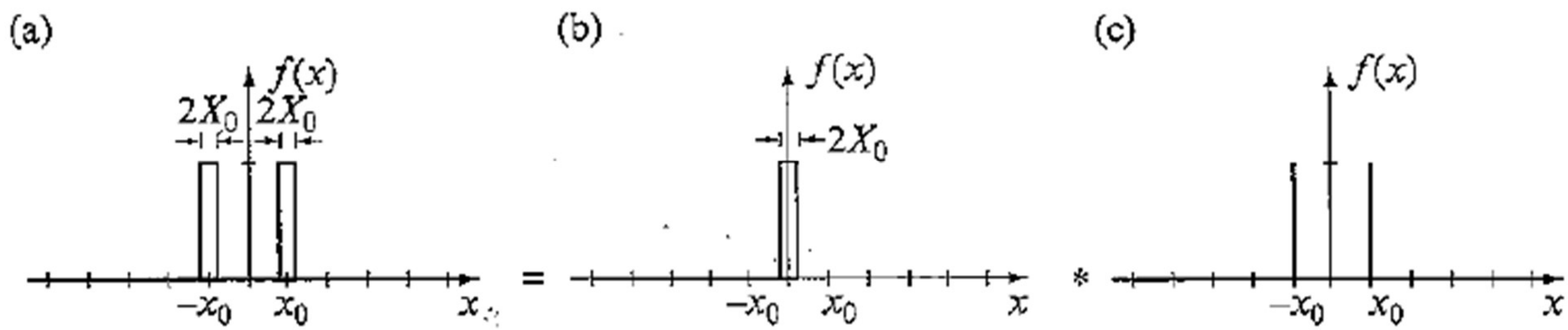
$$f(x) = 1 \text{ if } -(x_0 + X_0) \le x \le -(x_0 - X_0)$$

$$f(x) = 0 \text{ if } -(x_0 - X_0) < x < (x_0 - X_0)$$

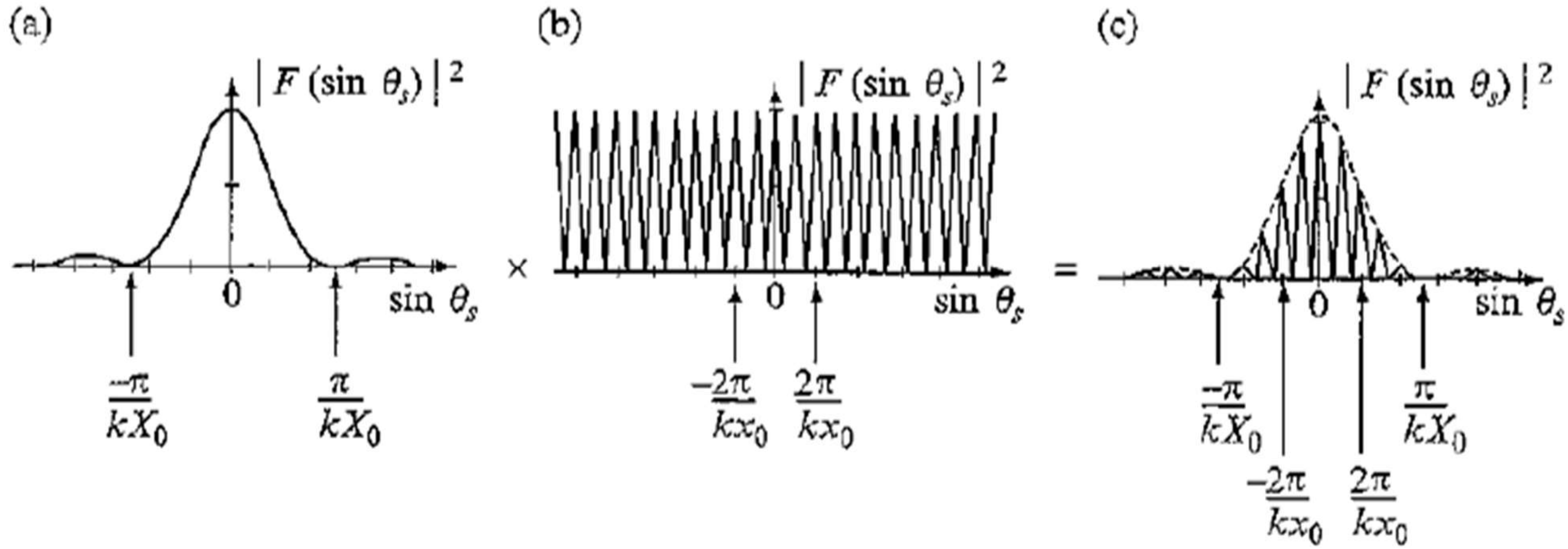
$$f(x) = 1 \text{ if } (x_0 - X_0) \le x \le (x_0 + X_0)$$

$$f(x) = 0 \text{ if } (x_0 + X_0) < x < \infty$$

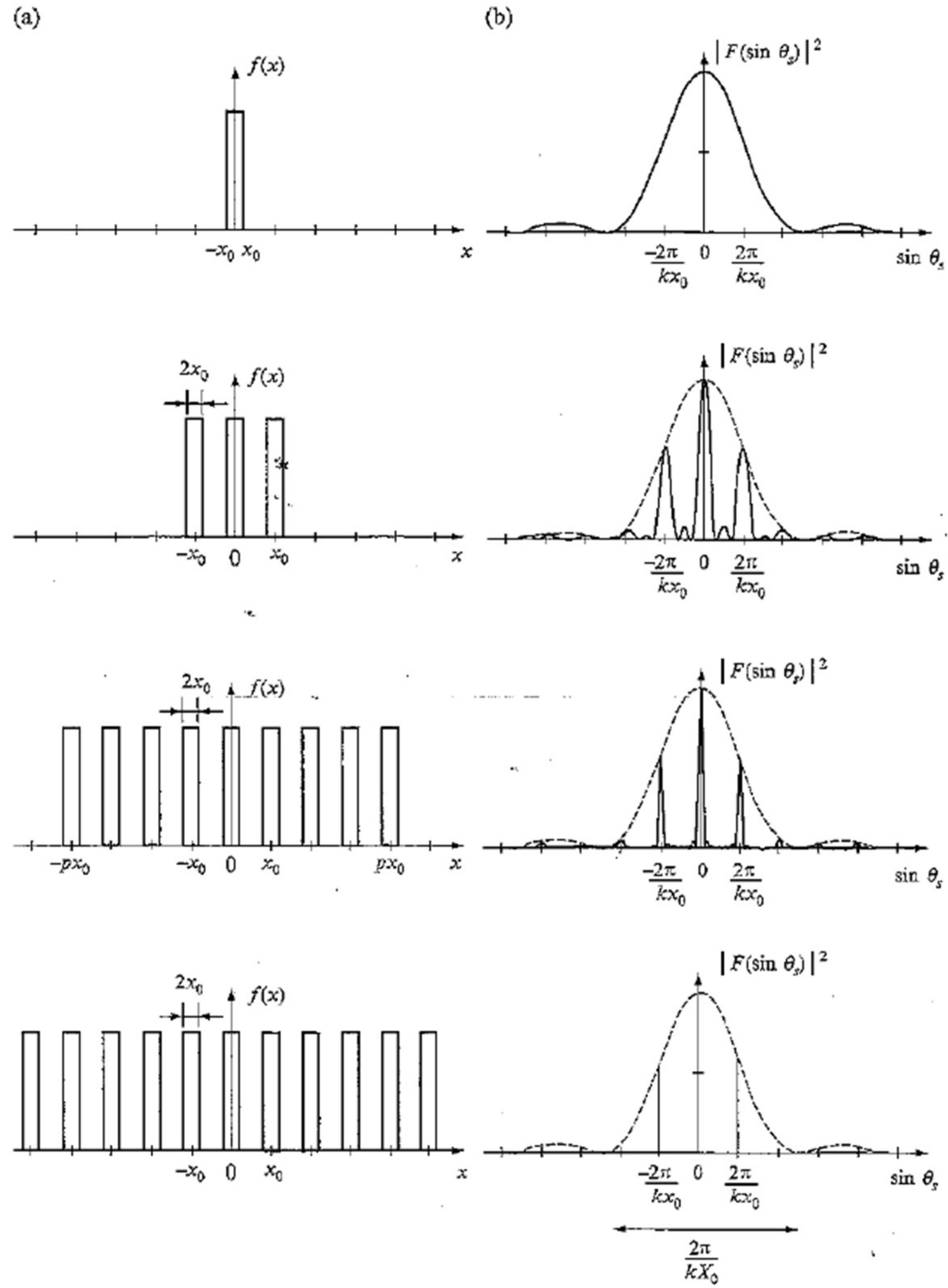
$$f(\text{two wide slits}) = f(\text{one wide slit}) * f(\text{two narrow slits})$$



Diffraction by Two Wide Slits



- 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
−x0 x0
|F(sin θs)|2
sin θs
−2π/kx0
0
2π/kx0
2x0
−x0
x0
−px0
px0
2π/kX0

- 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

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

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

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

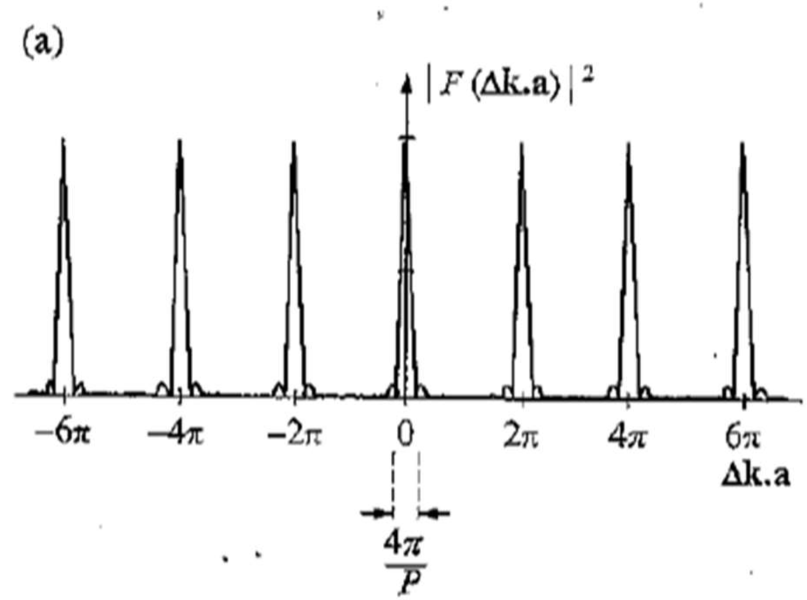
$$F(\Delta\mathbf{k}) = \int_{\text{all }\mathbf{r}} \sum_{\text{all } p,q,r} \delta(\mathbf{r} - [p\mathbf{a} + q\mathbf{b} + r\mathbf{c}]) e^{i\Delta\mathbf{k}\cdot\mathbf{r}} d\mathbf{r}$$

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

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

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

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



Diffraction by a 3D Object

$e^{i(\mathbf{k}\cdot\mathbf{r}_1-\omega t)}$ and $f(\mathbf{r}_1)d\mathbf{r}_1$

diffracted wave from element $d\mathbf{r}_1 = f(\mathbf{r}_1)e^{i(\mathbf{k}\cdot\mathbf{r}_1-\omega t)}d\mathbf{r}_1$

diffracted wave from element $d\mathbf{r}_2 = f(\mathbf{r}_2)e^{i(\mathbf{k}\cdot\mathbf{r}_2-\omega t)}d\mathbf{r}_2$

diffracted wave from all elements $d\mathbf{r}_n = \sum_n f(\mathbf{r}_n)e^{i(\mathbf{k}\cdot\mathbf{r}_n-\omega t)}d\mathbf{r}_n$

diffraction pattern $= \int_V f(\mathbf{r})e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}\,d\mathbf{r}$

diffraction pattern $= e^{-\omega t}\int_V f(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}\,d\mathbf{r}$

diffraction pattern $= \int_V f(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}\,d\mathbf{r}$

If $\mathbf{r}$ is outside the object, $f(\mathbf{r}) = 0$

diffraction pattern $= \int_{\text{all }\mathbf{r}} f(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}\,d\mathbf{r} \Rightarrow T[f(\mathbf{r})]$

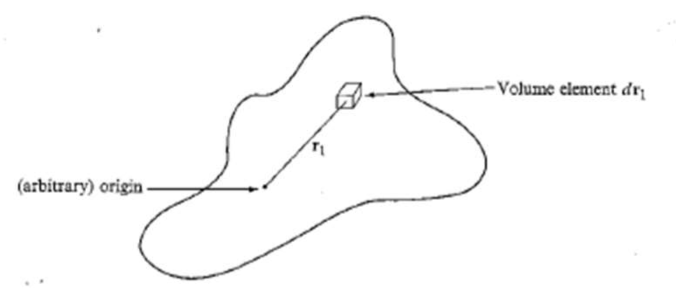


Fig. 6.5 *Diffraction by a volume element.* The volume element $d\mathbf{r}_1$ centred on $\mathbf{r}_1$ affects the waves in a manner which may be represented by the function $f(\mathbf{r})\,d\mathbf{r}_1$. A wave $e^{i(\mathbf{k}\cdot\mathbf{r}_1-\omega t)}$ is propagated, and the mathematical expression for the contribution of the volume element $d\mathbf{r}_1$ to the overall diffraction pattern must be some mathematical combination of $f(\mathbf{r})\,d\mathbf{r}_1$ and $e^{i(\mathbf{k}\cdot\mathbf{r}_1-\omega t)}$.

Thomson Scattering by a Single Electron

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

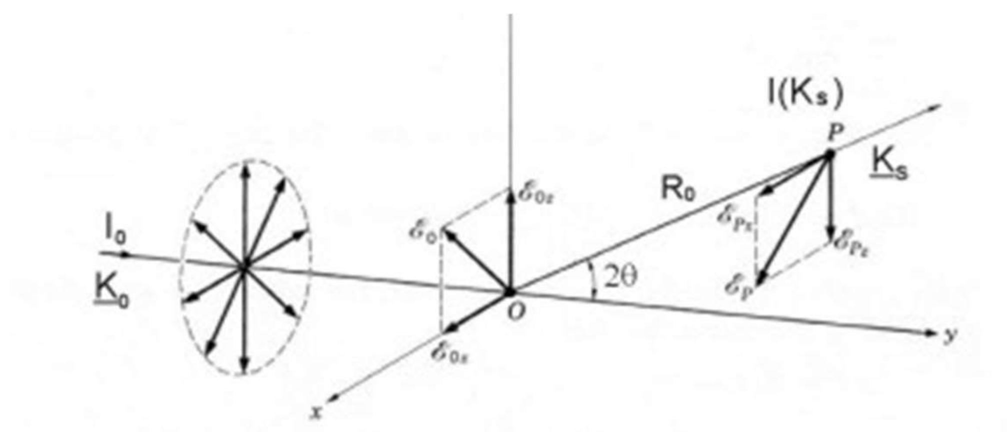
$$\frac{E_{scat}}{E_{in}} = \frac{e^2}{4\pi\varepsilon_0 rmc^2}\sqrt{\frac{1+\cos^2 2\theta}{2}}$$

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

$c =$ 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)

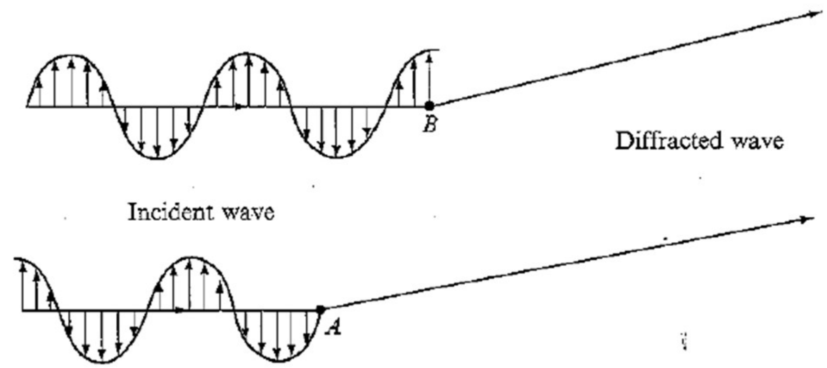
$$\left(E_{scat}\right)_A = f_e E_{in}$$

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

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

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

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



Remember

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

The amplitude function of a group of electrons is

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

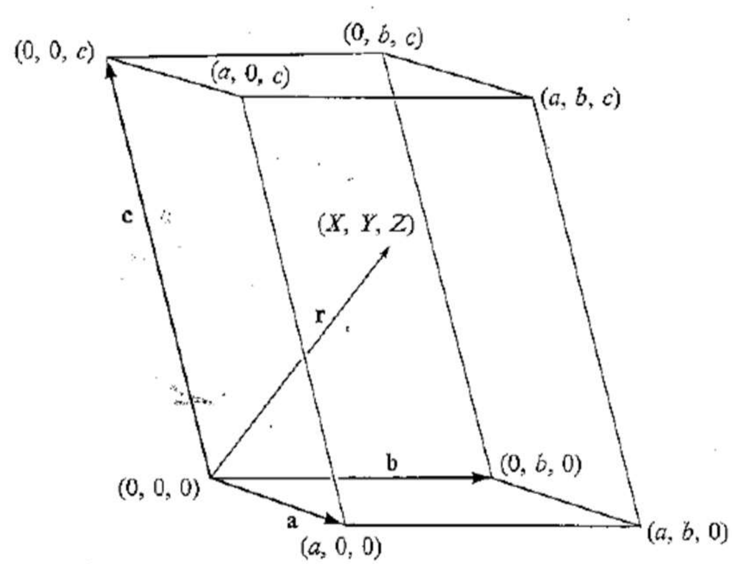
Substituting into $F(\Delta\mathbf{k})$ gives

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

Thomson Scattering by a Group of Electrons (III) or the Motif

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

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



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

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

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

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 $\rho(x, y, z)$

Bragg's Law

$$|\Delta \mathbf{k}| = 2k\sin\theta$$

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

$$|\Delta \mathbf{k}| = 2\pi S_{hkl}$$

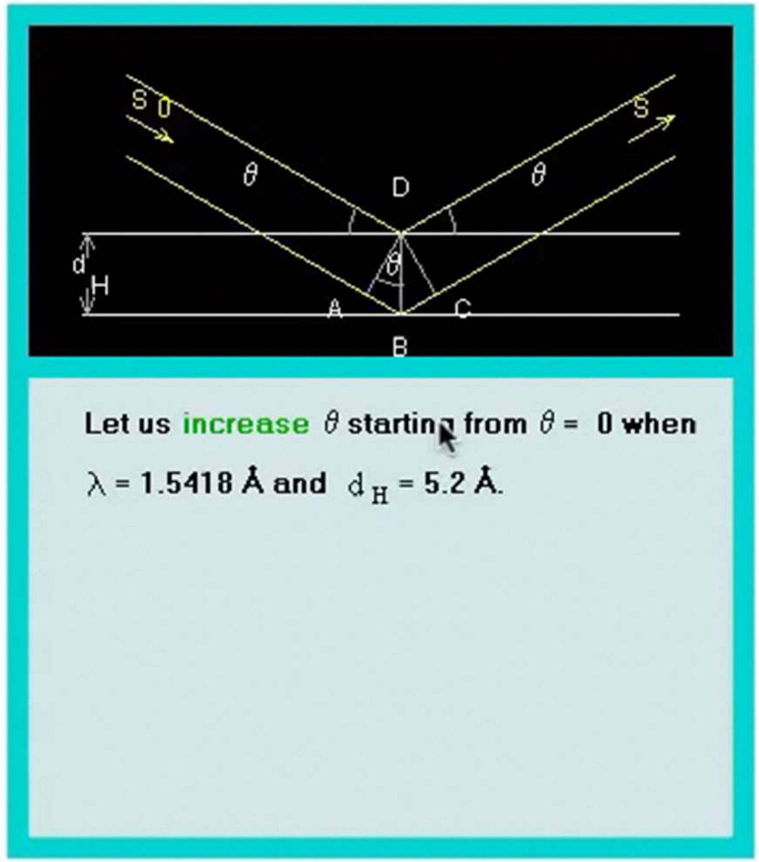
$$2\pi S_{hkl} = 2\frac{2\pi}{\lambda}\sin\theta$$

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

$$S_{hkl} = \frac{1}{d_{hkl}}$$

$$\frac{1}{d_{hkl}} = \frac{2\sin\theta}{\lambda}$$

$$\lambda = 2d_{hkl}\sin\theta$$



Thomson Scattering by a Group of Electrons (IV) or the Motif

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

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

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

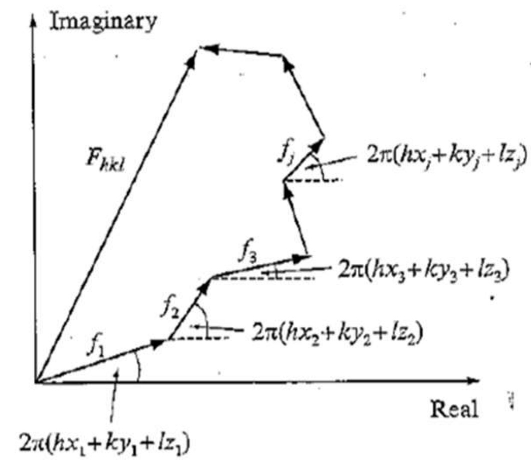
$$\Delta\mathbf{k}\cdot\mathbf{r} = 2\pi(h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*)\cdot(x\mathbf{a} + y\mathbf{b} + z\mathbf{c})$$

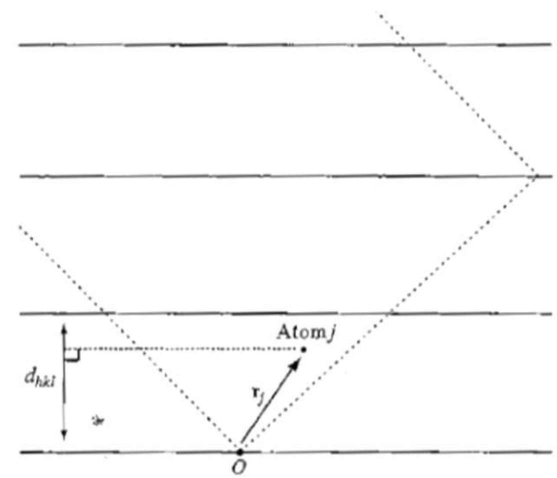
$$= 2\pi(hx + ky + lz)$$

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

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

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





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

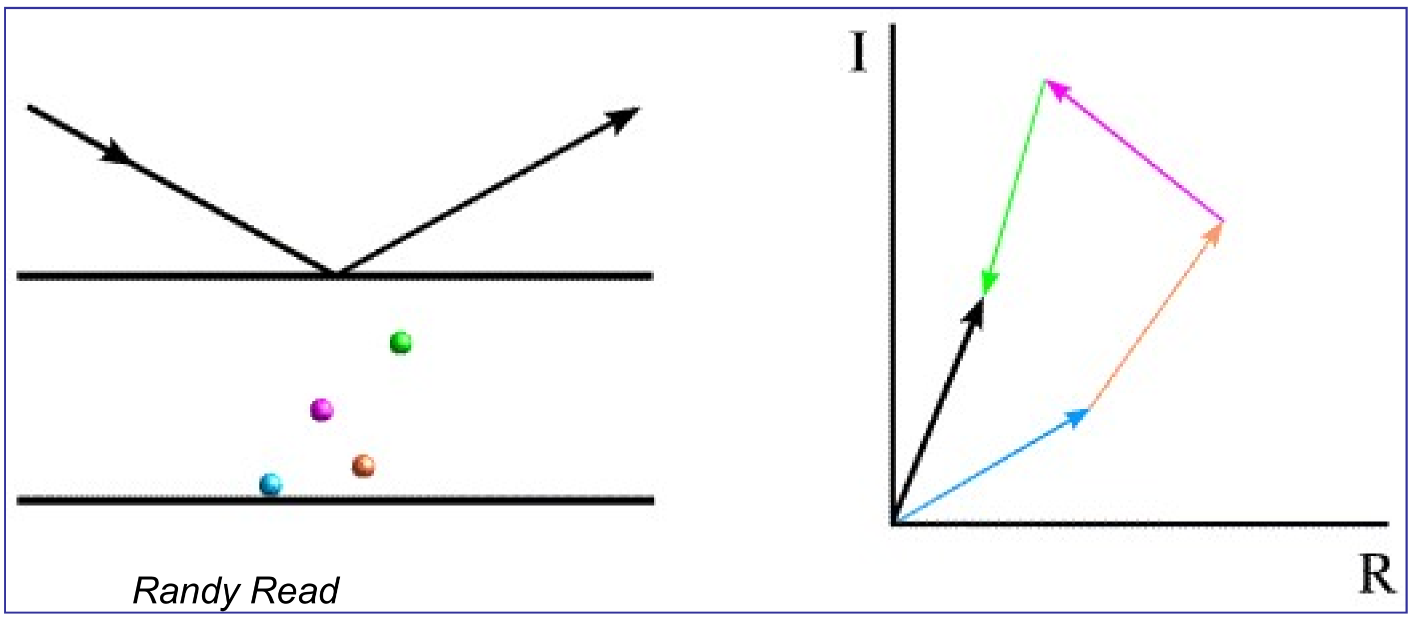
$$F_{hkl} = V \int_{x=0}^{x=1} \int_{y=0}^{y=1} \int_{z=0}^{z=1} \rho(x,y,z) e^{i\Delta\mathbf{k}\cdot(x\mathbf{a}+y\mathbf{b}+z\mathbf{c})}\, dx\ dy\ dz$$

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

- 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 $F_{hkl} = \sum_j f_j e^{2\pi i(hx+ky+lz)} = \left|F_{hkl}\right| e^{i\varphi}$ 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**.

The Atomic Scattering Factor

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

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

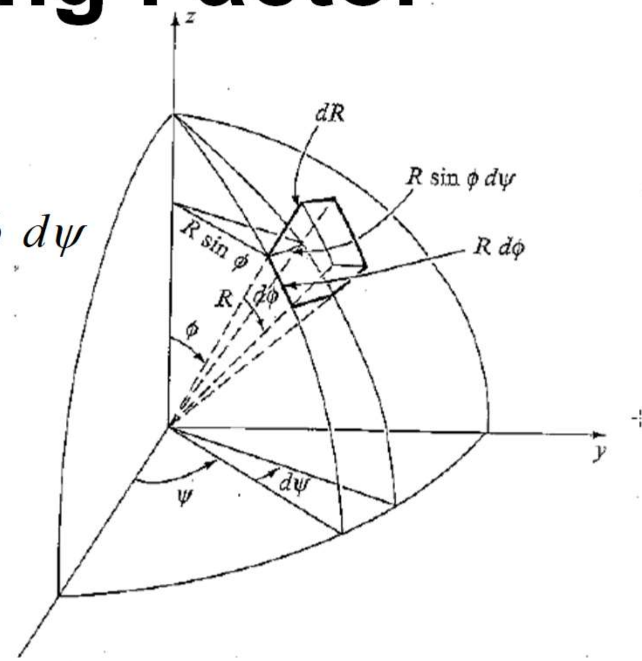
$$f_j = \int_{\psi=0}^{\psi=2\pi} \int_{\phi=0}^{\phi=\pi} \int_{R=0}^{R=\infty} \rho_j(R) e^{2\pi i S_{hkl} R \cos\phi} R^2 \sin\phi \; dR \; d\phi \; d\psi$$

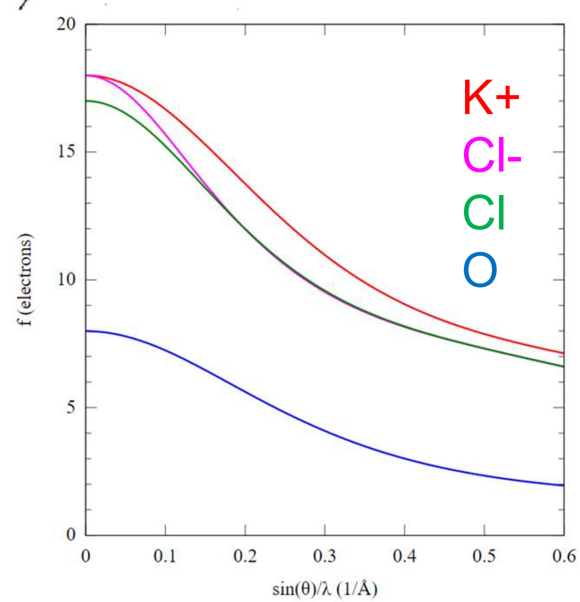
$$f_j = 2\pi \int_0^\infty R^2 \rho_j(R) \left(\frac{e^{2\pi S_{hkl} R} - e^{-2\pi S_{hkl} R}}{2\pi S_{hkl} R} \right) dR$$

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

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

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





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

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

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

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

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

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

Correction for Thermal Motion (II)

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

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

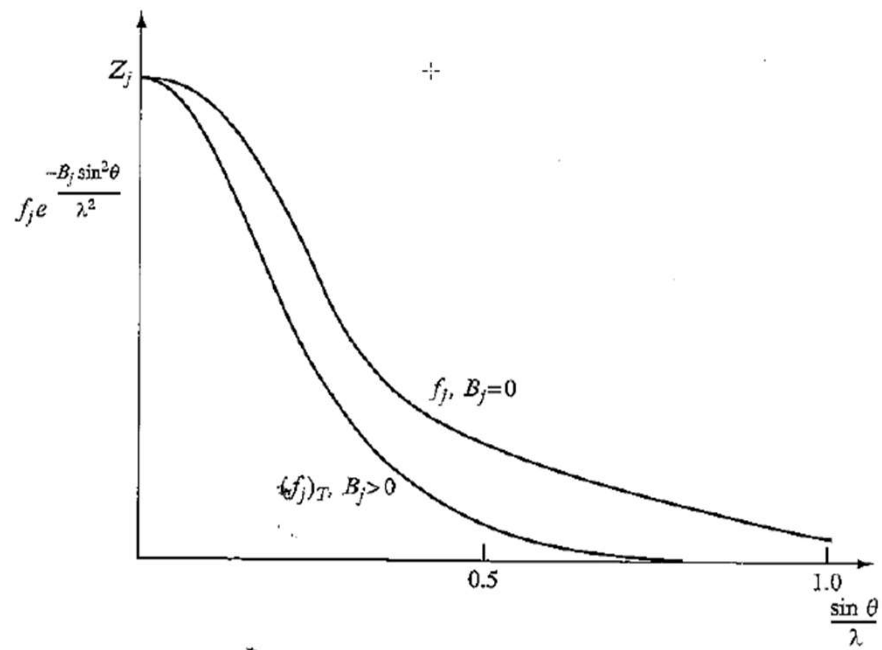
$$\text{Let us define } B_j = 8\pi^2 \overline{u_j^2}$$

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

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

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

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



Freidel's Law

Let's consider two centrosymmetrically disposed reflections:

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

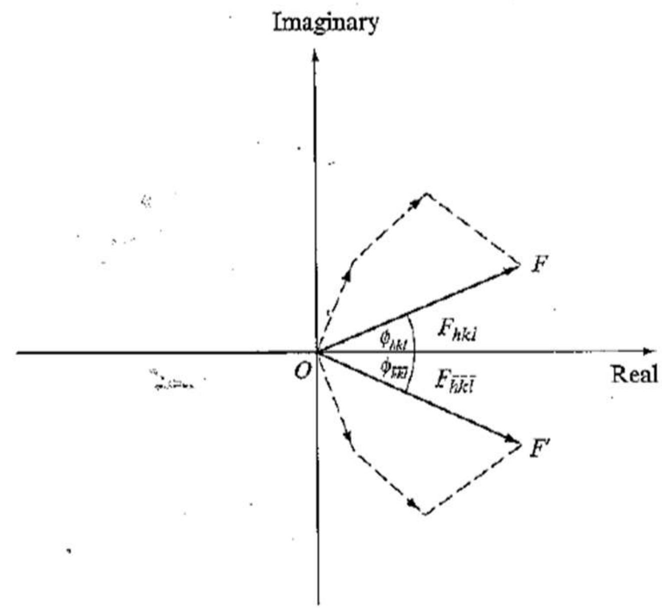
$$F_{\overline{hkl}} = \sum_j f_j e^{2\pi i(\bar{h}x_j + \bar{k}y_j + \bar{l}z_j)} = \sum_j f_j e^{-2\pi i(hx_j + ky_j + lz_j)}$$

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

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

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

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

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

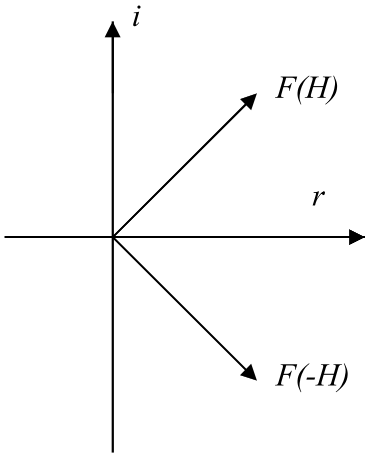
$$f = \sum_j \frac{\varphi_j}{1-\frac{\omega_j^2}{\omega_0^2}-i\frac{\kappa_j}{\omega_0}} = \sum_j \varphi_j \int_{\omega_j}^{\infty} \frac{w_j\,d\omega}{1-\frac{\omega_j^2}{\omega_0^2}-i\frac{\kappa_j}{\omega_0}} = f^0 + \sum_j \varphi_j(\xi_j + i\eta_j) = f^0 + f' + if''$$

Effect on Diffraction Data

- Form factor

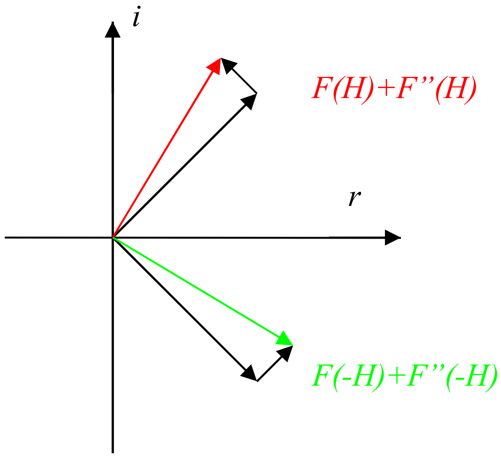
$$f = f^0 + \Delta f' + i\Delta f''$$

$$f = f^0 + f' + if''$$



- Structure Factor

$$F_{hkl} = \sum_j \left(f_j^0 + f_j' + if_j'' \right) \cdot e^{2\pi i \mathbf{h} \cdot \mathbf{r}_j}$$



Breakdown of Freidel's Law

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

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

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

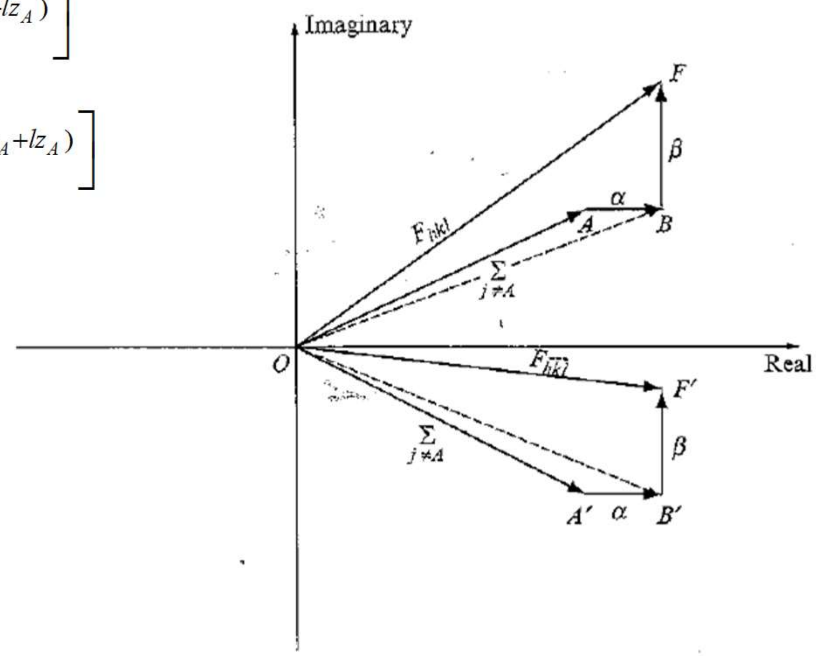
$$F_{\overline{hkl}} = \sum_j f_j e^{-2\pi i(hx_j+ky_j+lz_j)} + \left[\left(f_A^0 + f' + if''\right) e^{-2\pi i(hx_A+ky_A+lz_A)}\right]$$

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

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

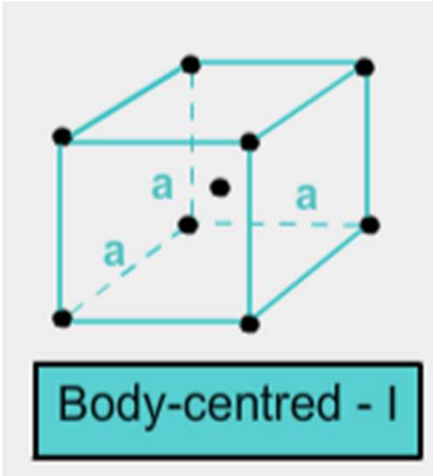
Furthrmore:

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



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

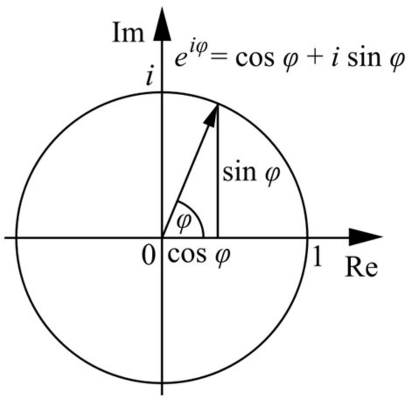


$$F_{hkl} = \sum_{j}^{j=N/2} \left(f_j e^{2\pi i(hx_j+ky_j+lz_j)} + f_j e^{2\pi i[h(x_j+1/2)+k(y_j+1/2)+l(z_j+1/2)]} \right)$$

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

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

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

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 $l = 0$

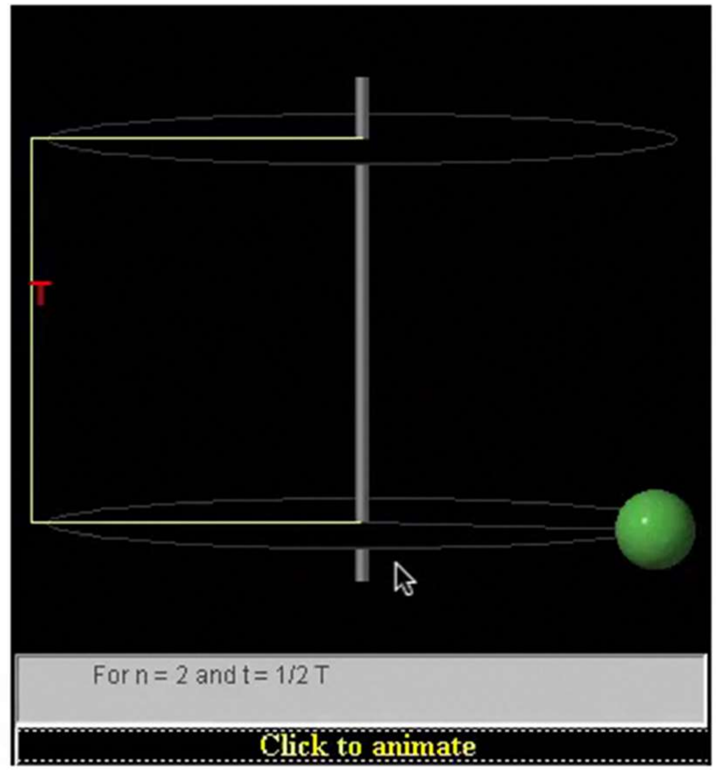
$$F_{hkl} = \sum_{j}^{j=N/2} f_j e^{2\pi i(hx_j + ky_j + lz_j)} \left(1 + e^{\pi i k}\right)$$

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

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

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

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



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

Textbooks and Resources Used

Jim Pflugrath and Lee Daniels, Rigaku Americas Corp.

Crystals, X-rays and Proteins: Comprehensive Protein Crystallography, by D. Sherwood and J. Cooper, Oxford University Press, © 2011

Fundamentals of Crystallography, 2nd Ed., C. Giacovazzo ed. Oxford University Press, © 2002

Understanding Single Crystal X-ray Crystallography, D. Bennett, Wiley-VCH, © 2010

International Tables for Crystallography, Volume A, Space Group Symmetry, T. Hahn, Springer, 2002

Dauter and Jaskolski, *J. Appl. Cryst.* (2010), **43**, 1150-1171

http://escher.epfl.ch/software/

http://www.ysbl.york.ac.uk/~cowtan/sfapplet/sfintro.html

https://see.stanford.edu/Course/EE261