

STRUCTURE FACTORS & THE FOURIER SYNTHESIS

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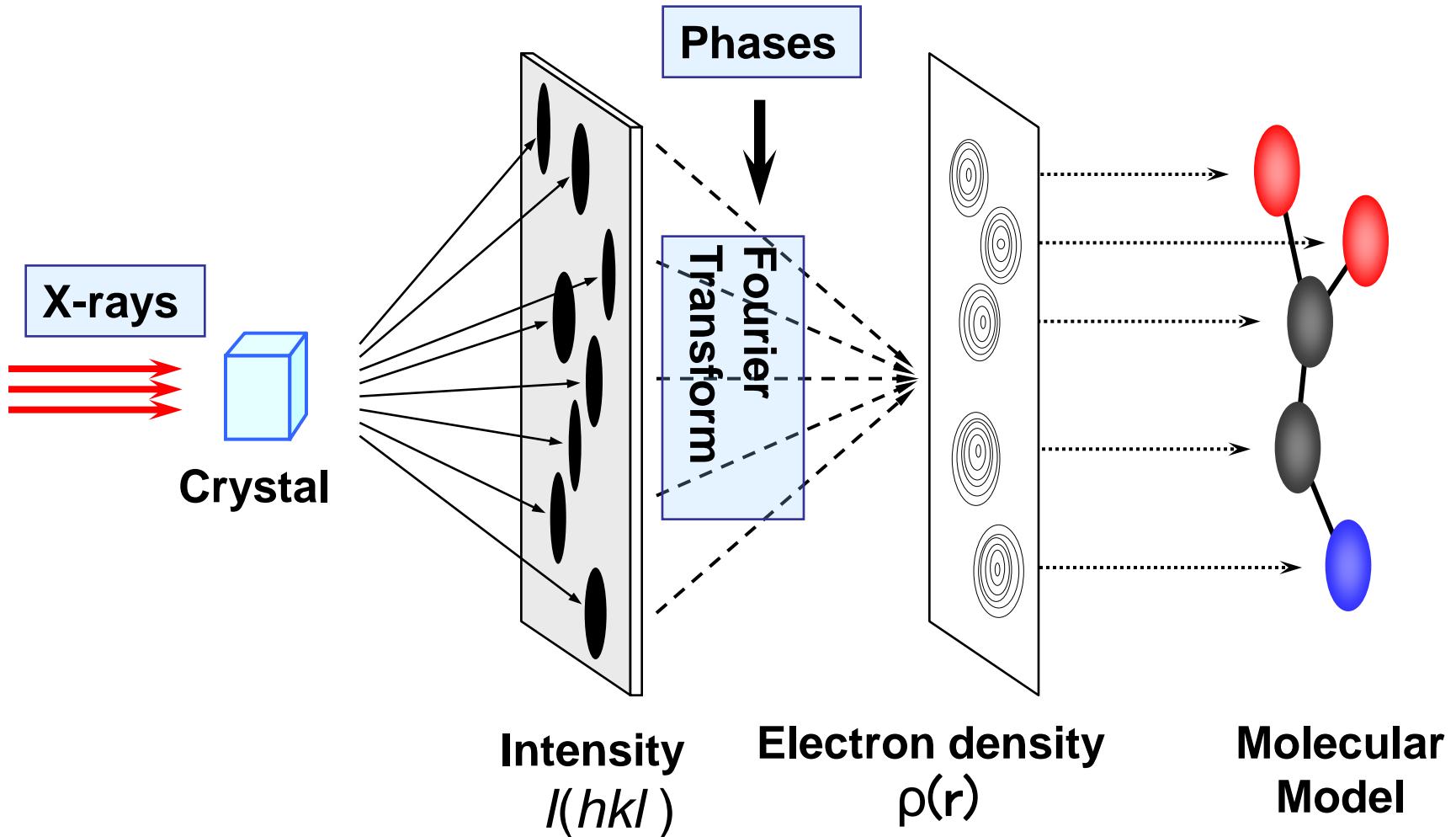


Joseph Ferrara, PhD,

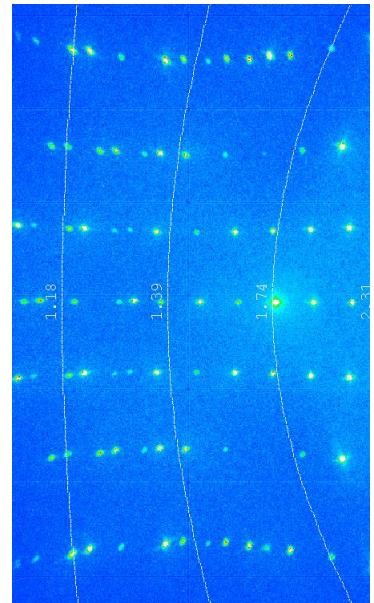
A GROUP PROJECT...



35000 ft view of X-ray Structure Analysis



Structure Factor and Intensity



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

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

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

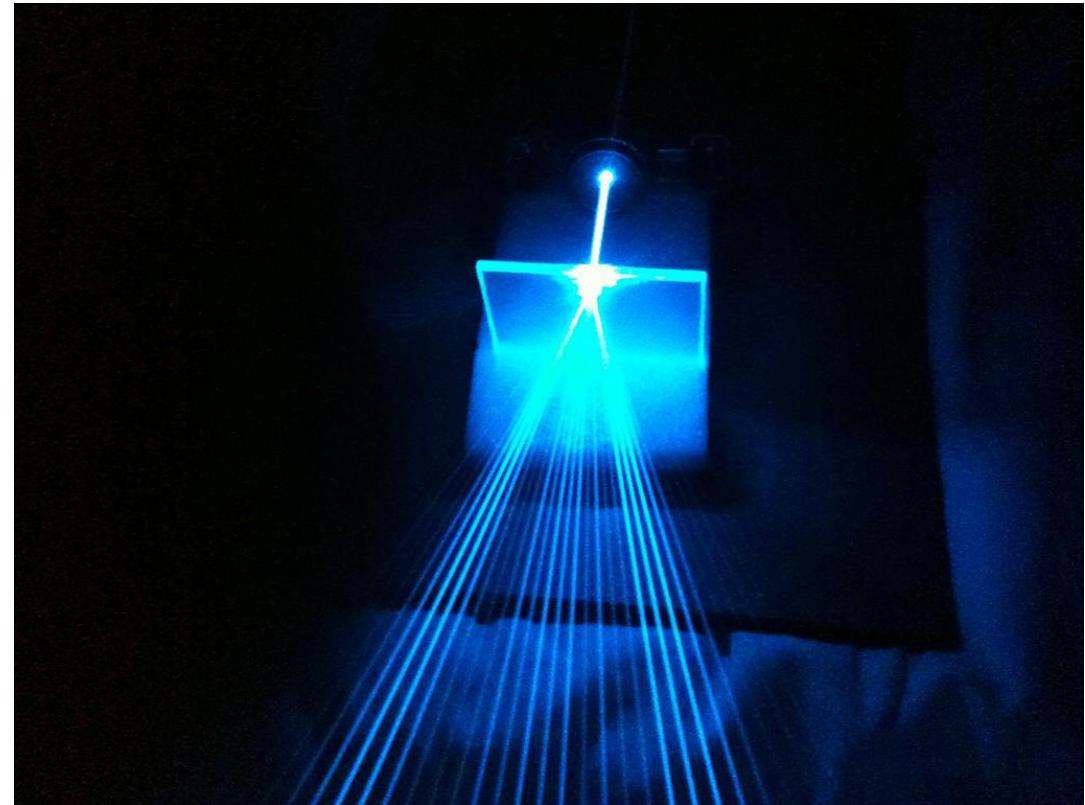
$$\epsilon = \cos^{-1}(\xi \csc 2\theta)$$

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

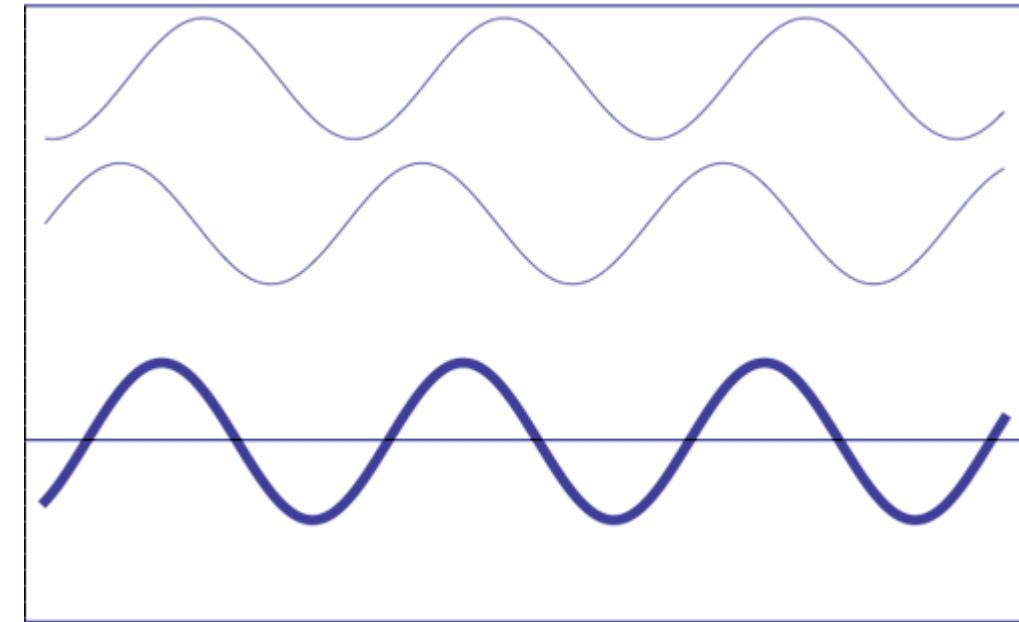
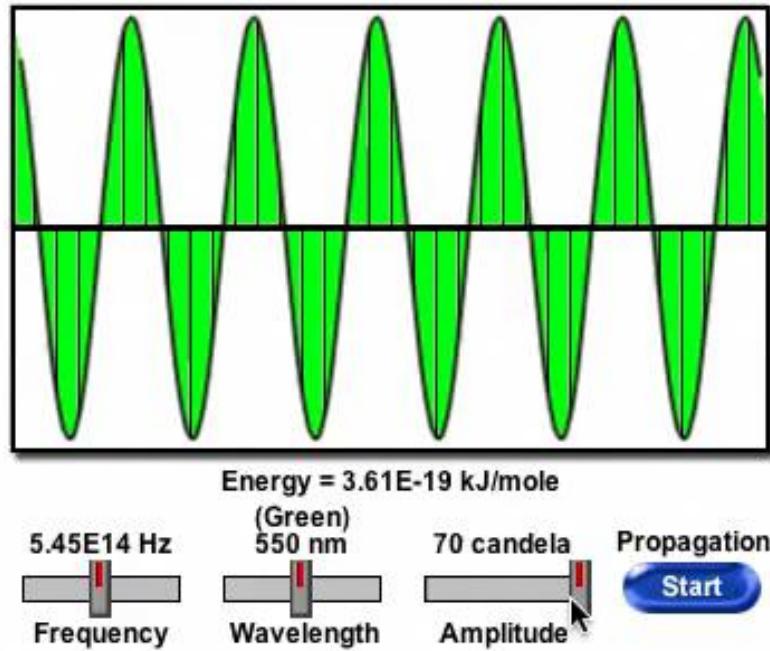
$$F_{hkl} = \sum_j f_j e^{2\pi i (hx_j + ky_j + lz_j)}$$

SCATTERING

- Scattering is the result of an interaction of electromagnetic radiation with a charged particle, predominately electrons.
 - Thompson/Rayleigh
 - elastic scattering
 - Compton
 - inelastic scattering

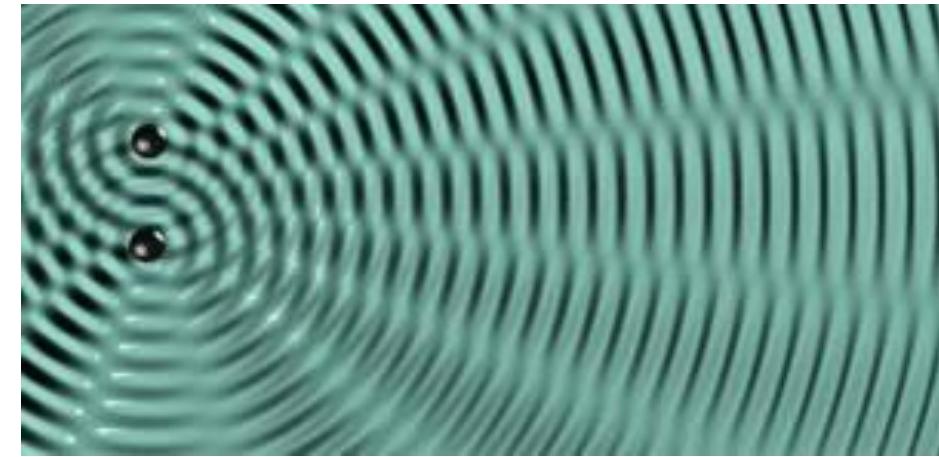
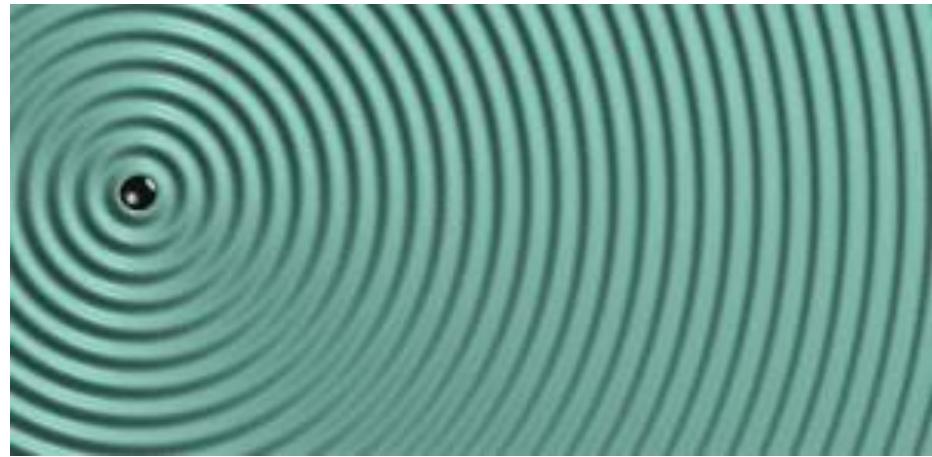


WAVES



- Direction of propagation
- Amplitude
- Wavelength

WAVES



COMPLEX NUMBERS



imgflip.com



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

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

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

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

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

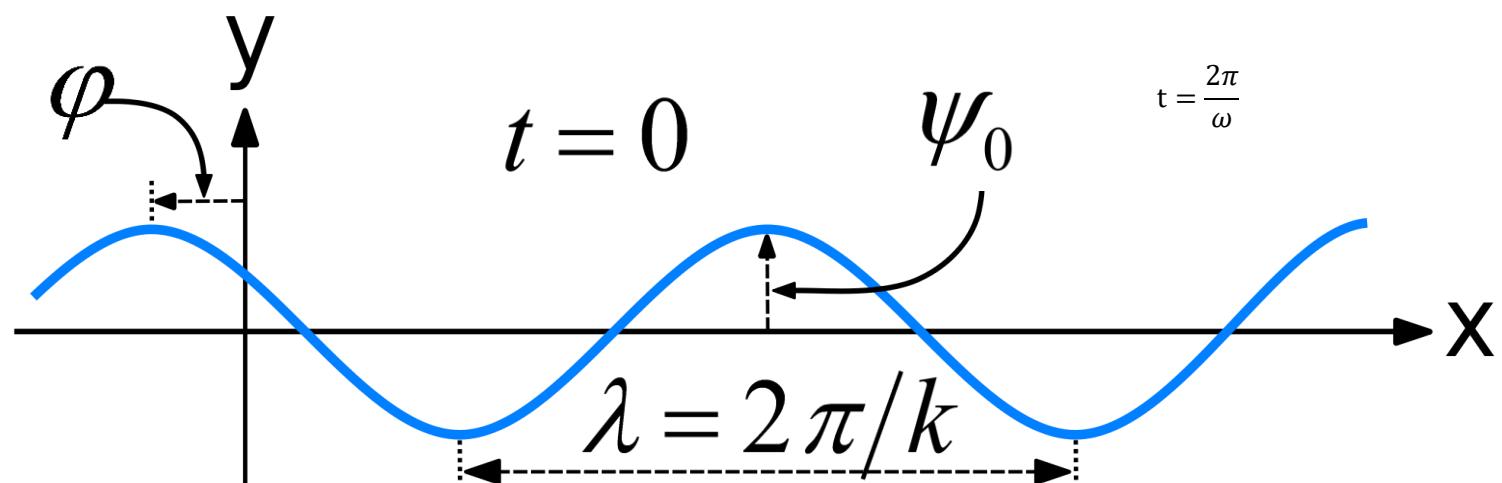
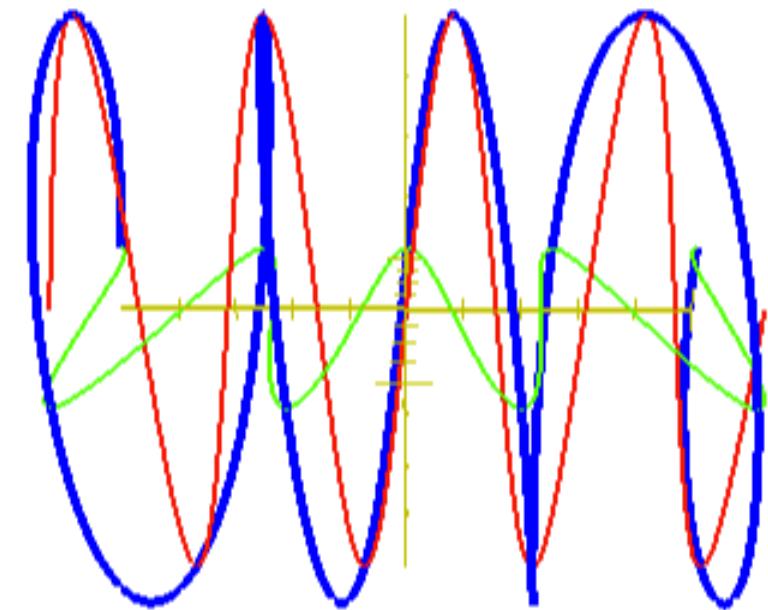
$$\mathbf{k} \cdot \mathbf{r} = (k_x x + k_y y + k_z z)$$

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

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

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

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

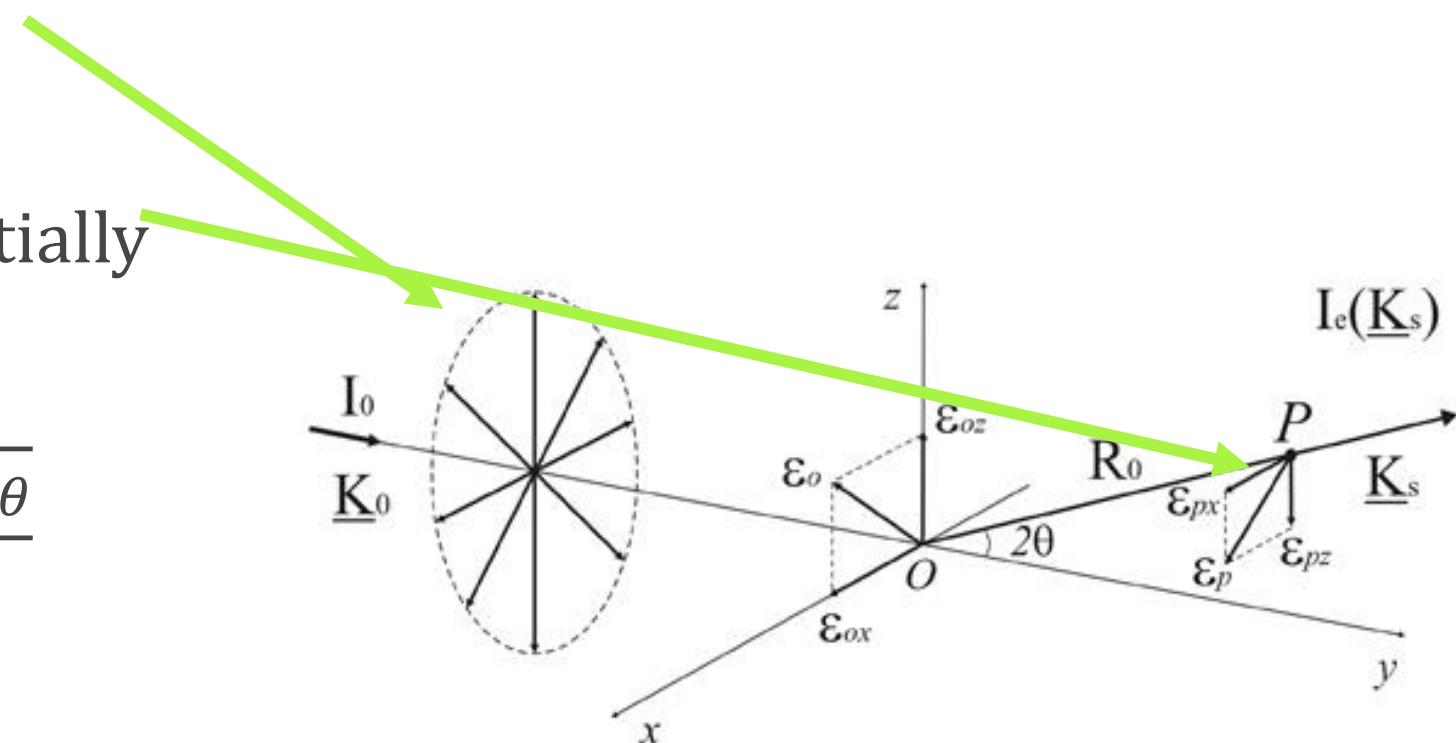


THOMPSON SCATTERING OF 1 ELECTRON

- The incoming light is not polarized
- The scattered light is partially polarized

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

- r = interaction radius
- 2θ = deflection angle

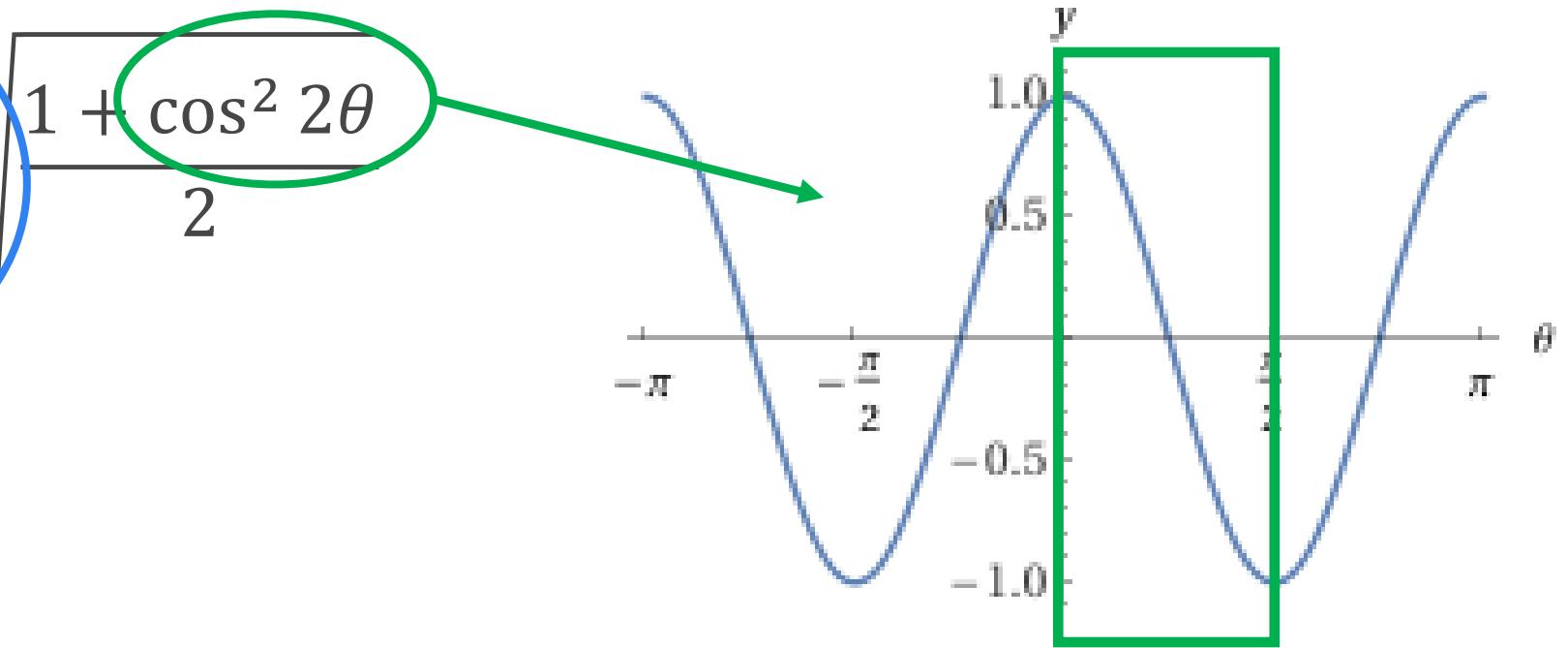


[Crystallography. Scattering and diffraction](#)

EXTENDING THOMPSON SCATTERING

$$\frac{E_{scat}}{E_{in}} = \frac{e^2}{4\pi\epsilon_0 r m c^2} \sqrt{1 + \cos^2 2\theta}$$

$$f_e = \frac{e^2}{4\pi\epsilon_0 r m c^2}$$



$$\frac{E_{scat}}{E_{in}} = f_e \rho(\mathbf{r})$$

This part gets more interesting if the incoming X-rays are polarized, but we're going to ignore it for now.

The Atomic Scattering Factor

$$d\mathbf{R} = R^2 \sin f \, dR \, df \, dy \text{ and } \mathbf{S}_{hkl} \times \mathbf{R} = S_{hkl} R \cos f$$

$$f_j = \int_{\text{atom}} r_j(\mathbf{R}) e^{2\rho i S_{hkl} \times \mathbf{R}} d\mathbf{R} = \int_{\text{atom}} r_j(R) e^{2\rho i S_{hkl} R \cos f} R^2 \sin f \, dR \, df \, dy$$

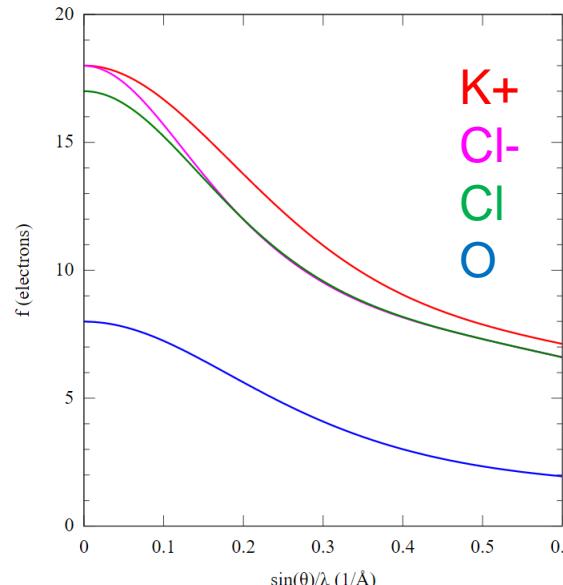
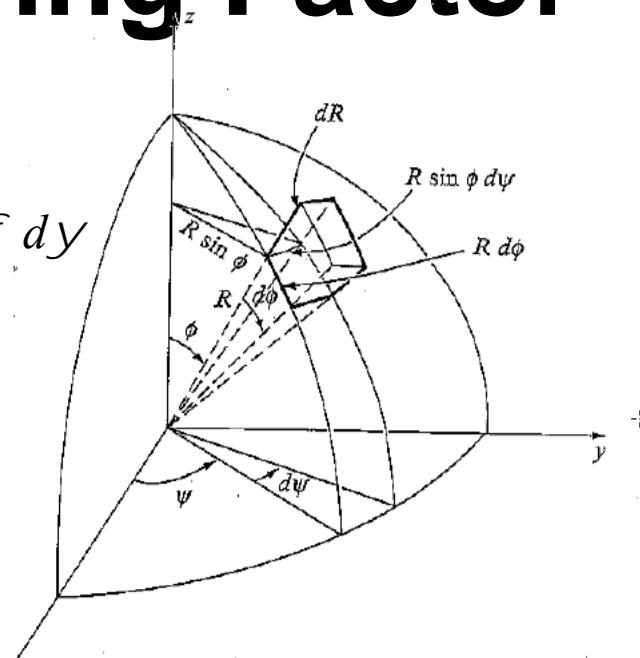
$$f_j = \int_{y=0}^{y=2\rho} \int_{f=0}^{f=\rho} \int_{R=0}^{R=\sqrt{\chi}} r_j(R) e^{2\rho i S_{hkl} R \cos f} R^2 \sin f \, dR \, df \, dy$$

$$f_j = 2\rho \int_0^{\sqrt{\chi}} R^2 r_j(R) \left[\frac{e^{2\rho S_{hkl} R}}{2\rho S_{hkl} R} - \frac{e^{-2\rho S_{hkl} R}}{2\rho S_{hkl} R} \right] dR$$

$$f_j = 4\rho \int_0^{\sqrt{\chi}} R^2 r_j(R) \left[\frac{\sin 2\rho S_{hkl} R}{2\rho S_{hkl} R} \right] dR$$

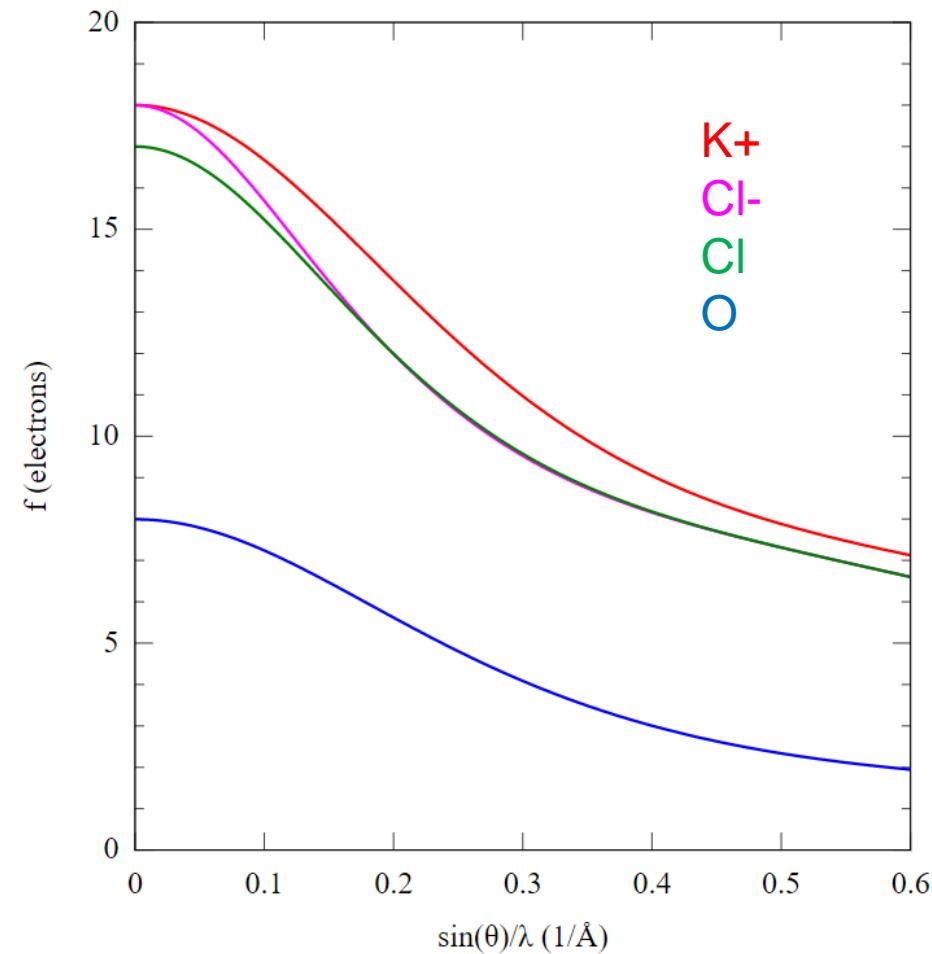
$$S_{hkl} = \frac{2 \sin q}{l}$$

$$f_j = 4\rho \int_0^{\sqrt{\chi}} R^2 r_j(R) \left[\frac{\sin q}{4\rho \sin q} \frac{R}{l} \right] dR$$



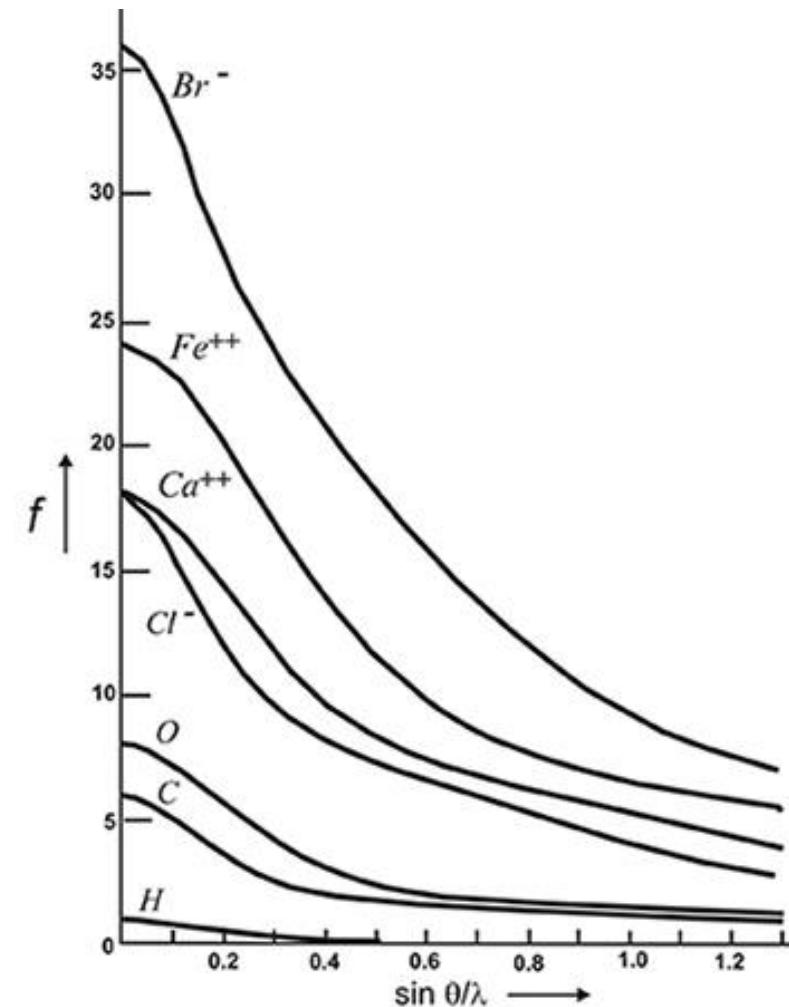
ATOMIC SCATTERING FACTORS(FOR X-RAYS)

- Max scattering power is the number of electrons
- Notice the fall-off differs for atoms/ions with same total electron #
- Scattering factors are different for different probes (e.g., Neutrons, electrons)



ATOMIC SCATTERING FACTORS(FOR X-RAYS)

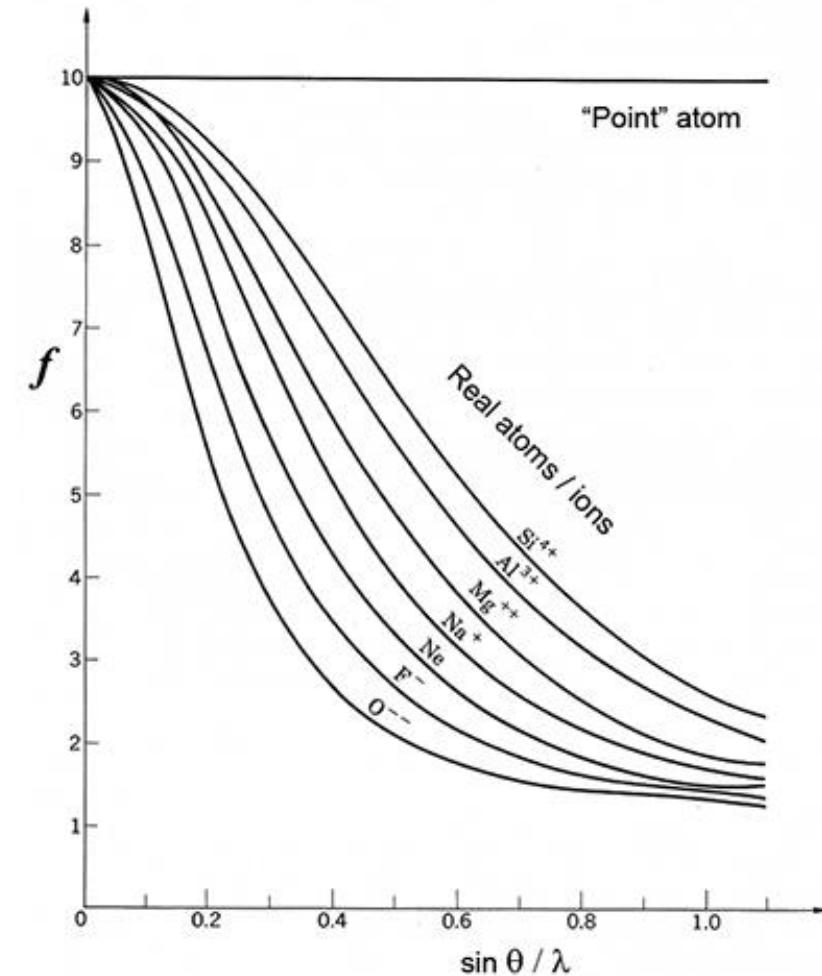
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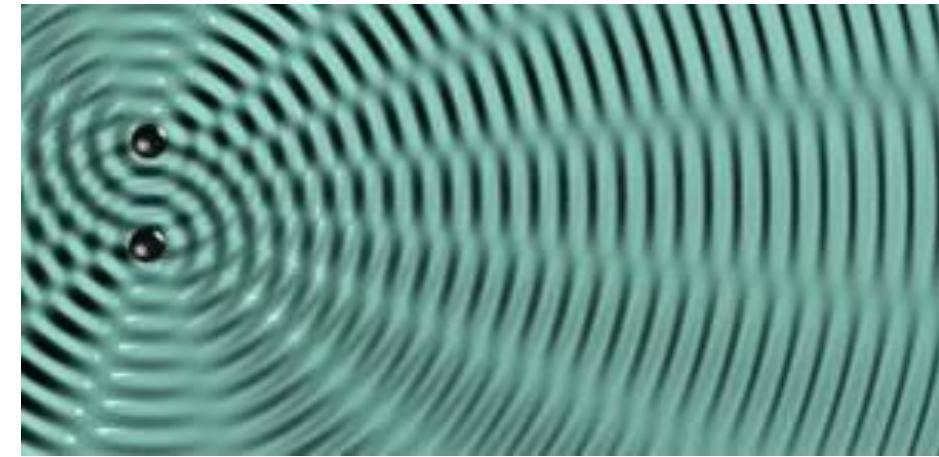
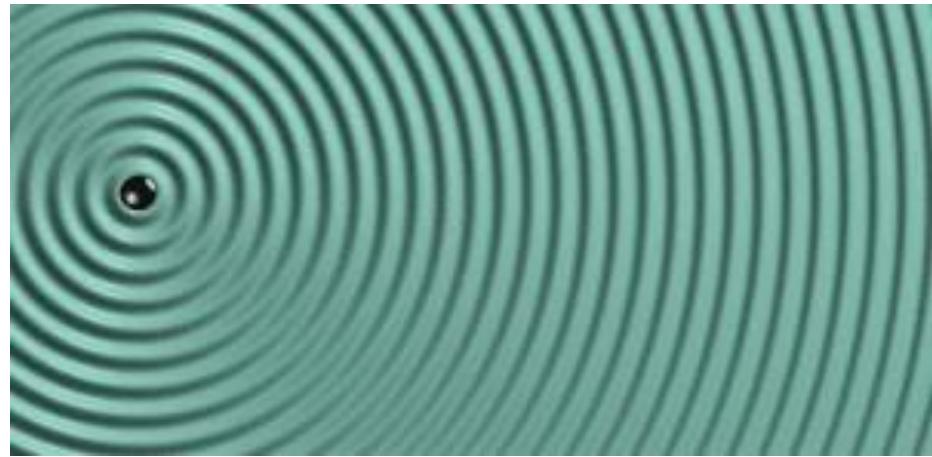
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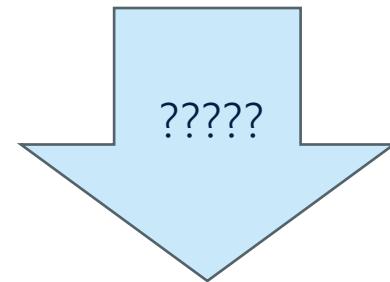
WAVES



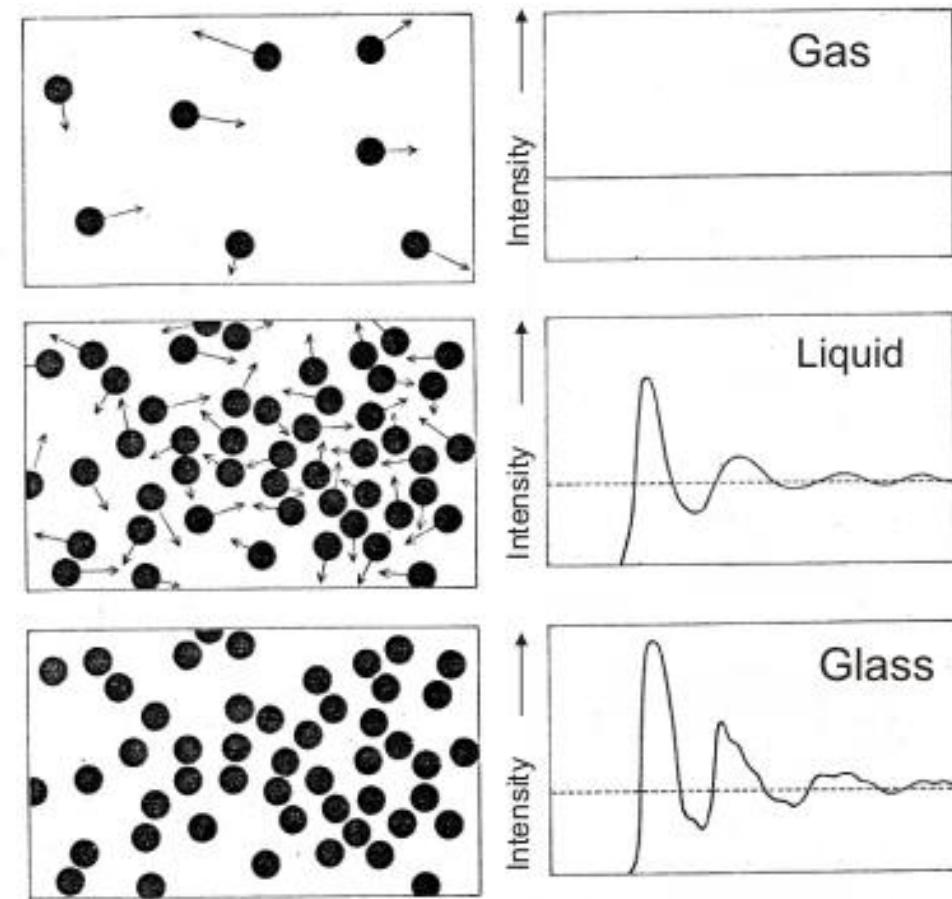
PAIR DISTRIBUTION FUNCTION

$$S(Q) = \frac{I_{\text{coh}} - \langle f^2 \rangle + \langle f \rangle^2}{\langle f \rangle^2}$$

$$\langle f \rangle = \sum_i^n c_i f_i \quad \langle f^2 \rangle = \sum_i^n c_i f_i^2$$



$$g_{ab}(r) = \frac{1}{N_a N_b} \sum_{i=1}^{N_a} \sum_{j=1}^{N_b} \langle \delta(|\mathbf{r}_{ij}| - r) \rangle$$

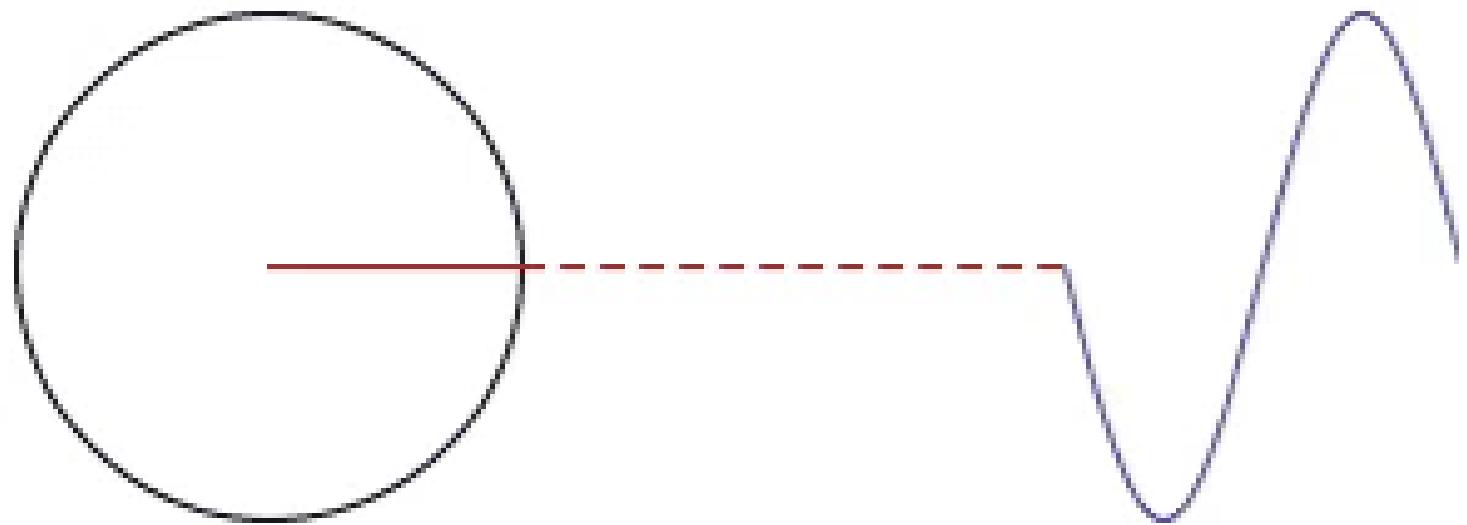


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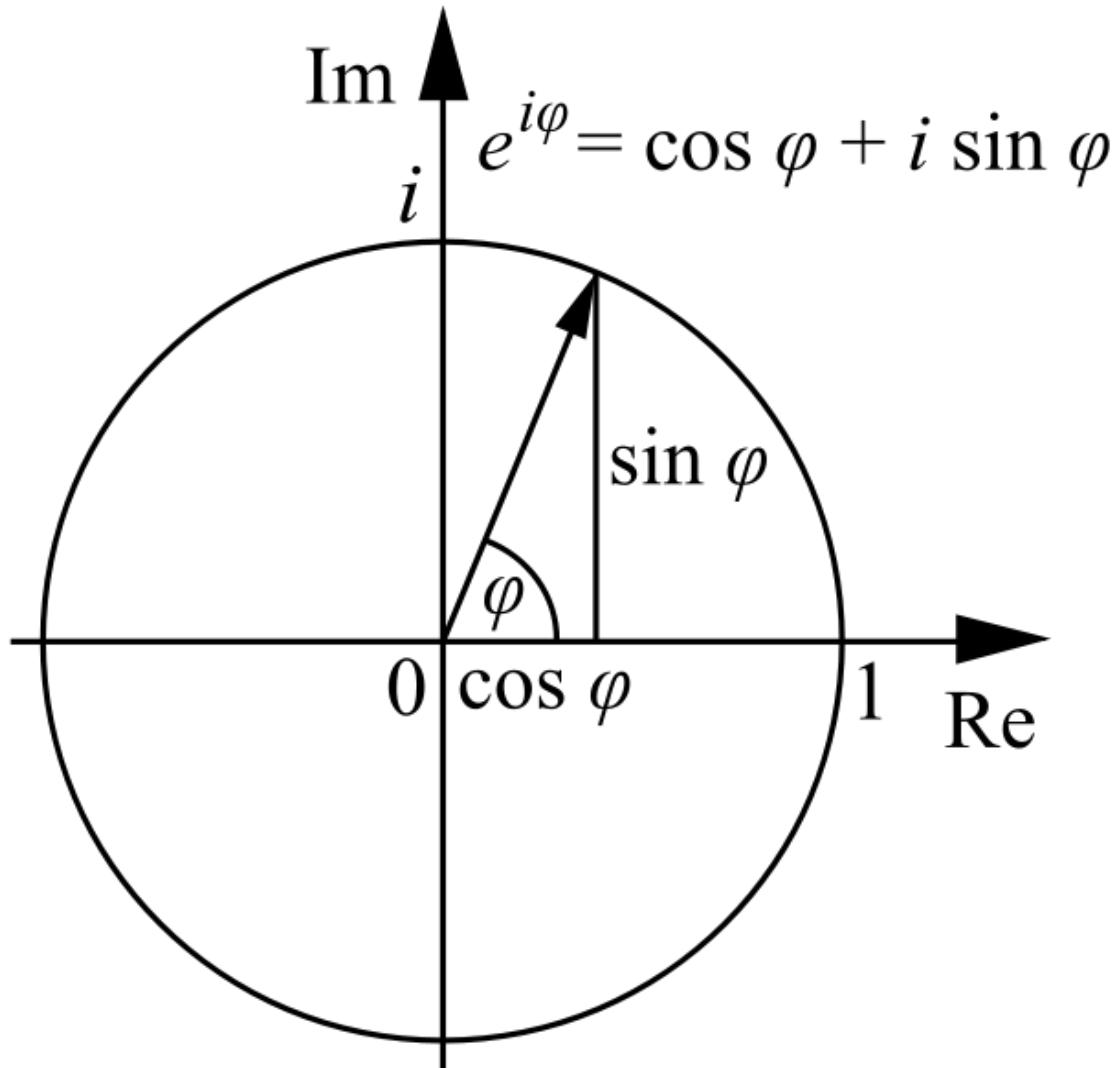
[PDF Analysis](#)

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



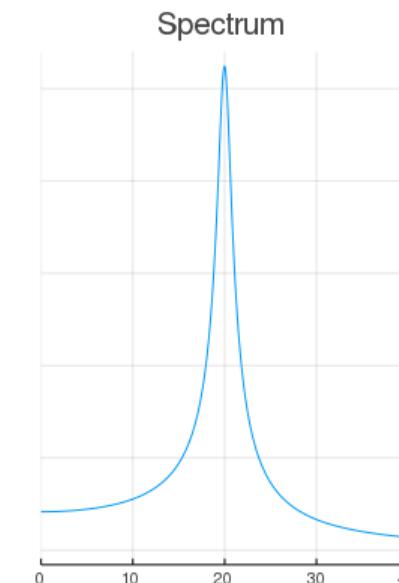
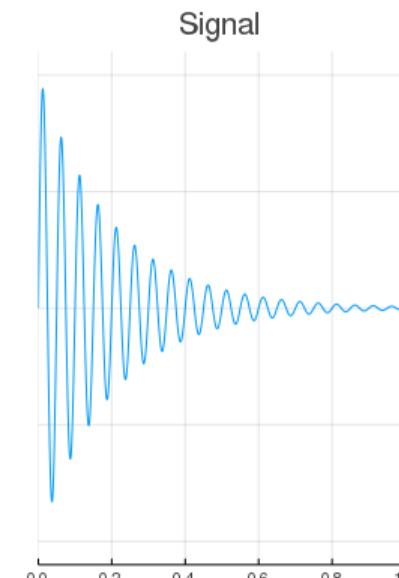
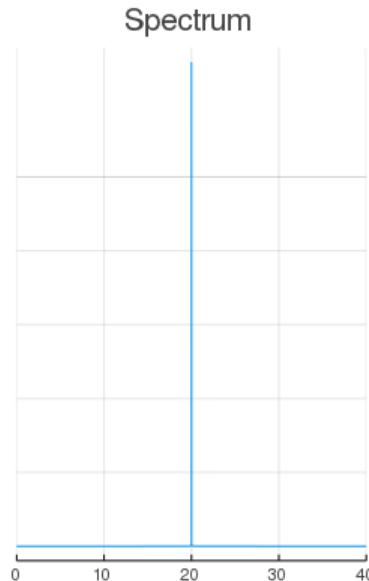
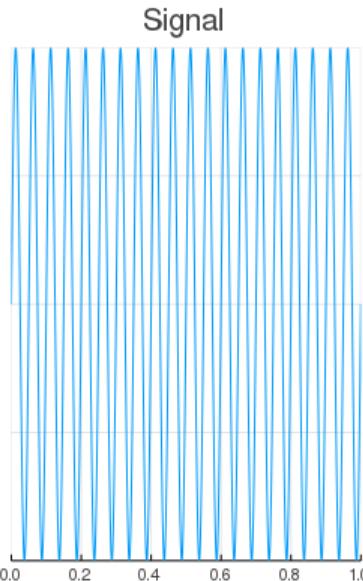
The Fourier Transform

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

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

In three dimensions this is generalized to:

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



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

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

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

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

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

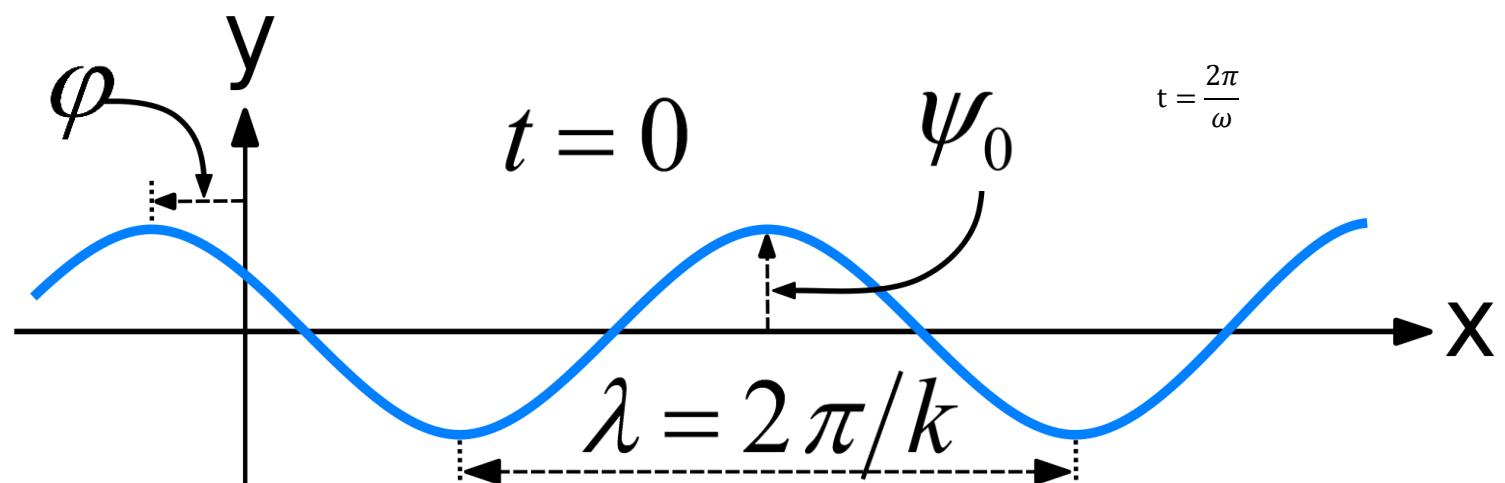
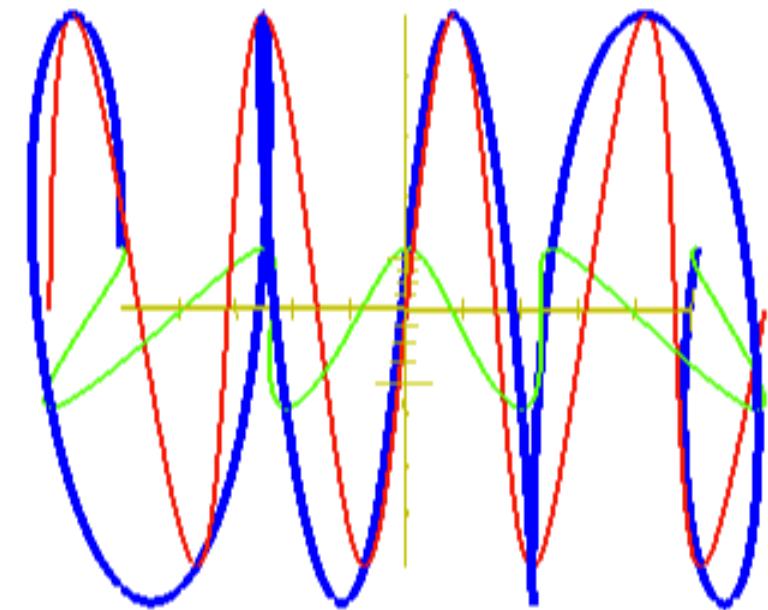
$$\mathbf{k} \cdot \mathbf{r} = (k_x x + k_y y + k_z z)$$

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

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

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

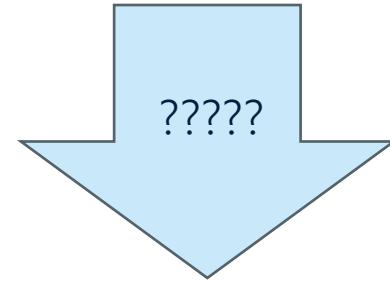
$$I = |\psi(\mathbf{r}, t)|^2$$



PAIR DISTRIBUTION FUNCTION

$$S(Q) = \frac{I_{\text{coh}} - \langle f^2 \rangle + \langle f \rangle^2}{\langle f \rangle^2}$$

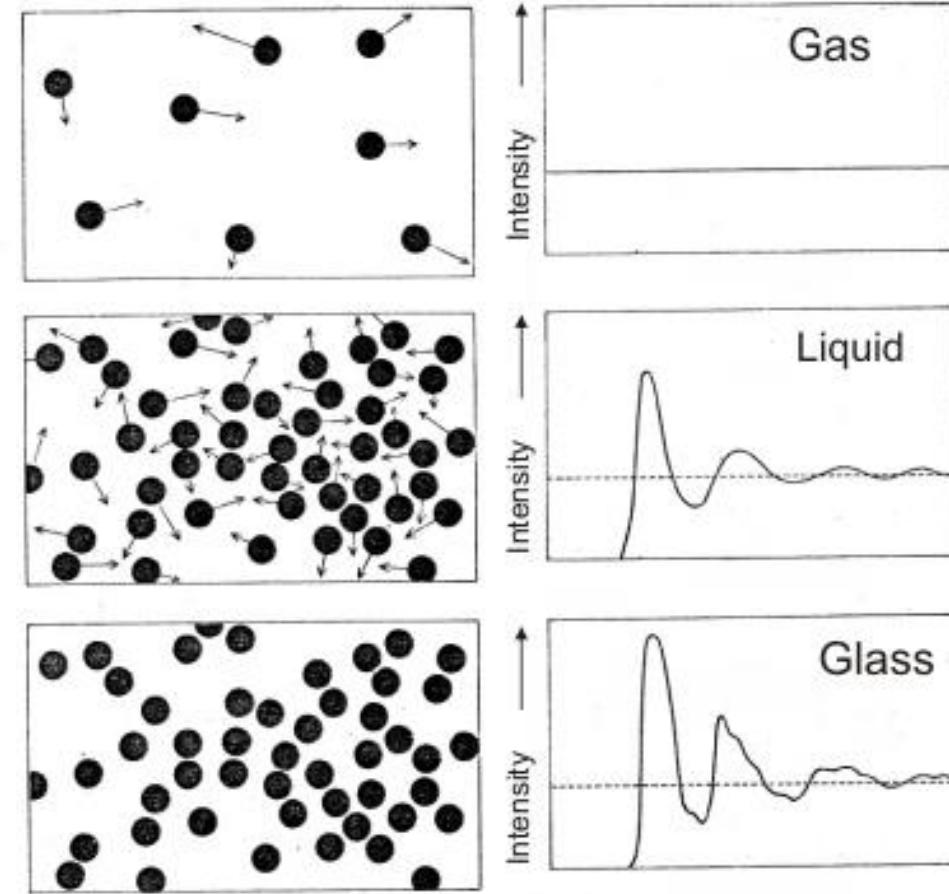
$$\langle f \rangle = \sum_i^n c_i f_i \quad \langle f^2 \rangle = \sum_i^n c_i f_i^2$$



$$g_{ab}(r) = \frac{1}{N_a N_b} \sum_{i=1}^{N_a} \sum_{j=1}^{N_b} \langle \delta(|\mathbf{r}_{ij}| - r) \rangle$$

[Crystallography. Scattering and diffraction](#)

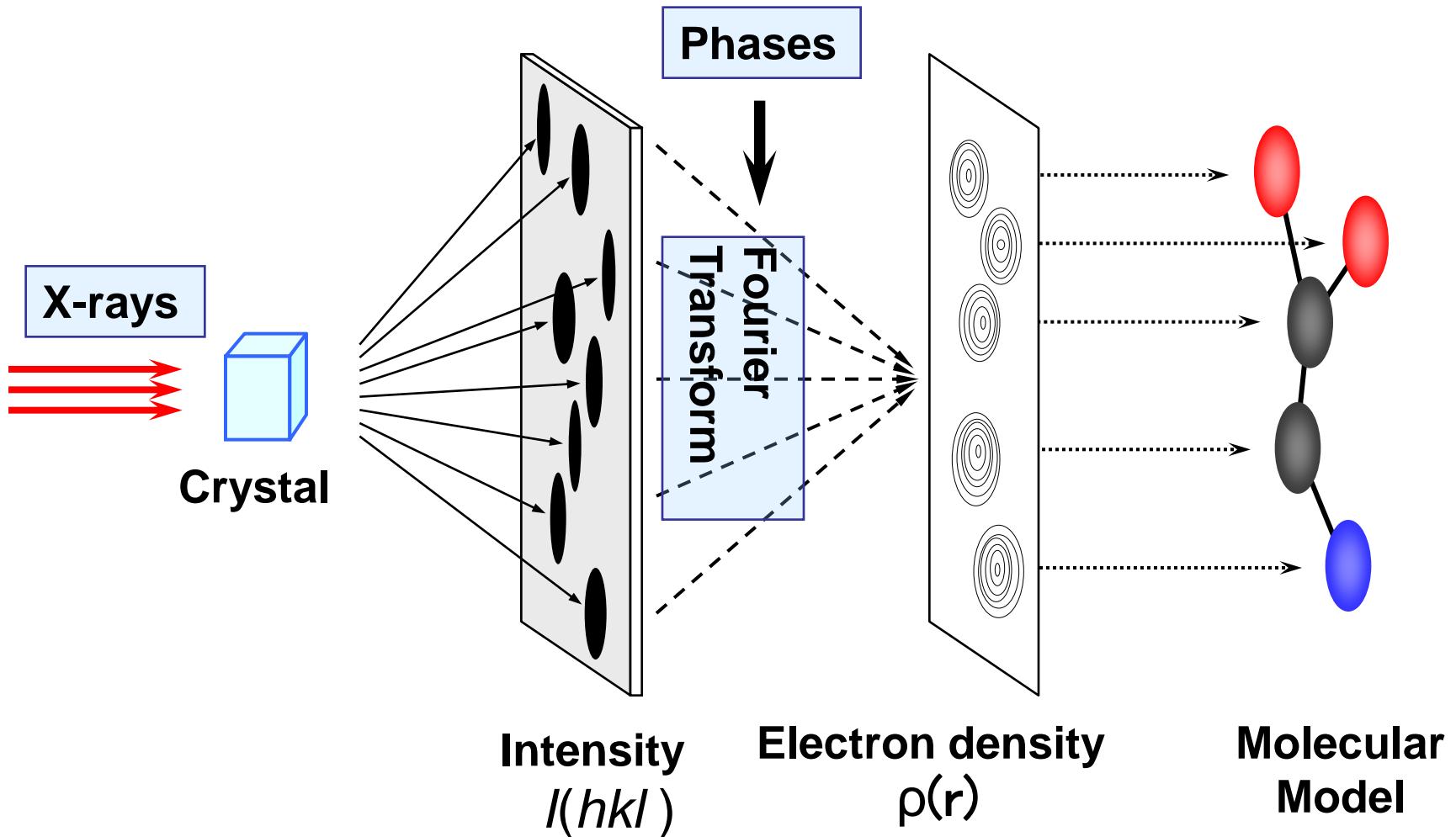
[PDF Analysis](#)



THE POWER OF CRYSTALLOGRAPHY

- Satisfying Bragg's Law means amplification of the scattering in discrete(ish) points.
- All these reflections give us vastly more data points than the radial integration of PDF/SAXS/etc
- We just need to understand how this periodicity affects our intensity data.

35000 ft view of X-ray Structure Analysis



Thomson Scattering by a Group of Electrons (III)

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

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

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

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

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

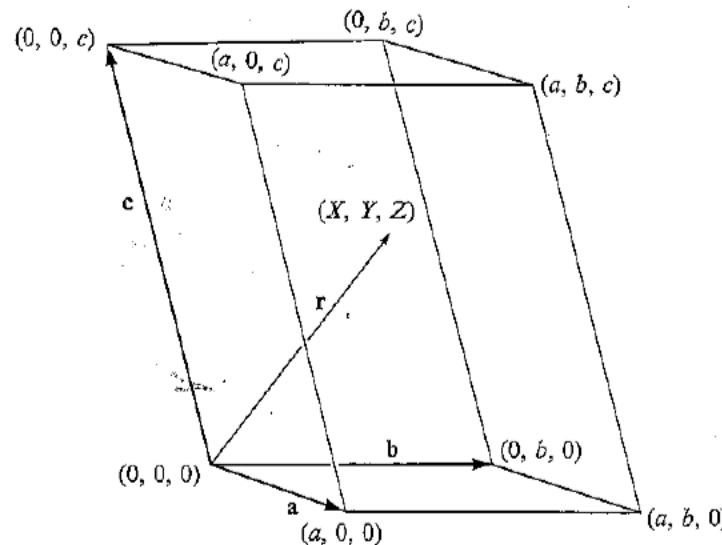
X, Y and Z represent absolute coordinates and

x, y and z represent fractional coordinates.

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

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

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



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 $\rho(x, y, z)$

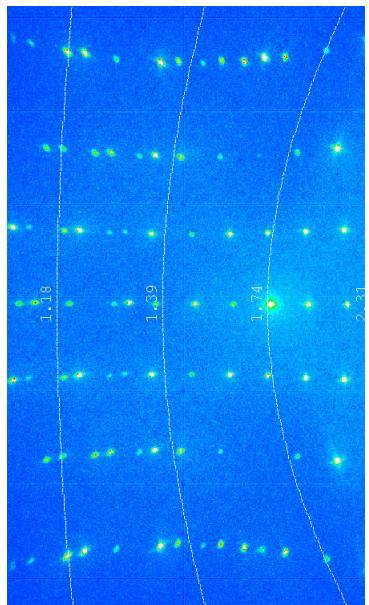
$$\rho(x, y, z) = \frac{1}{V} \int_{\text{all } \Delta\mathbf{k}} F_{rel}(\Delta\mathbf{k}) e^{-i\Delta\mathbf{k}\cdot(x\mathbf{a}+y\mathbf{b}+z\mathbf{c})} d(\Delta\mathbf{k})$$

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

hkl values are discrete so we can rewrite this as:

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

Structure Factor and Intensity



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

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

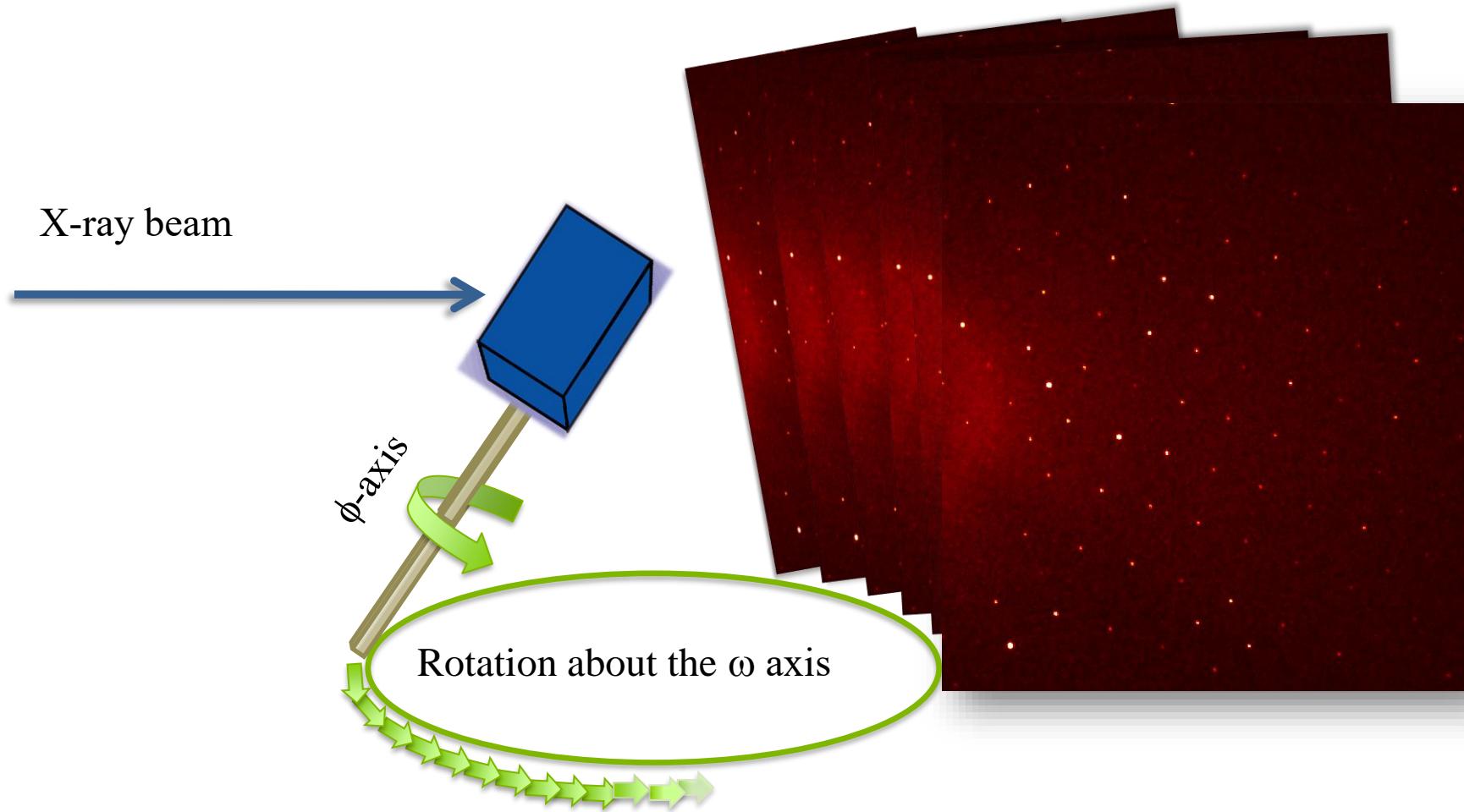
$$p_{hkl} = \frac{((\cos \epsilon)^2 + (\sin \epsilon)^2 (\cos 2\theta)^2) + (\sin \epsilon)^2 + (\cos \epsilon)^2}{2}$$

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

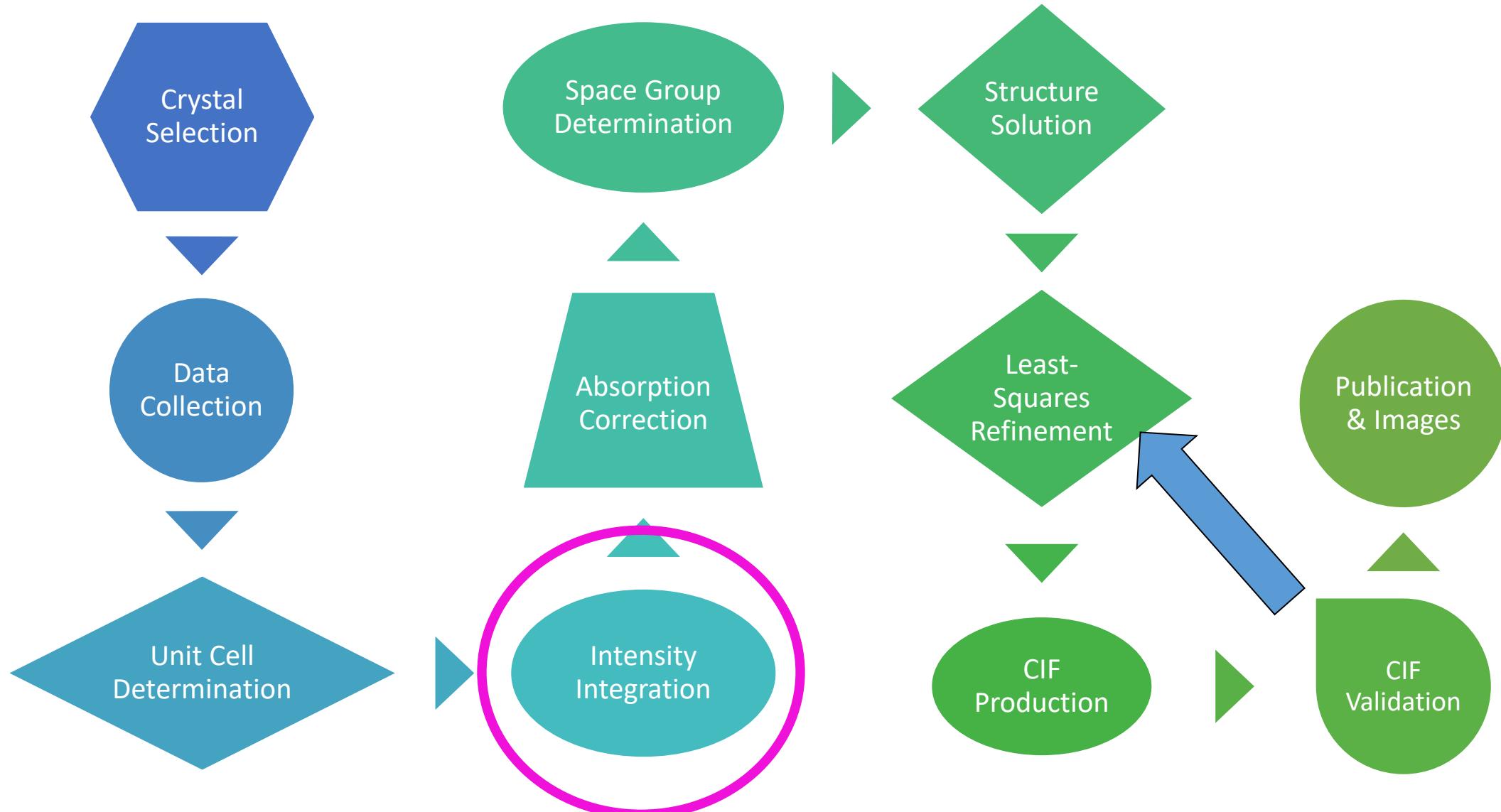
$$A_{hkl} = \frac{I_{hkl}}{I_0} = e^{-\mu t}$$

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

Data Collection Schematic



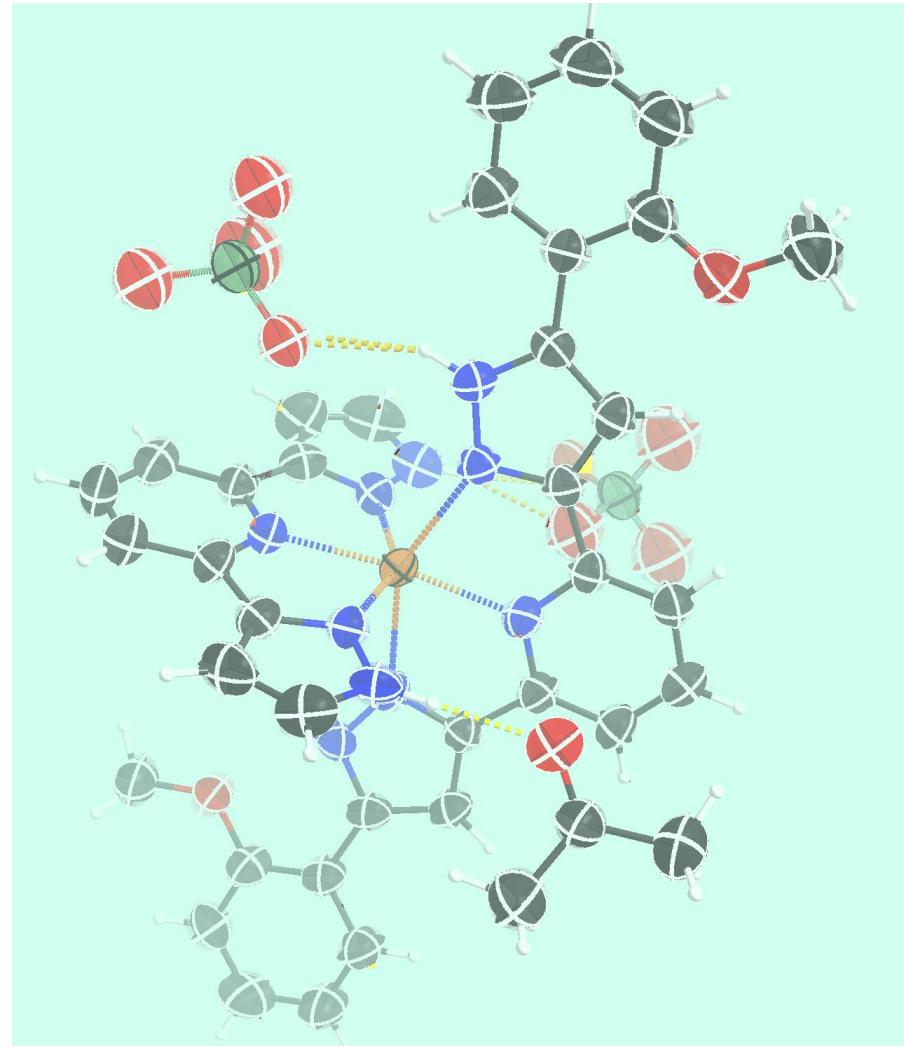
Crystal to Structure



From Reflections to Structure



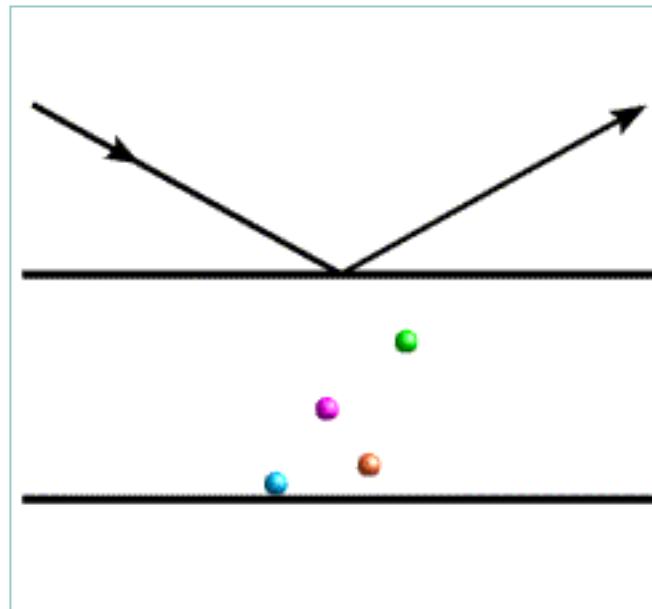
-5	10	-3	0.01	0.45
-6	10	-3	-0.28	0.49
-7	10	-3	-0.28	0.52
-8	10	-3	1.63	0.56
12	9	-3	1.15	0.68
-12	-9	3	0.64	0.66
11	9	-3	5.65	0.82
-11	-9	3	6.17	0.77
10	9	-3	-0.14	0.65
-10	-9	3	-0.17	0.48
9	9	-3	2.01	0.72
-9	-9	3	2.11	0.51
8	9	-3	4.10	0.72
8	9	-3	6.25	0.82
-8	-9	3	5.89	0.63
7	9	-3	9.05	0.95
-7	-9	3	9.79	0.79
6	9	-3	4.40	0.72
-6	-9	3	7.25	0.65
5	9	-3	8.03	0.84
-5	-9	3	7.17	0.73
4	9	-3	5.66	0.71
-4	-9	3	4.98	0.65
3	9	-3	1.28	0.51
-3	-9	3	1.40	0.46
2	9	-3	18.66	1.23
-2	-9	3	16.45	1.18
1	9	-3	8.06	0.84
-1	-9	3	7.75	0.75
0	9	-3	17.88	1.22



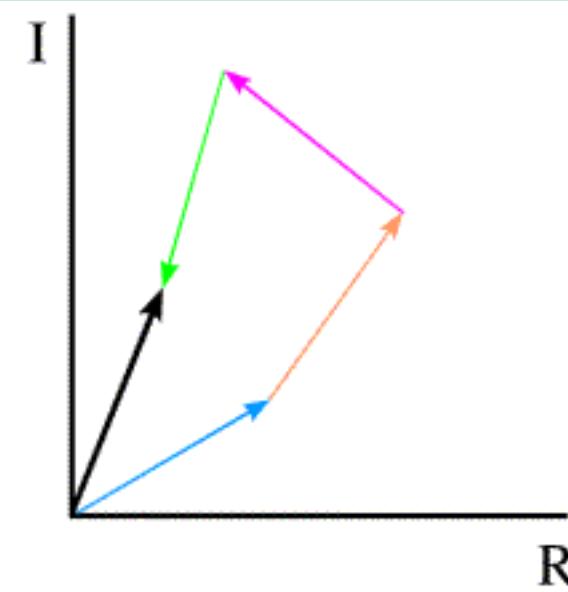
What does $F_{hkl} = \sum_j f_j e^{2\pi i(hx+ky+lz)} = |F_{hkl}|e^{i\varphi}$ mean?

- All atoms contribute to F_{hkl}
- 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



Randy Read

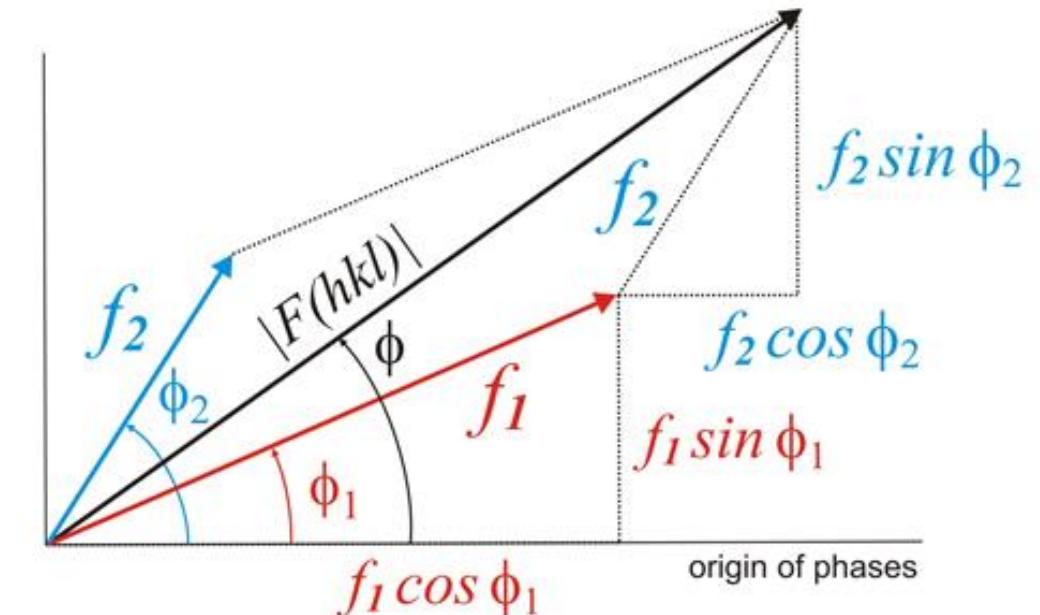


Atomic structure factors
add as **complex numbers**,
or **vectors**.

THE STRUCTURE FACTOR

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

$$F_{hkl} = |F_{hkl}| e^{i\varphi}$$



A(real)

B(imaginary)

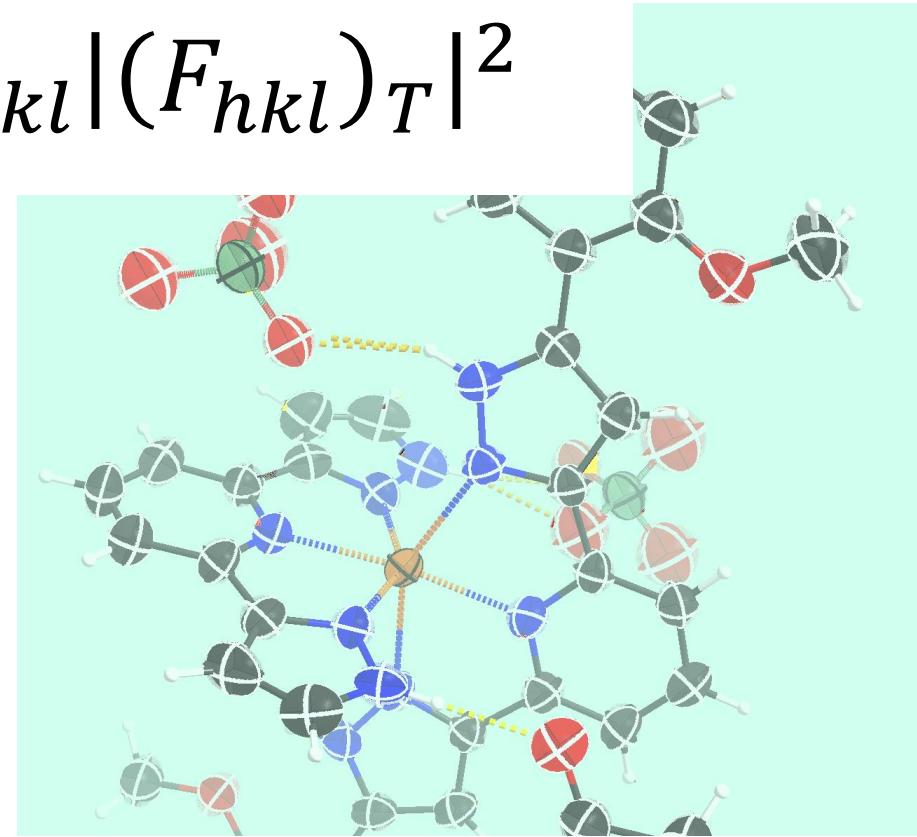
$$F_{hkl} = \sum_{j=1}^n f_j \cos [2\pi(hx_j + ky_j + lz_j)] + i \sum_{j=1}^n f_j \sin [2\pi(hx_j + ky_j + lz_j)]$$

Crystallography. Scattering and diffraction. The structure factor

FROM REFLECTIONS TO STRUCTURE

$$I_{hkl} = \frac{I_0}{\omega} VKL_{hkl} p_{hkl} A_{hkl} e_{hkl} |(F_{hkl})_T|^2$$

11	9	-3	5.65	0.82
-11	-9	3	6.17	0.77
10	9	-3	-0.14	0.65
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9	9	-3	2.01	0.72
-9	-9	3	2.11	0.51
8	9	-3	4.10	0.72
8	9	-3	6.25	0.82
-8	-9	3	5.89	0.63
7	9	-3	9.05	0.95
-7	-9	3	9.79	0.79
6	9	-3	4.40	0.72
-6	-9	3	7.25	0.65
5	9	-3	8.03	0.84
-5	-9	3	7.17	0.73
4	9	-3	5.66	0.71
-4	-9	3	4.98	0.65
3	9	-3	1.28	0.51
-3	-9	3	1.40	0.46
2	9	-3	18.66	1.23
-2	-9	3	16.45	1.18
1	9	-3	8.06	0.84
-1	-9	3	7.75	0.75
0	9	-3	17.88	1.22



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

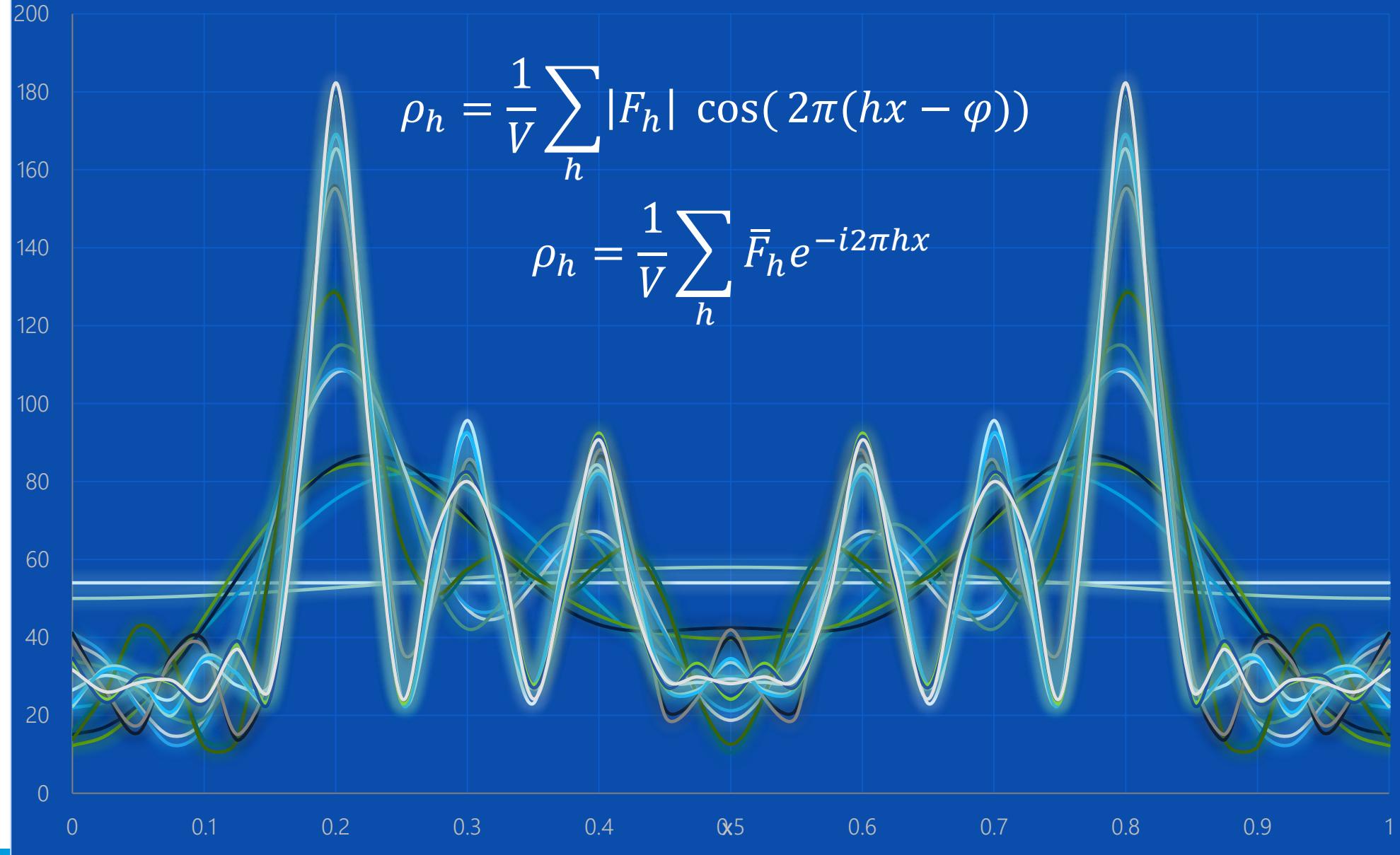
1D FOURIER EXAMPLE

A(real) B(imaginary)

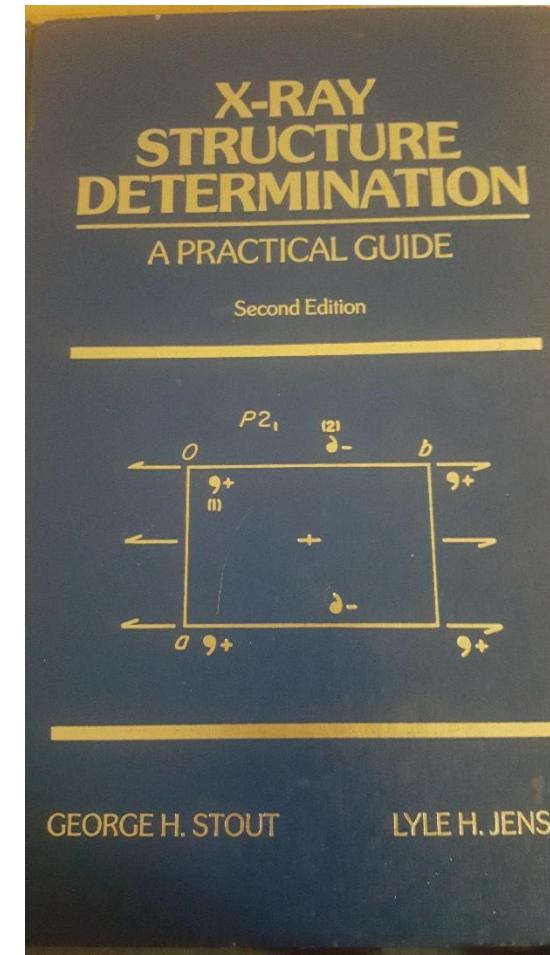
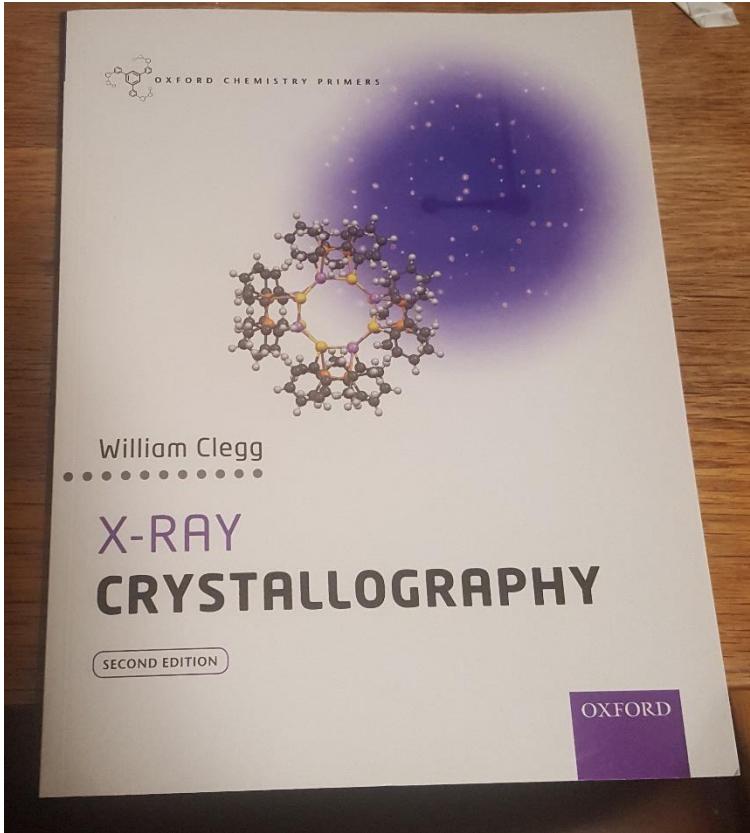
$$F(hkl) = \sum_{j=1}^n f_j \cos [2\pi(hx_j + ky_j + lz_j)] + i \sum_{j=1}^n f_j \sin [2\pi(hx_j + ky_j + lz_j)]$$

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

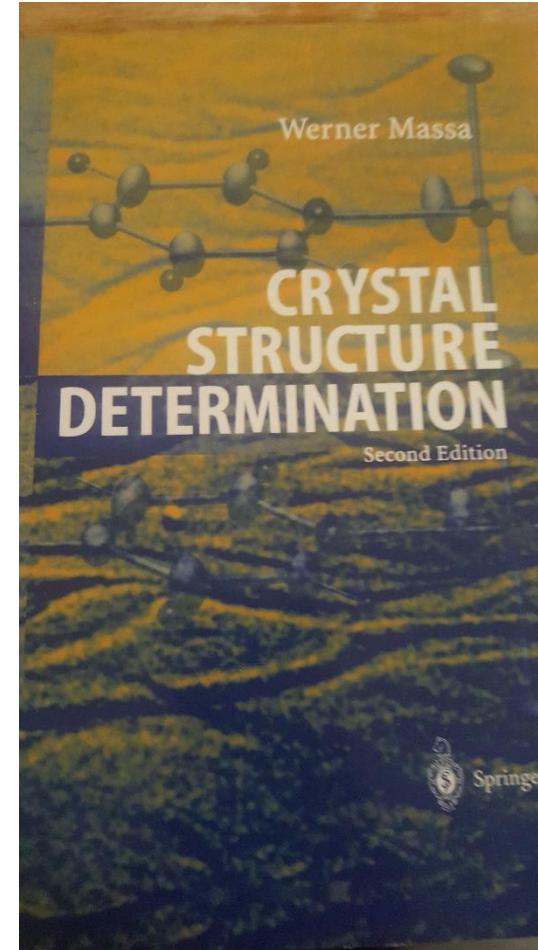
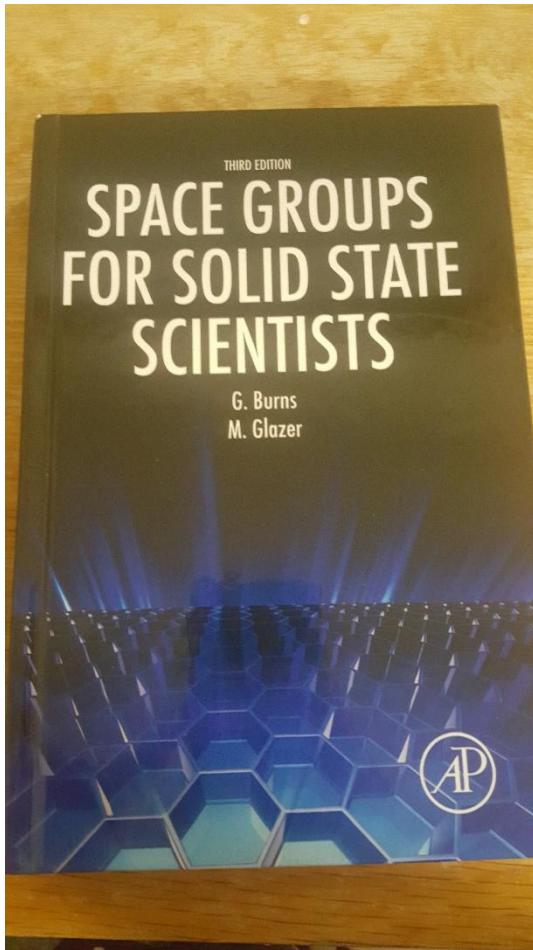
1-D Electron Density Map



FOR MORE INFORMATION



EVEN MORE INFORMATION



TEXTBOOKS AND RESOURCES USED

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>

[XRayView \(theraj.org\)](http://theraj.org)



THANK YOU



WHO WE ARE

A Brief History

Since its inception in 1951, Rigaku has been at the forefront of analytical and industrial instrumentation technology. Today, with hundreds of major innovations to their credit, the Rigaku group of companies are world leaders in the fields of general X-ray diffraction, thin film analysis, X-ray fluorescence spectrometry, small angle X-ray scattering, protein and small molecule X-ray crystallography, Raman spectroscopy, X-ray optics, semiconductor metrology, X-ray sources, computed tomography, nondestructive testing and thermal analysis.



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● Rigaku Offices and Subsidiaries

● Major Distributors