Diffraction basics

Electromagnetic radiation

Diffraction phenomena depend on the interaction of the electromagnetic radiation with electrons of atoms in the sample.

Electromagnetic radiation: dual nature!

Electromagnetic Wave

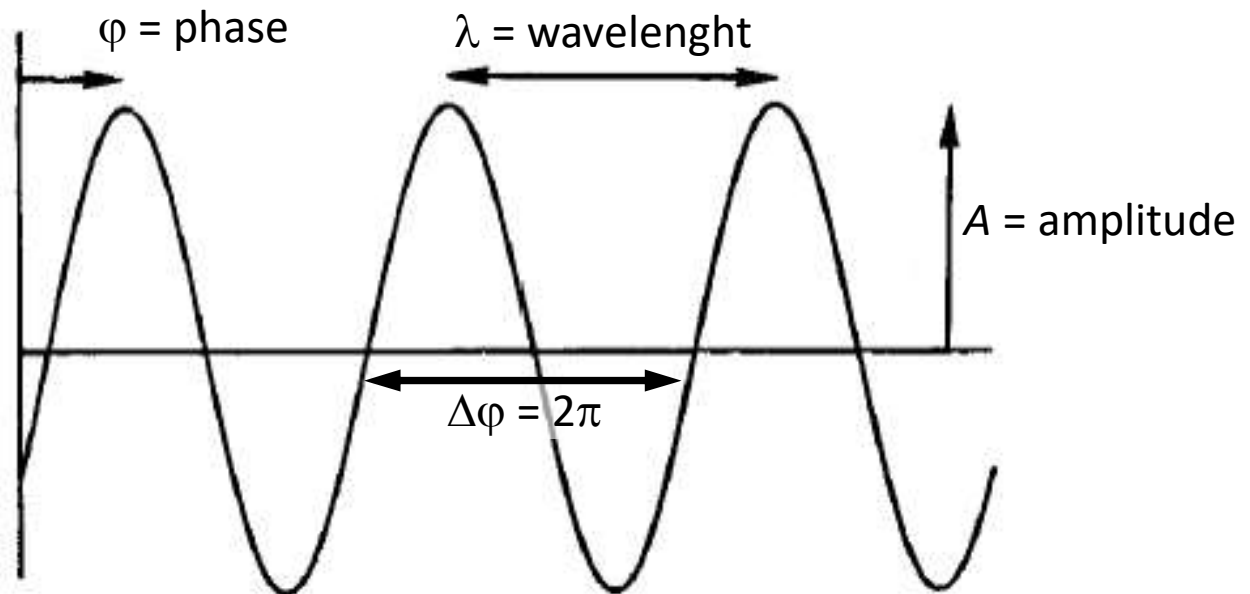— Electric field — Magnetic field
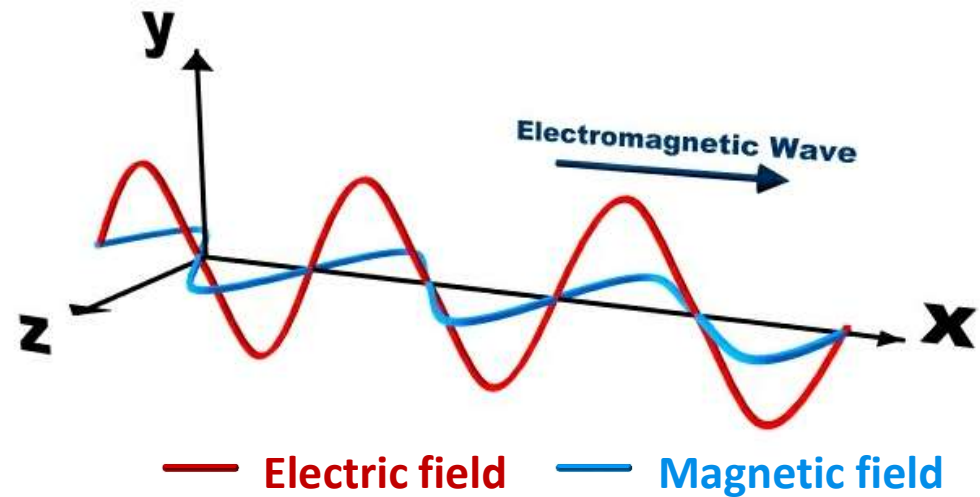
ν = frequency

c = speed of light

$$\nu \cdot \lambda = c$$

E = energy

$$E = h \cdot \nu$$

I = intensity

$$I \propto A^2$$

φ = phase λ = wavelenght

A = amplitude

$$\Delta\varphi = 2\pi$$

X-rays

Radiation Type	Radio	Microwave	Infrared	Visible	Ultraviolet	X-ray	Gamma ray
Wavelength (m)	10^3	10^{-2}	10^{-5}	0.5×10^{-6}	10^{-8}	10^{-10}	10^{-12}
Approximate Scale of Wavelength	Buildings	Butterflies	Needle Point	Protozoans	Molecules	Atoms	Atomic Nuclei
	Humans						

Frequency (Hz) 10^4 10^8 10^{12} 10^{15} 10^{16} 10^{18} 10^{20}
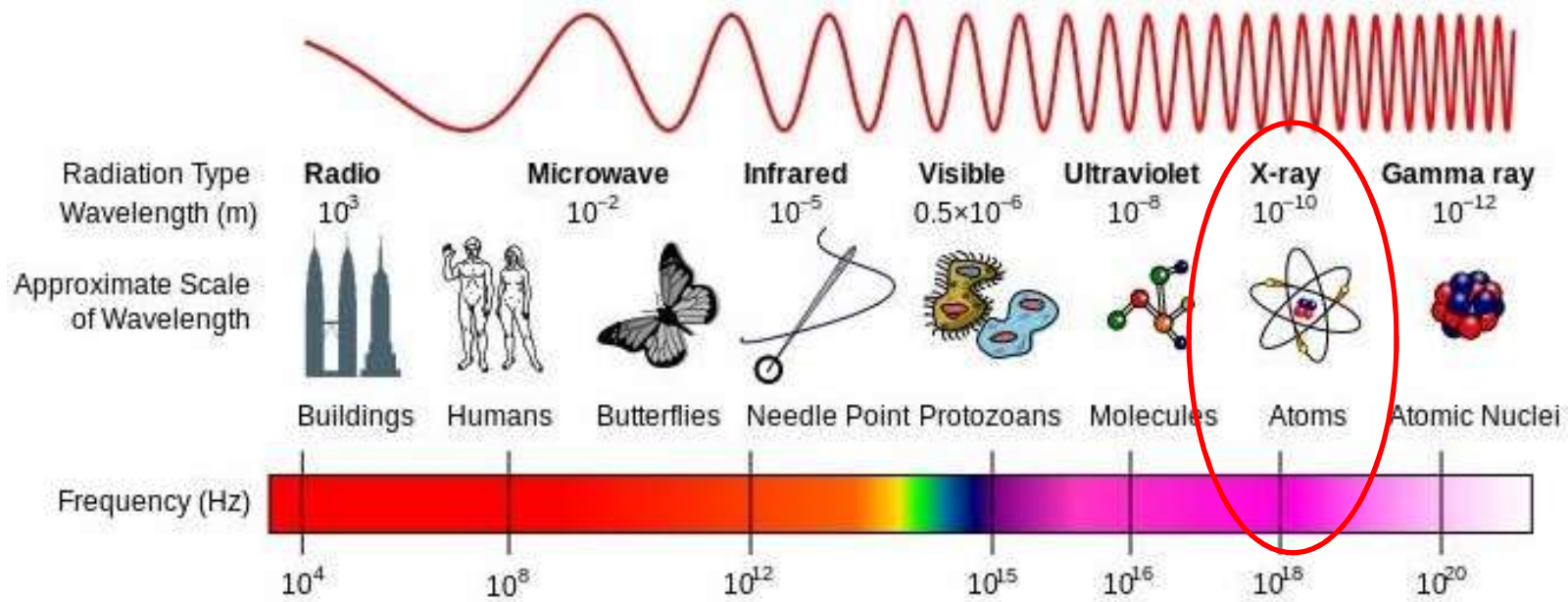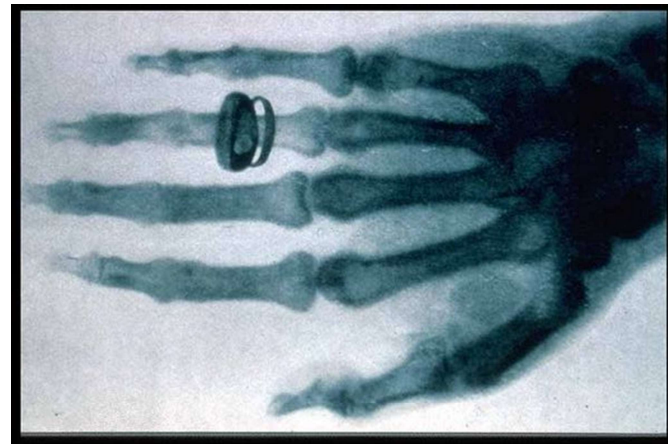
Discovered in 1895 by Röntgen (first Nobel laureate in Physics, in 1901).
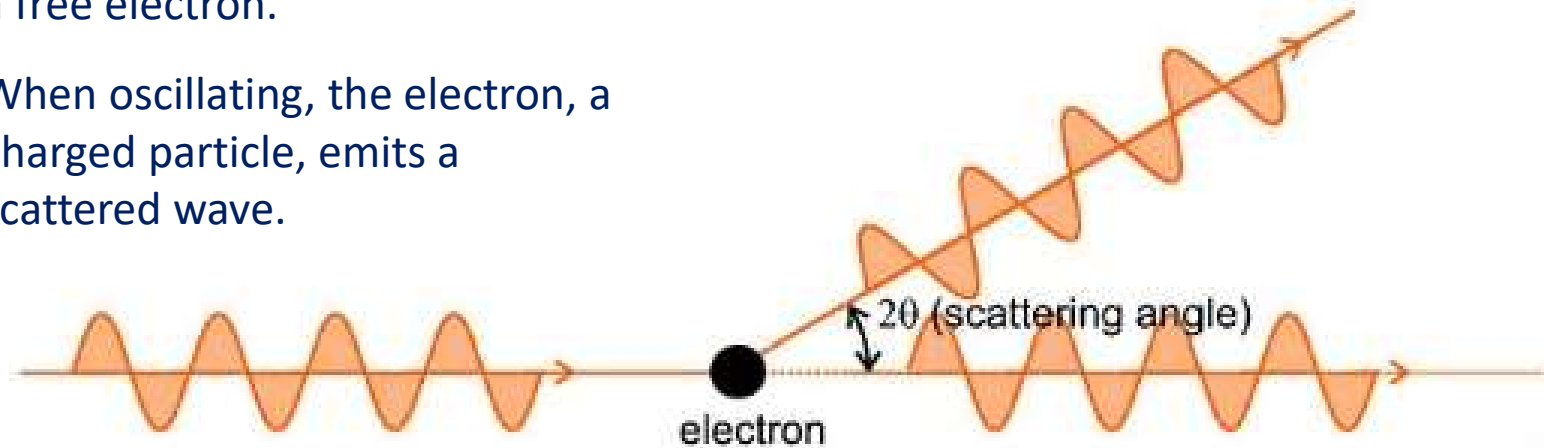
X-rays interact with matter according to atomic number of atoms, i.e. according to the number of electrons that each atom has.

Scattering of X-rays by a free electron

The electric (and magnetic) filed of the electromagnetic radiation causes oscillation in a free electron.

When oscillating, the electron, a charged particle, emits a scattered wave.

electron

99% of the radiation is transmitted, 1% interacts with the electron.

Inelastic scattering: change in frequency of the emitted radiation (not considered for diffraction, only contributes to background)

Elastic scattering: electron emits a wave of the same frequency, with an angle 2θ. No energy loss.

- For a free electron, the angle 2θ covers all the possible values, i.e. each direction in space as an equal probability.

- The **cross section** (integration in space of the scattering probability) is low.
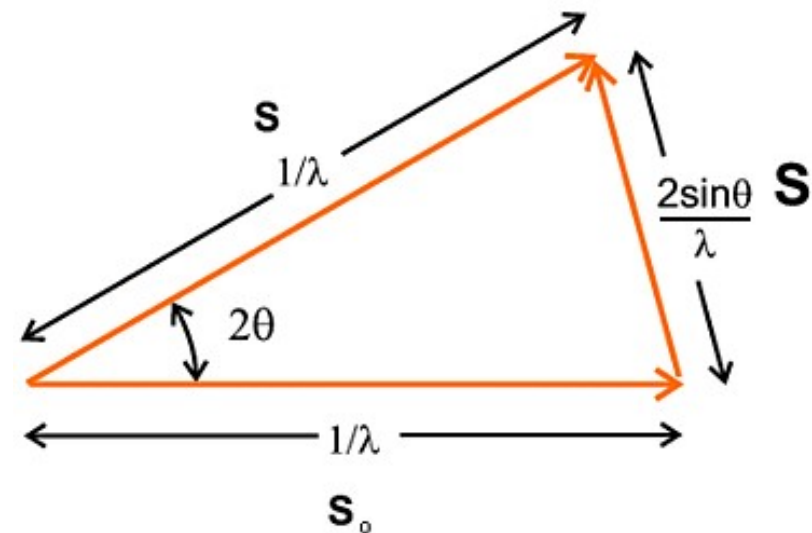
Diffraction geometry:

$$S = s - s_o$$
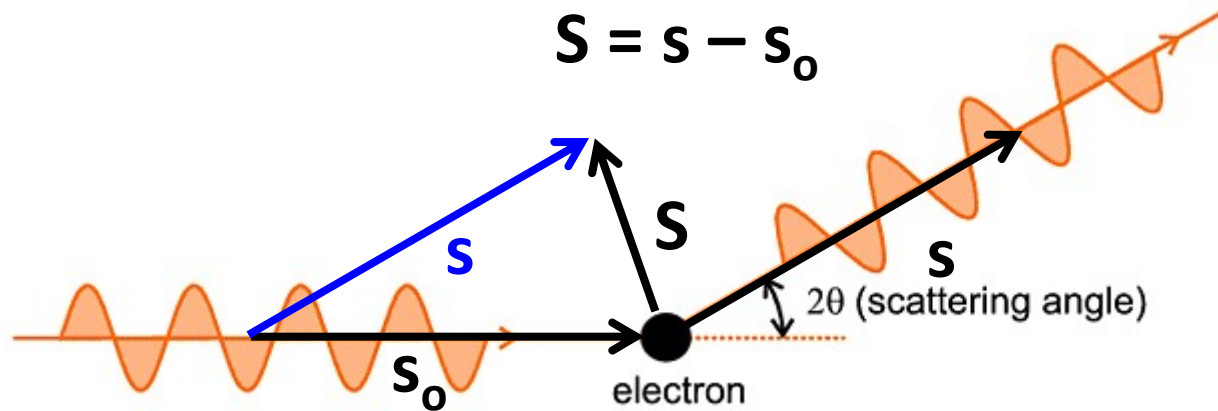
s_o Direction of incident wave

s Direction of diffracted wave

S Scattering vector

For vectors representing the incident and diffracted wave, the module is the inverse of the wavelength:

$$|s| = |s_o| = 1/\lambda$$

By application of trigonometric laws:

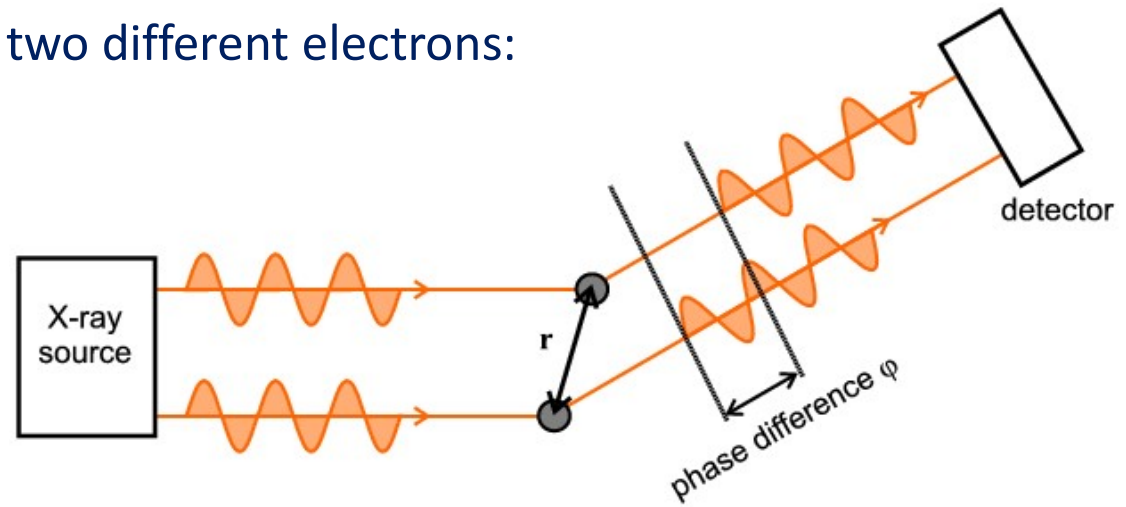$$|S| = \frac{2\sin\theta}{\lambda}$$
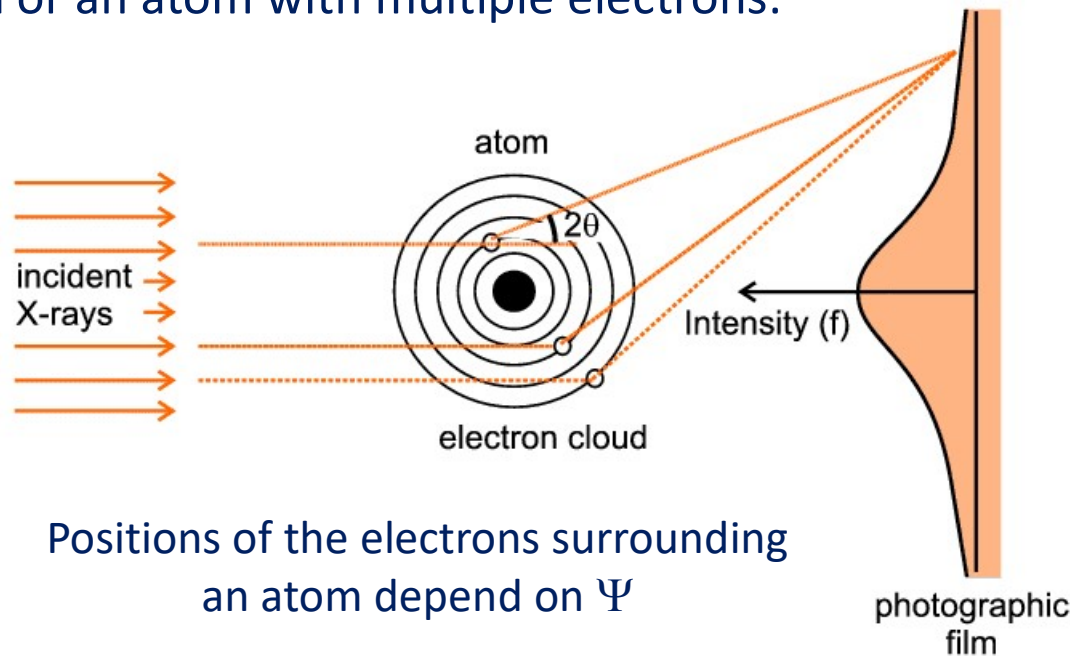
Scattering of X-rays from an atom

When a photon interacts with two different electrons:

Due to distance between electrons, change in phase between diffracted waves: interference!
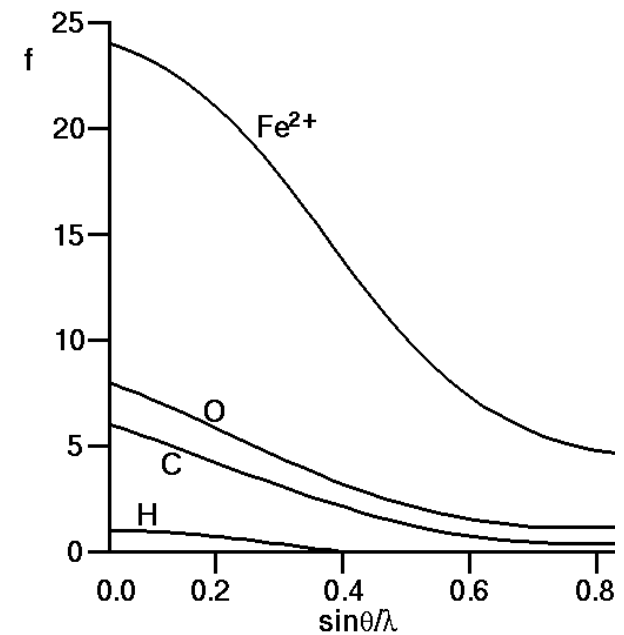
Interference is constructive at $2\theta = n(2\pi)$, but is reduced at different values of θ.

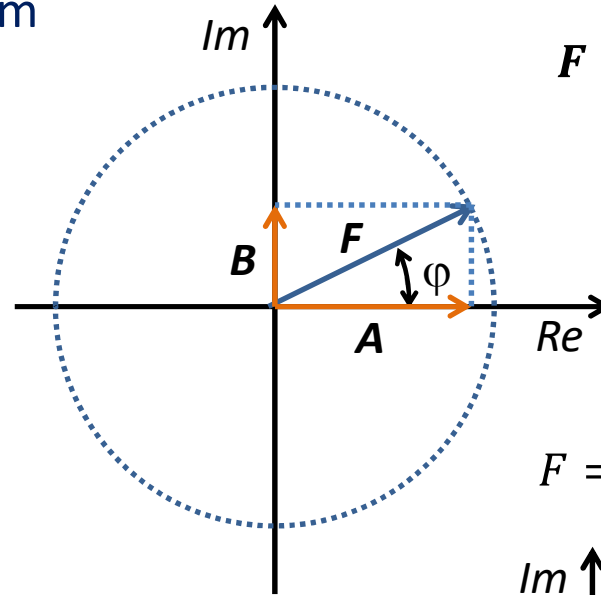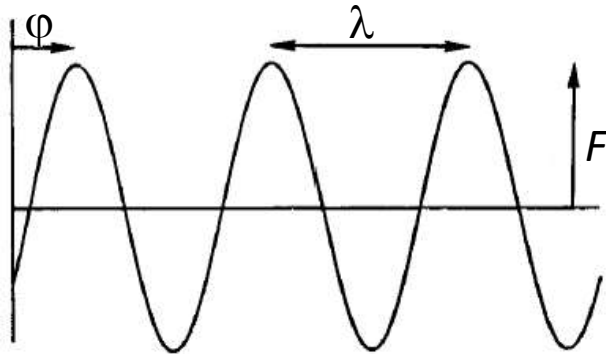For an atom with multiple electrons:

Positions of the electrons surrounding an atom depend on Ψ

Argand diagram

To describe interference, each wave can be represented as a complex number in the Argand diagram

$$F = |F|\cos\varphi + |F|\, i \sin\varphi$$

$$F = A + i\, B$$

$$A = |F|\cos\varphi$$

$$B = |F|\sin\varphi$$
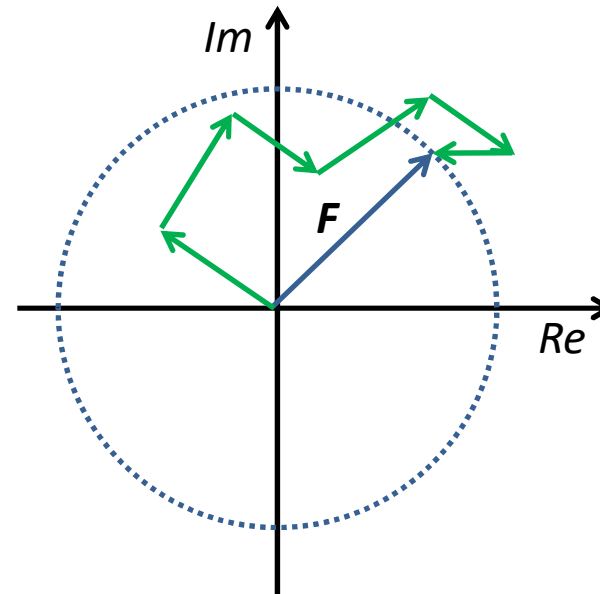
$$F = |F| = (A^2 + B^2)^{1/2}$$

Using Euler's expression:

$$e^{i\varphi} = \cos\varphi + i\sin\varphi$$

$$F = |F|(\cos\varphi + i\sin\varphi) \qquad F = F\, e^{i\varphi}$$
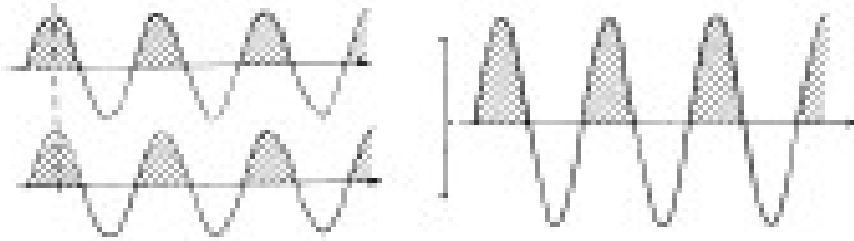
To describe the interference of multiple waves in an atom:

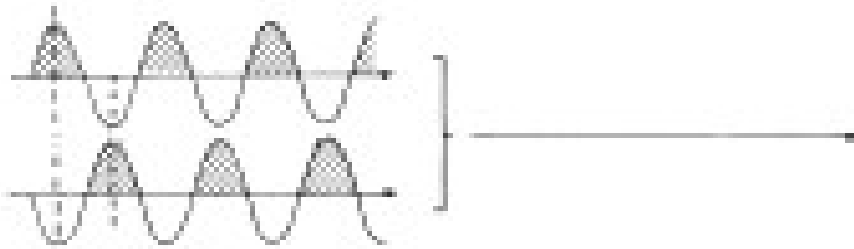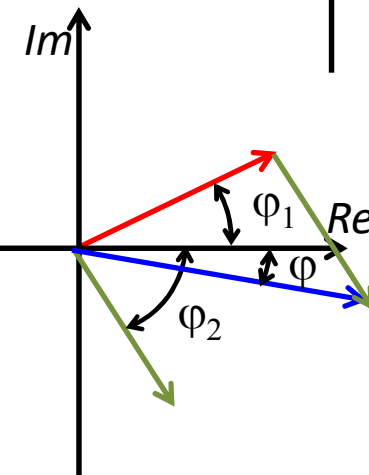$$F = \sum_{j} F_j\, e^{i\varphi_j}$$

Interference

Constructive interference

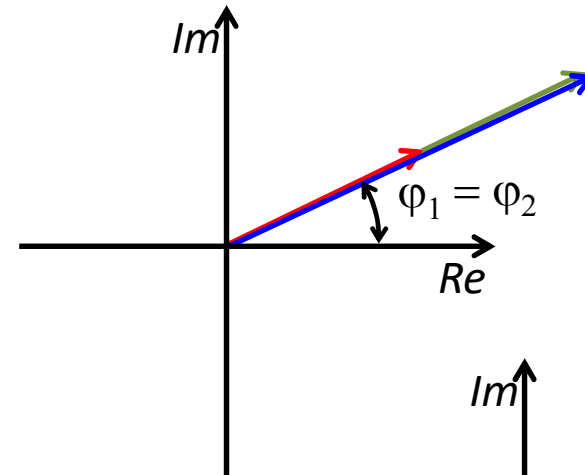$\varphi_1 = \varphi_2$

Destructive interference

$\varphi_2 = \varphi_1 + \pi$

φ_1

General interference

φ_1

φ

φ_2
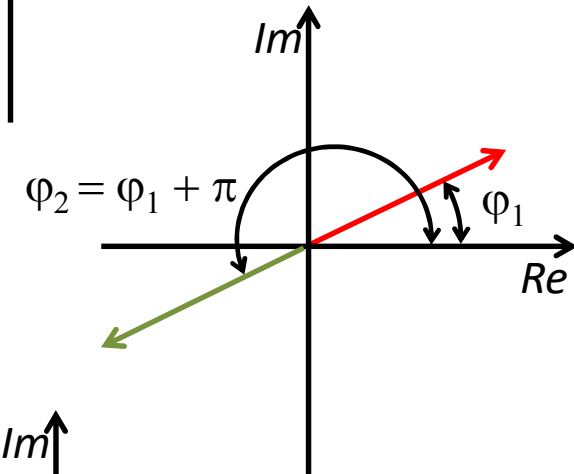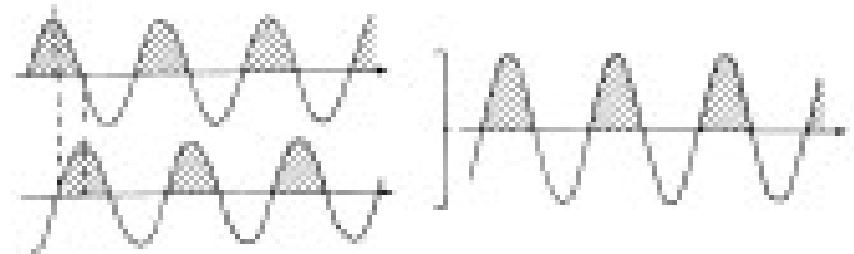
Atomic scattering factor

Contribution of elettrons to the scattered wave in a specific direction (2θ):

$$\Delta p = \Delta p_d - \Delta p_i$$

$$\Delta p = \lambda(\mathbf{s} - \mathbf{s_o}) \cdot \mathbf{r}$$

$$\Delta p = \lambda \, \mathbf{S} \cdot \mathbf{r}$$

$$\Delta\varphi = (2\pi/\lambda) \, \Delta p$$

$$\Delta\varphi = 2\pi \, \mathbf{S} \cdot \mathbf{r}$$

$$\Delta p_i = \lambda(\mathbf{s_o} \cdot \mathbf{r})$$

$$\Delta p_d = \lambda(\mathbf{s} \cdot \mathbf{r})$$
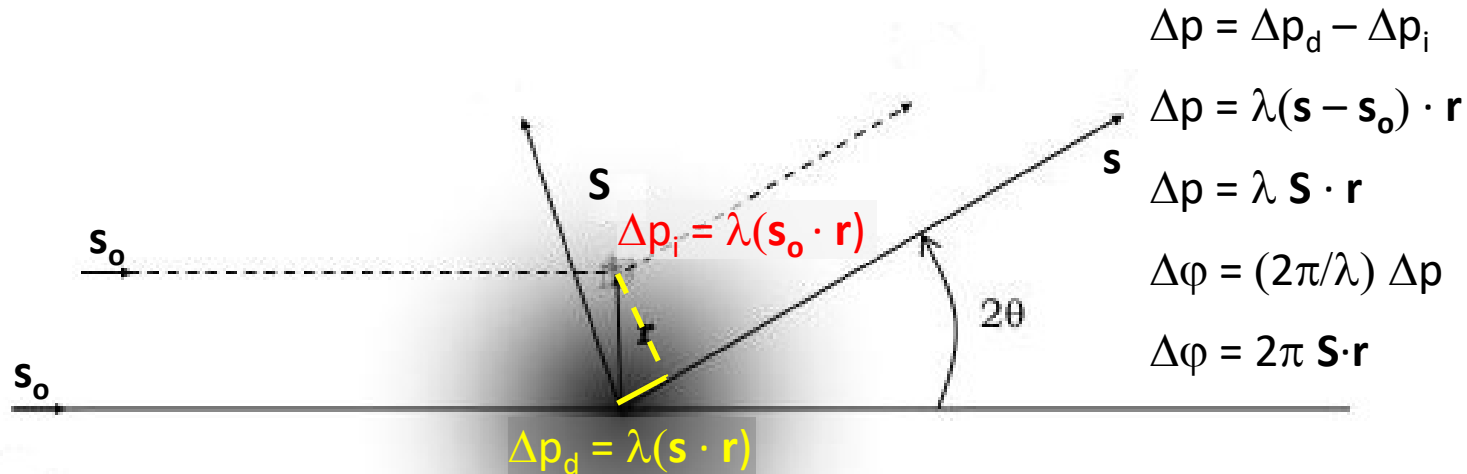
The whole scattering from the atom can be calculated as the sum of the contibution of each electron. Or, more precisely, by considering its electron density and integrating over the atom volume:

$$f_{2\theta} = f_{\mathbf{S}} = \int_{\mathbf{r}}^{V} \rho(\mathbf{r}) \exp(2\pi i \, \mathbf{S} \cdot \mathbf{r}) \, d\mathbf{r}$$

In mathematical terms, this is the Fourier transform of the electron density:

$$f_{\mathbf{S}} = FT[\rho(\mathbf{r})]$$

Atomic displacement: B-factor

How to account for thermal movement of atoms? And additional static or dynamic displacement effects?

Consider an isotropic atomic displacement. It can be quantified by the isotropic displacement parameter, or **B-factor** of the atom, connected with the mean square isotropic displacement of the atomic coordinates from their equilibrium $\langle u_{iso}^2 \rangle$:

$$B_{iso} = 8\pi^2 \langle u_{iso}^2 \rangle$$

The atomic displacement induces a further attenuation on the scattering factor of the atom, that can be calculated as:

$$f_S^B = f_S^0 \exp(-B_{iso}(\sin\theta/\lambda)^2)$$

The B-factor is correlated with the occupancy factor *n* of an atom in a specific position and, therefore, the effects of thermal movement and partial occupancy cannot be distinguished.
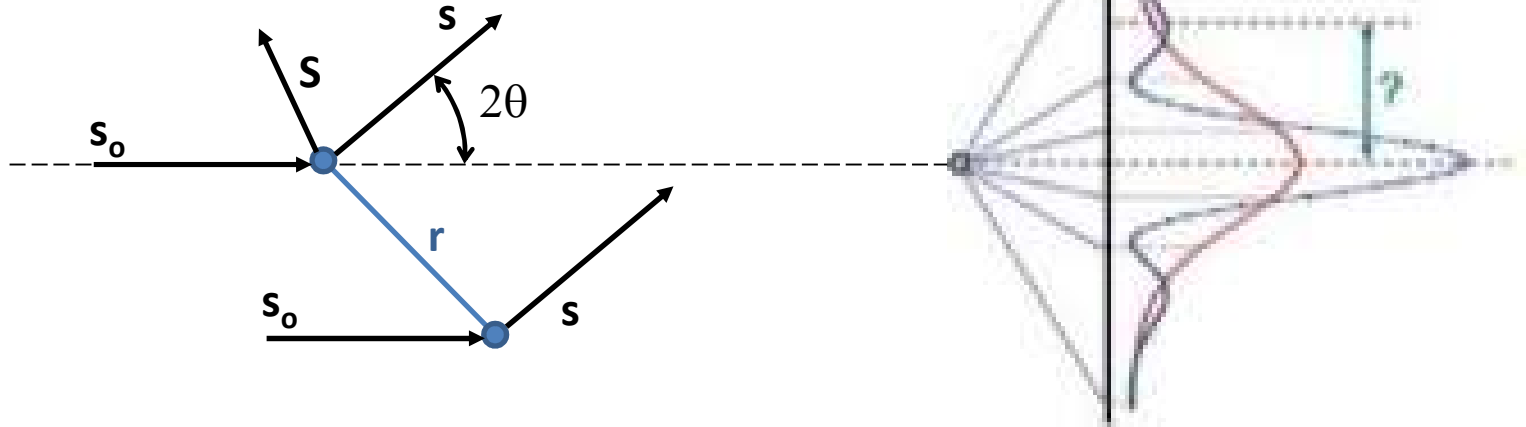
Anisotropy: B becomes a tensor.
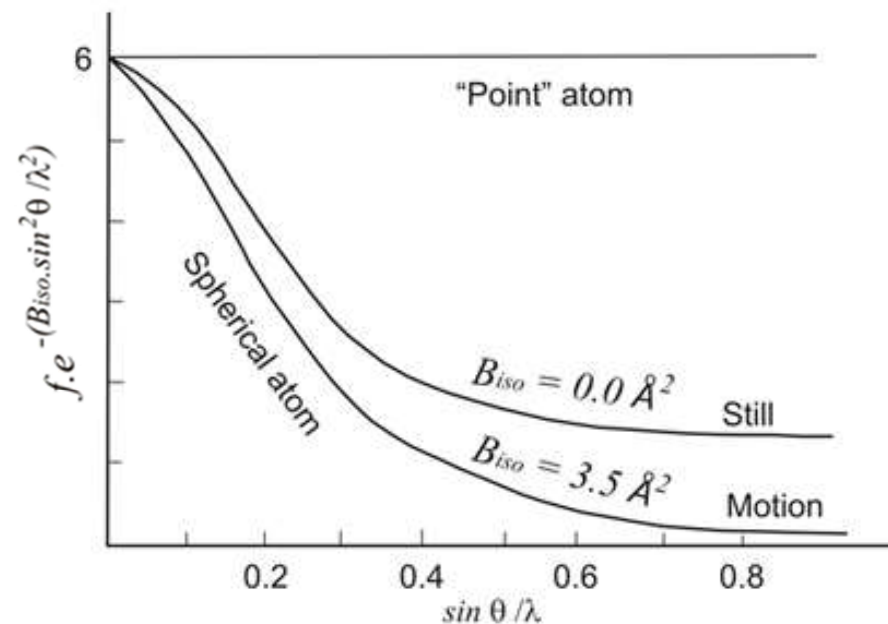
Scattering from adjacent atoms

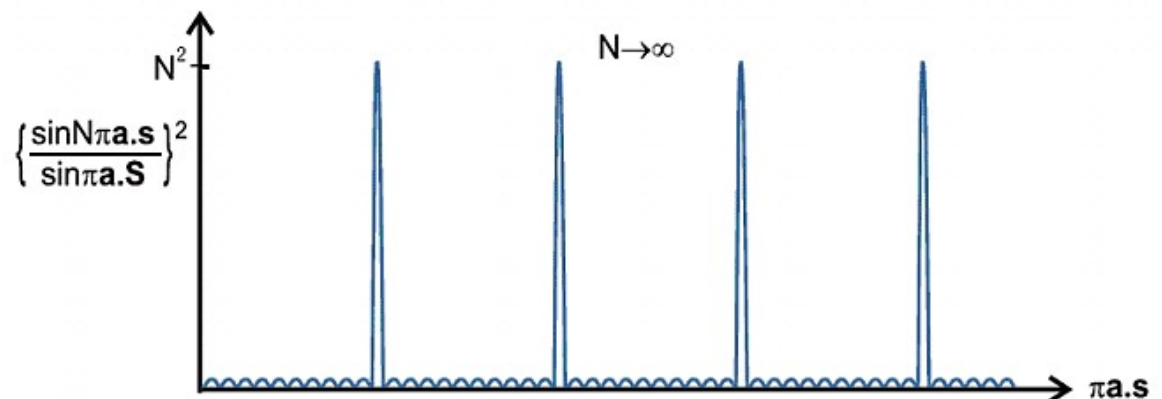As in the case of two electrons:

Phase difference: $\Delta\varphi = 2\pi\, \mathbf{S}\cdot\mathbf{r}$
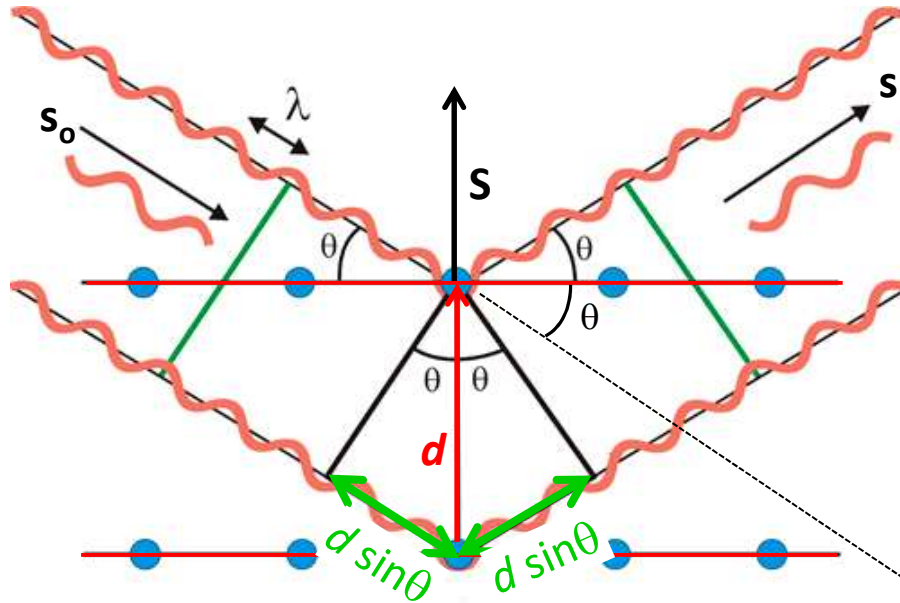

The maximum scattering intensity is obtained when: $\Delta\varphi = 2\pi\, \mathbf{S}\cdot\mathbf{r} = 2\pi n$

or $\mathbf{S}\cdot\mathbf{r} = n$ (Laue condition)

In presence of an infinite lattice of equally spaced atoms (crystal lattice!), the peaks of maximum scattering intensity become sharper

Bragg's law

Interpretation of the diffraction condition as a reflection on the lattice planes:

Considering the diffraction on lattice planes, the path difference is
$$\Delta p = 2d \sin \theta$$
Scattered intensity is measurable only when
$$\Delta p = n \cdot \lambda$$

**Bragg's law:** $2d \sin \theta = n \cdot \lambda$

According to the construction of the reciprocal lattice:
$$\frac{1}{d_{hkl}} = d^*_{hkl} = \frac{2 \sin \theta}{n\lambda}$$

The vector d^*_{hkl}, defined in the reciprocal space is prependicular to the family of planes and therefore collinear with the diffraction vector **S**.

d^*_{hkl} depends on the unit cell parameters, a,b,c and α,β,γ.

Diffraction from a molecule

Considering a molecule of N atoms, each diffracted beam in the direction perpendicular to the family of planes (hkl) can be expressed as interference of all atomic scattered waves in the same direction, with the corresponding module and phase.
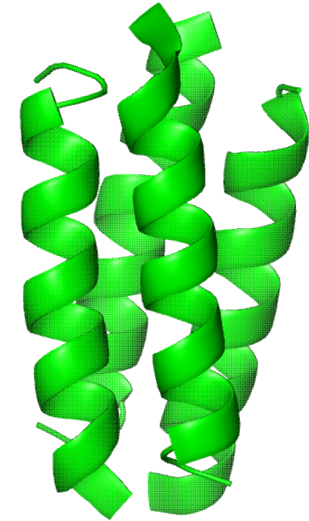
Considering the representation in the Argan diagram:

$$F_S = \sum_j^N F_j e^{i\varphi_j} = \sum_j^N f_{S,j}^B \exp(2\pi i S \cdot r_j)$$

The vector r_j represents the position of an atom in the real lattice and can be expressed as: $r_j = x_j a + y_j b + z_j c$

The vector S, in diffraction conditions, coincides with the vector d_{hkl}^*, perpendicular to the family of planes (hkl) and can be expressed as: $S = h a^* + k b^* + l c^*$

The scalar product $S \cdot r_j$ becomes:

$$S \cdot r_j = h x_j a^* a + h y_j a^* b + h z_j a^* c + k x_j b^* a + k y_j b^* b + k z_j b^* c$$
$$+ l x_j c^* a + l y_j c^* b + l z_j c^* c$$

Considering the relations defining the reciprocal space:

$$S \cdot r_j = h x_j + k y_j + l z_j$$

$$a^* a = 1, \quad a^* \perp b, \ a^* \perp c$$
$$b^* b = 1, \quad b^* \perp a, \ b^* \perp c$$
$$c^* c = 1, \quad c^* \perp a, \ c^* \perp b$$

$$F_h = \sum_j^N f_{h,j}^B \exp(2\pi i h \cdot x_j)$$

Considering the B-factor expression: $\quad f_{\boldsymbol{h}}^{B} = f_{\boldsymbol{h}}^{0}\exp(-B_{iso}(\sin\theta/\lambda)^2)$

$$F_{\boldsymbol{h}} = \sum_{j}^{N} f_{\boldsymbol{h},j}^{0}\exp\!\left(-B_j(\sin\theta/\lambda)^2\right)\exp\!\left(2\pi i\boldsymbol{h}\cdot\boldsymbol{x}_j\right)$$

Considering occupancy factor of each atom, n_j:

$$F_{\boldsymbol{h}} = \sum_{j}^{N} n_j f_{\boldsymbol{h},j}^{0}\exp\!\left(-B_j(\sin\theta/\lambda)^2\right)\exp\!\left(2\pi i\boldsymbol{h}\cdot\boldsymbol{x}_j\right)$$

In the Argan diagram:

$$\boldsymbol{F} = |\boldsymbol{F}|\cos\varphi + |\boldsymbol{F}|\,i\,\sin\varphi \qquad\qquad \boldsymbol{F} = \boldsymbol{A} + i\,\boldsymbol{B}$$

$$F = |\boldsymbol{F}| = (A^2 + B^2)^{1/2}$$

$$\varphi_j = 2\pi\boldsymbol{h}\boldsymbol{x}_j = \tan^{-1}(B_{\boldsymbol{h}}/A_{\boldsymbol{h}})$$
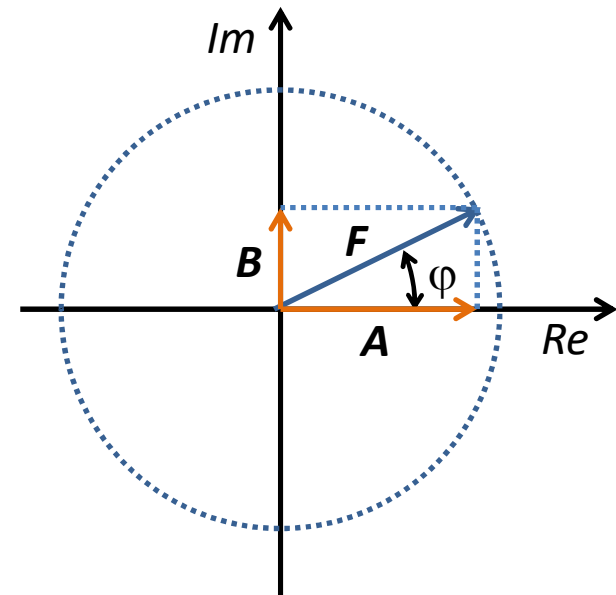
Ewald sphere

Useful construction of a sphere with radius $1/\lambda$

It respresents the diffraction conditions: a point P*(hkl) of the reciprocal space is in diffraction conditions when its vector in the reciprocal space coincides with **S**, the diffraction vector.
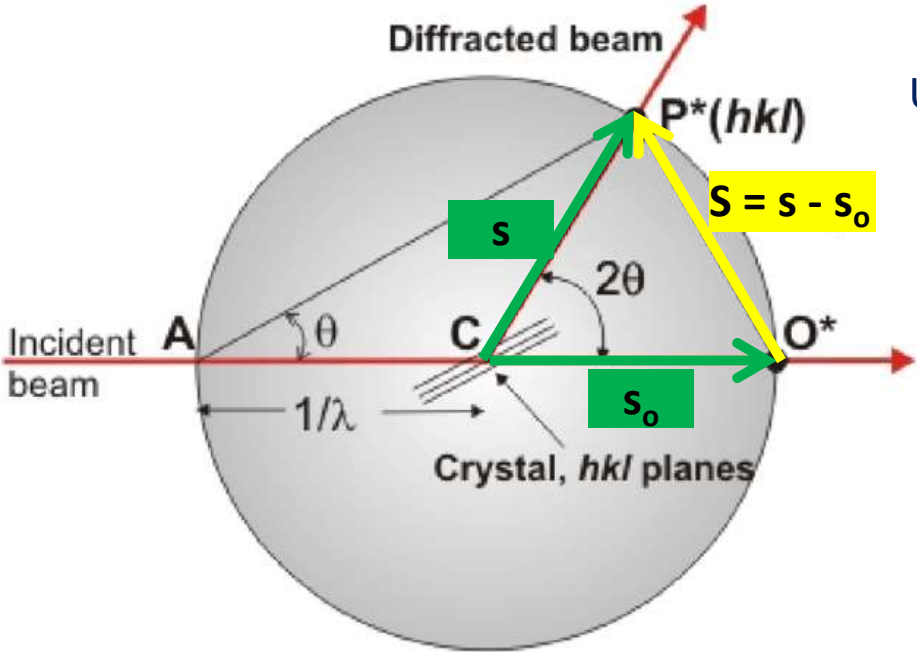
In 2D:

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

Reciprocal lattice

In 3D:
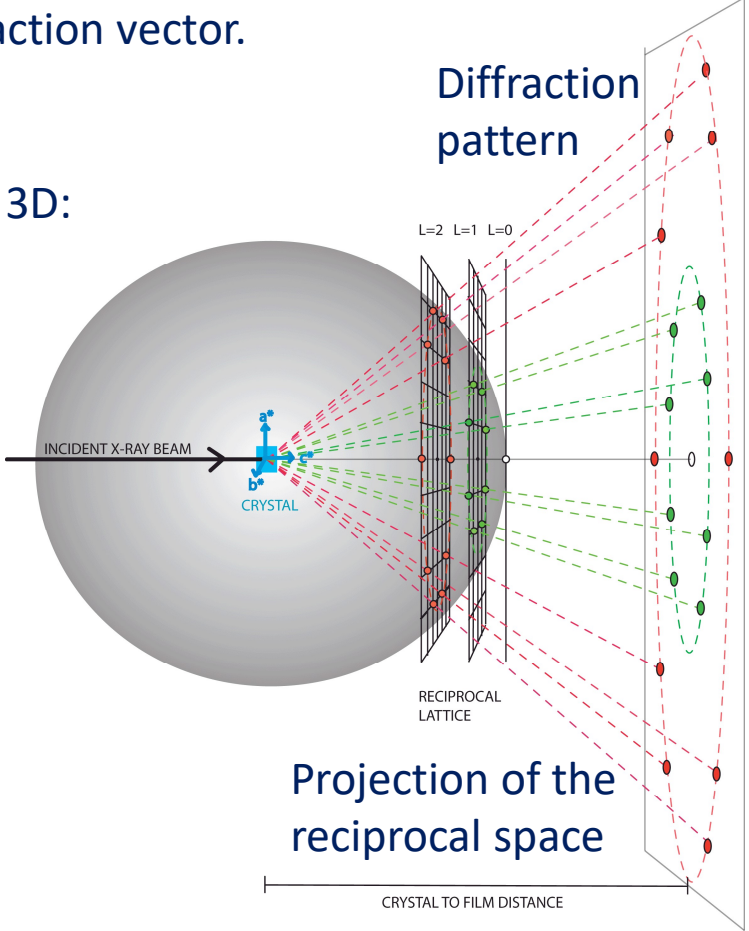
Diffraction pattern

Projection of the reciprocal space

Diffraction experiment

X-Ray source

X-Ray beam
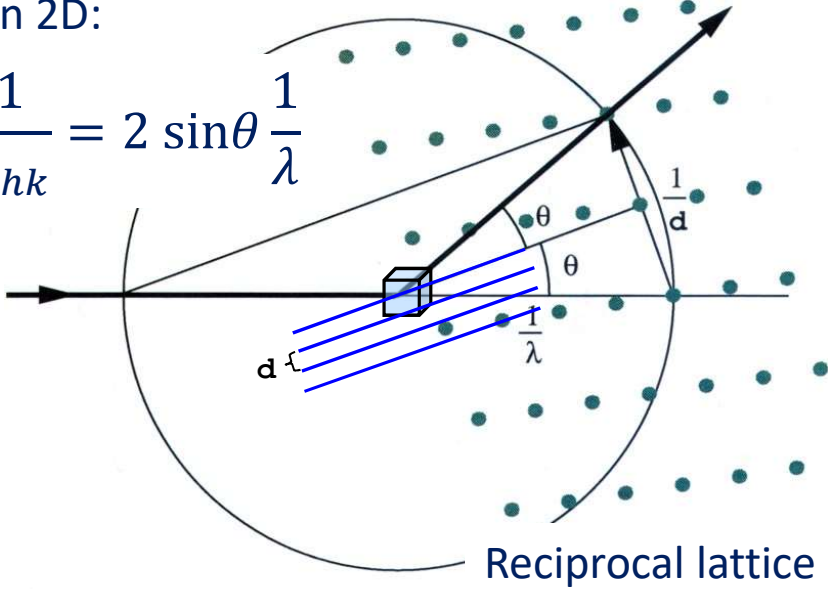
Crystal

Detector

Goniometer

Diffraction pattern

q_z

q_y

direct

Ewald sphere

detector
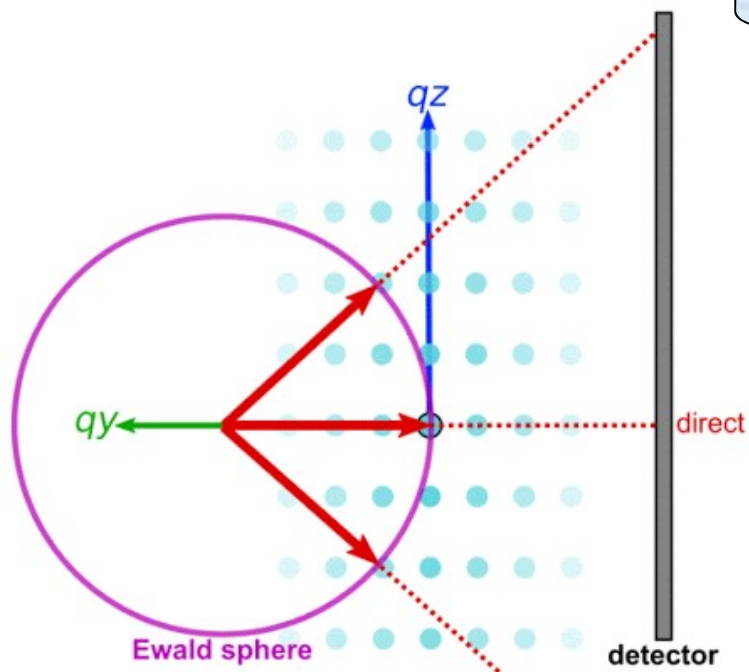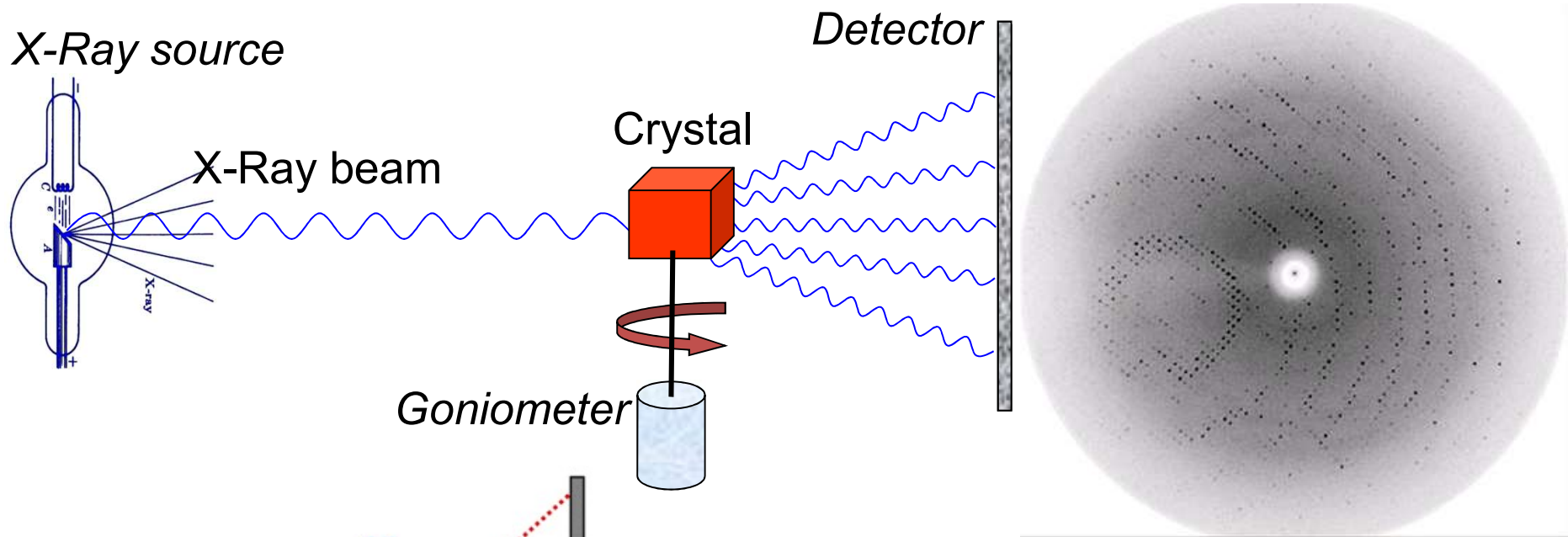
Rotation of the crystal allows to bring in reflection conditions different nodes of the reciprocal lattice.

In an ideal diffraction experiment, the largest possible portion of the reciprocal space should be measured.

Diffraction experiment

Diffraction data are collected while the crystal rotates, each diffracted beam obtained from a node of the reciprocal lattice.

The number of reflections that can be collected depends on:

➢ Wavelenght: with larger wavelenght or smaller wavelenght?

   Smaller wavelenght allows a larger sphere

➢ Detector dimension: larger detector or smaller detector?

   Larger detector allows collection of

   reflections at high θ

➢ Crystal-to-detector distance: closer?

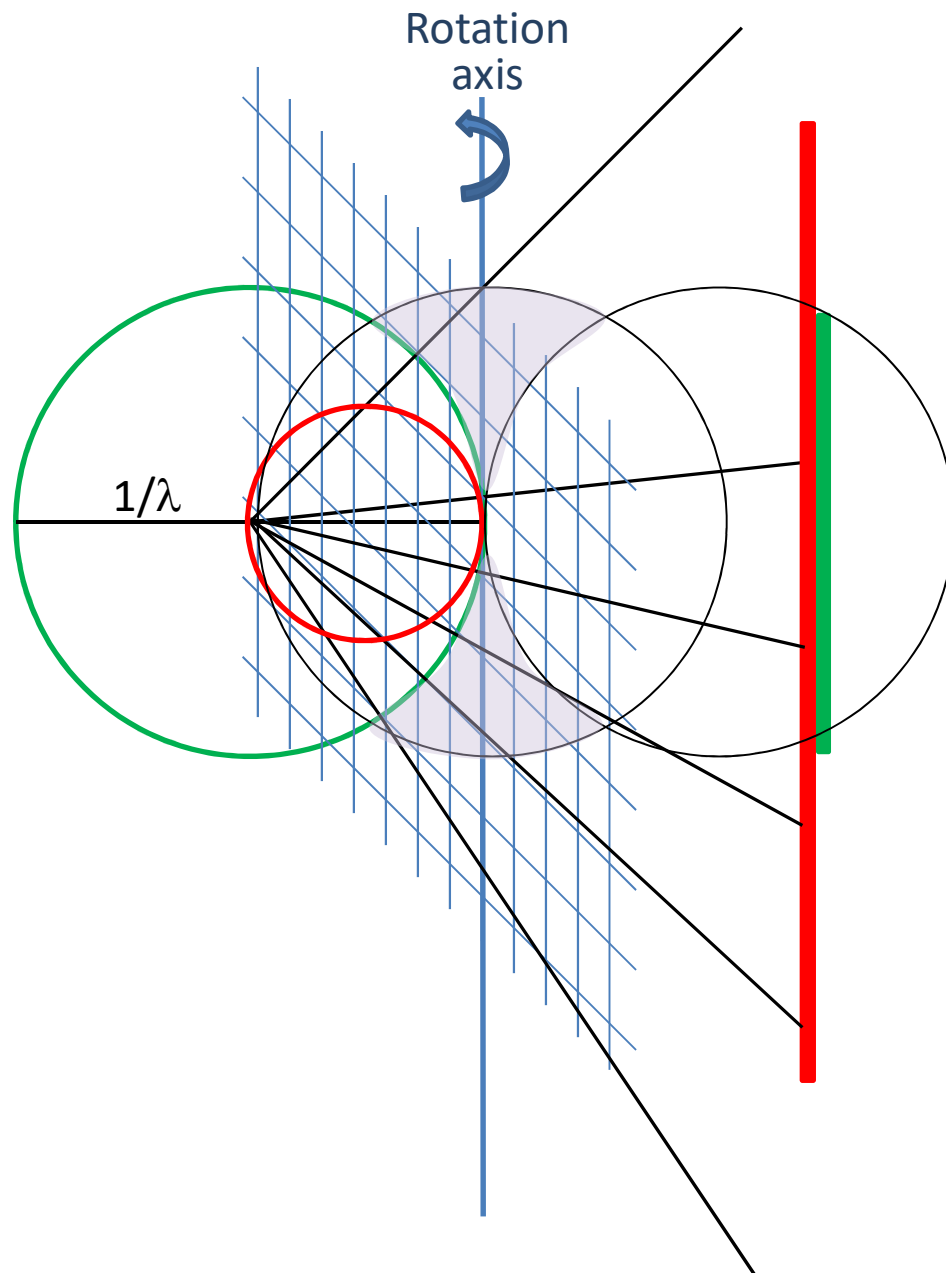➢ Diffraction limit of the crystal (depends on crystal order → B-factor attenuation)

➢ Radiation damage

A portion of the reciprocal space cannot be sampled with the rotation of the crystal around a single axis (some goniometers have a more complex geometry...)

Lorentz-polarization corrections
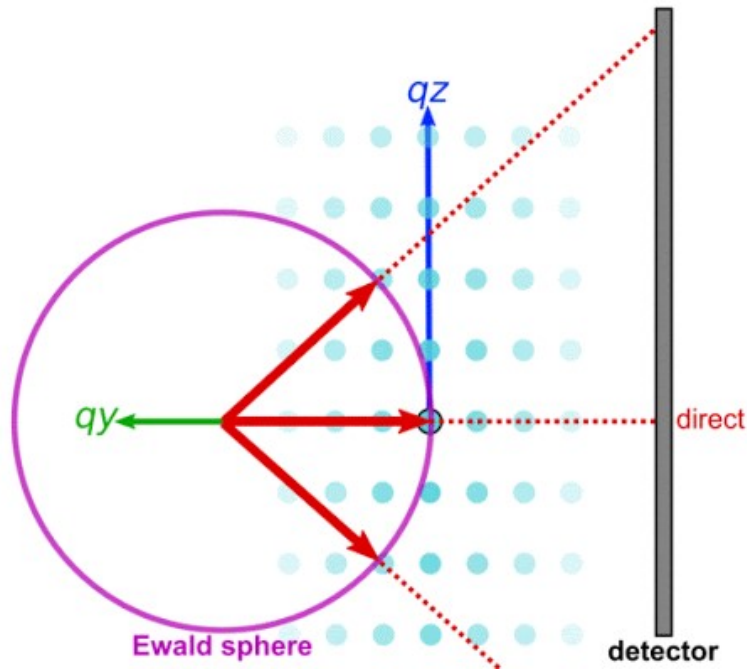
Nodes of the reciprocal lattice cross the Ewald sphere for different intervals: nodes close to the rotation axis take longer, nodes far from the rotation axis are faster.

Lorentz factor = correction of the intensity of the measured beam required to take into account the time each node takes to transit through the Ewald sphere.

$$L_h = 1/h \cdot (e_R \times s_o)$$

(e_R direction of the rotation axis)

In addition, in case of unpolarized X-ray source, a further correction is required to consider the polarization, **polarization factor**:

$$P_\theta = (1 + \cos^2 2\theta)/2$$

Lorentz-polarization factors are usually applied during data analysis by software.

Diffraction data and Friedel pairs

Intensity of a beam diffracted from a specific family of planes h (hkl):

$$I_h \propto F_h^* \cdot F_h = |F_h|(\cos\varphi_h - i\sin\varphi_h) \cdot |F_h|(\cos\varphi_h + i\sin\varphi_h)$$

$$F_h^2 = (A - iB) \cdot (A + iB)$$

$$A = |F|\cos\varphi \quad \text{and} \quad B = |F|\sin\varphi$$

$$I_h \propto A^2 + B^2$$

Conjugate of F_h: $F_h^* = |F_h|(\cos\varphi_h - i\sin\varphi_h)$

$$F_h^* = |F_h|(\cos(-\varphi_h) + i\sin(-\varphi_h))$$

Considering that $\quad \varphi_h = 2\pi h \cdot x \quad \Rightarrow \quad \varphi_{\bar{h}} = -\varphi_h$

$$F_{\bar{h}} = |F_{\bar{h}}|(\cos(-\varphi_h) + i\sin(-\varphi_h)) = F_h^*$$

Intensity of a beam diffracted from a specific family of planes $\bar{h}$ ($\bar{h}\bar{k}\bar{l}$):

$$I_{\bar{h}} \propto F_{\bar{h}}^* \cdot F_{\bar{h}} = (A + iB) \cdot (A - iB) = A^2 + B^2$$
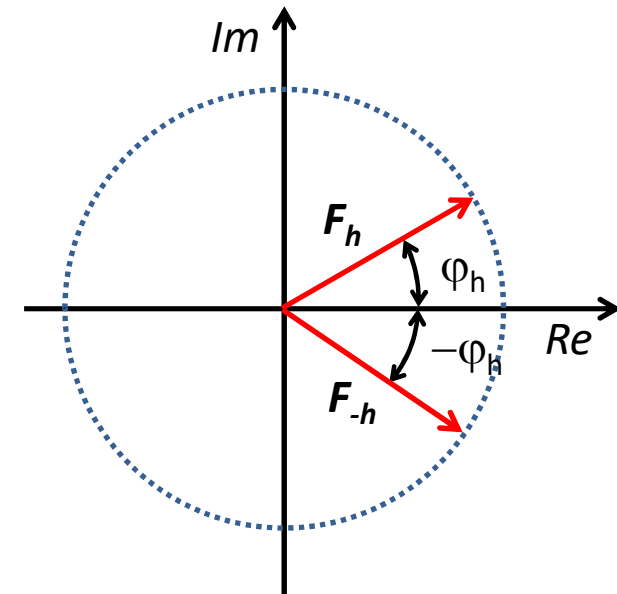
$I_h = I_{\bar{h}}$ **Friedel pairs = reflections from families of planes in opposite directions**

Symmetry in the reciprocal space

From the definition of the reciprocal lattice, we know that the reciprocal space is **centrosymmetric**, even when the molecule in the real space is not (e.g. a protein).

$\Rightarrow$ we only need to collect *half* of the reciprocal space.

What about the symmetry elements of the real space?

Each symmetry element of the real space corresponds to a symmetry element in the reciprocal space.

For example:

4-fold axis along z

$$x' = Sx$$

$$S = \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$\Rightarrow$

$$h' = hS$$

(hkl) and $(k\bar{h}l)$ are equivalent in reciprocal space

(xyz) and $(y\bar{x}z)$ are equivalent in real space

An asymmetric unit can be defined also in the reciprocal space. Its dimension and symmetry depend on the symmetry of the real space.

Asymmetric unit of the reciprocal space

Due to the symmetry of the reciprocal lattice, only part of the reciprocal lattice needs to be determined.

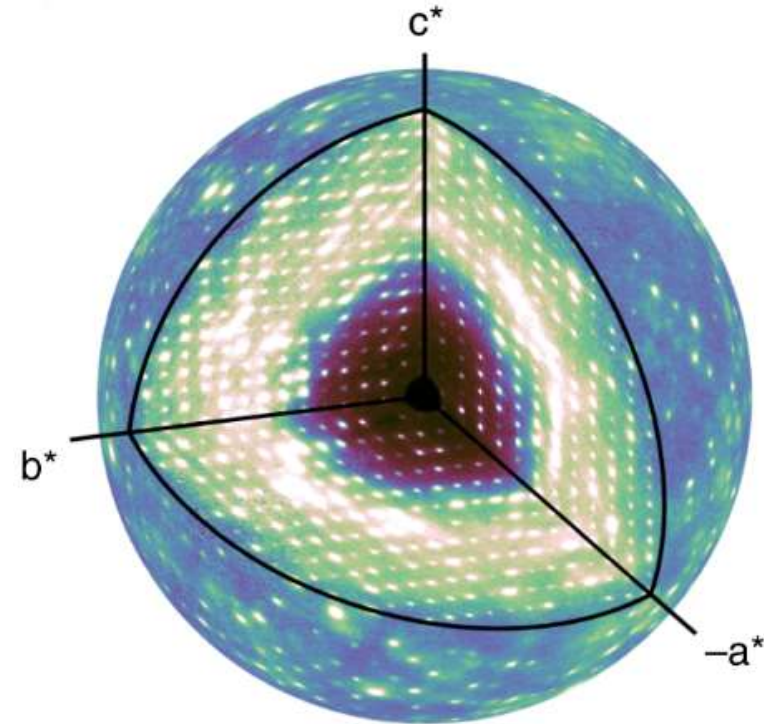For an orthorhombic space group, only an octave of the reciprocal space needs to be measured,

$$h > 0, \, k > 0, \, l > 0,$$

considering:

- Friedel pairs: $I_{hkl} = I_{\bar{h}\bar{k}\bar{l}}$

- Bijvoet mates (reflections related by a symmetry element of the reciprocal space)

  e.g. $I_{hkl} = I_{k\bar{h}l}$ for a tetragonal lattice with a 4-fold axis along c

  e.g. $I_{hkl} = I_{\bar{h}\bar{k}l}$ for a 2-fold axis along c

Symmetry of real lattices   +   centrosymmetry of reciprocal lattice

= 11 groups of symmetry **Laue classes**

Unit cell dimentions	Crystal system	Laue classes
$a, b, c, \alpha, \beta, \gamma$	Triclinic	$\bar{1}$
a, b, c, β ($\alpha, \gamma=90°$)	Monoclinic	$2/m$
a, b, c ($\alpha=\beta=\gamma=90°$)	Orthorhombic	mmm
a, c ($b=a, \alpha=\beta=\gamma=90°$)	Tetragonal	$4/m$
		$4/mmm$
a, c ($b=a, \alpha=\beta=90°, \gamma=120°$)	Trigonal	$\bar{3}$
		$\bar{3}m$
	Hexagonal	$6/m$
		$6/mmm$
a ($b=a, c=a, \alpha=\beta=\gamma=90°$)	Cubic	$m\bar{3}$
		$m\bar{3}m$

Systematic absences

In presence of translational elements (centering or screw axes) in the real lattice, some diffracted intensities are systematically equal to 0.

Consider a 2_1 axis along the z direction:

1) From each atom in (x,y,z), we obtain a symmetric atom in $(-x,-y,z+\frac{1}{2})$

2) The scattering function has to take into account the sum of each pair of atoms:

$$F = \sum f \cos 2\pi(hx + ky + lz) + \sum f \cos 2\pi(h\bar{x} + k\bar{y} + l(z + {}^1/_2))$$

3) Using the trigonometric equation: $\cos a + \cos b = 2 \cos \dfrac{a+b}{2} \cos \dfrac{a-b}{2}$

$$\cos 2\pi(hx + ky + lz) + \cos 2\pi(h\bar{x} + k\bar{y} + l(z + {}^1/_2)) =$$
$$= 2 \cos \pi(2lz + l/2) \cos \pi(2hx + 2ky - l/2)$$

4) For reflections with $h = 0$ and $k = 0$,

in case $l = 2n$: $\quad F = \sum f 2 \cos \pi(4nz + n) \cos \pi(-n)$

in case $l = 2n+1$: $\quad F = \sum f 2 \cos \pi \left(4nz + z + \dfrac{n}{2} + \dfrac{1}{2}\right) \cos \pi \left(-n - \dfrac{1}{2}\right) = 0$

$$\cos\left(-n\pi - \frac{\pi}{2}\right) = 0$$

When a screw axis is present along the z direction, diffraction intensities for ($00l$) reflections are present only when $l = 2n$ (i.e. l is even)

Systematic absences

In presence of translational elements (centering or screw axes) some diffracted intensities are systematically equal to 0.

Consider a 2_1 axis along the z direction:

1) From each atom in (x,y,z), we obtain a symmetric atom in

2) The scattering function has to take into account the sum of

$$F = \sum f \cos 2\pi(hx + ky + lz) + \sum f \cos 2\pi(h\bar{x} + k\ $$

3) Using the trigonometric equation: $\cos a + \cos b = 2 \cos$

$$\cos 2\pi(hx + ky + lz) + \cos 2\pi(h\bar{x} + k\bar{y} + l(z + {}^1/$$
$$= 2 \cos\pi(2lz + l/2) \cos\pi(2hx + 2ky - l/2)$$

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in case $l = 2n+1$: $F = \sum f 2 \cos\pi\left(4nz + z + \frac{n}{2} + \frac{1}{2}\right) \cos\pi\left(-n - \frac{1}{2}\right) = 0$

$$\cos\left(-n\pi - \frac{\pi}{2}\right) = 0$$

On the crystallographic tables, for each space group

Reflection conditions

General:

$h00: h = 2n$
$0k0: k = 2n$
$00l: l = 2n$

When a screw axis is present along the z direction, diffraction intensities for $(00l)$ reflections are present only when $l = 2n$ (i.e. l is even)
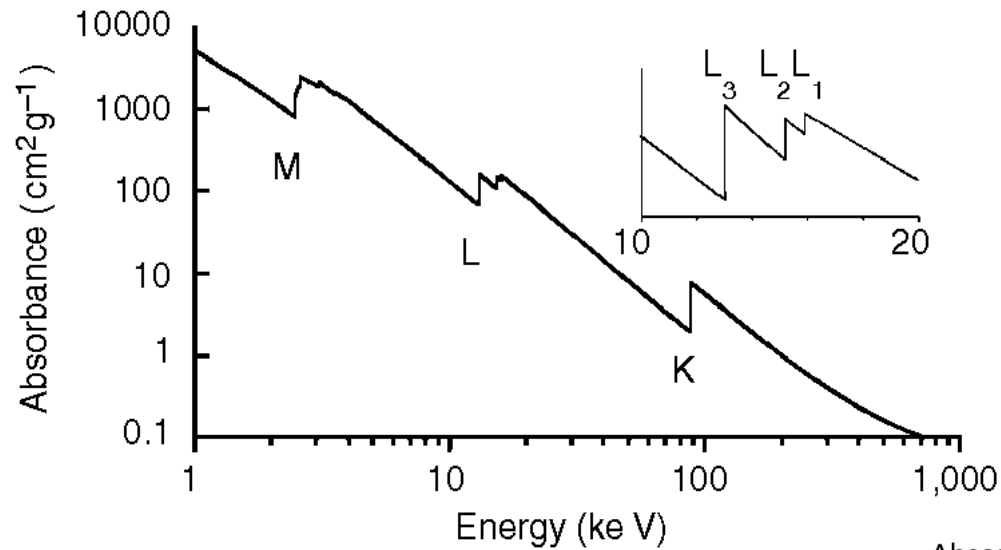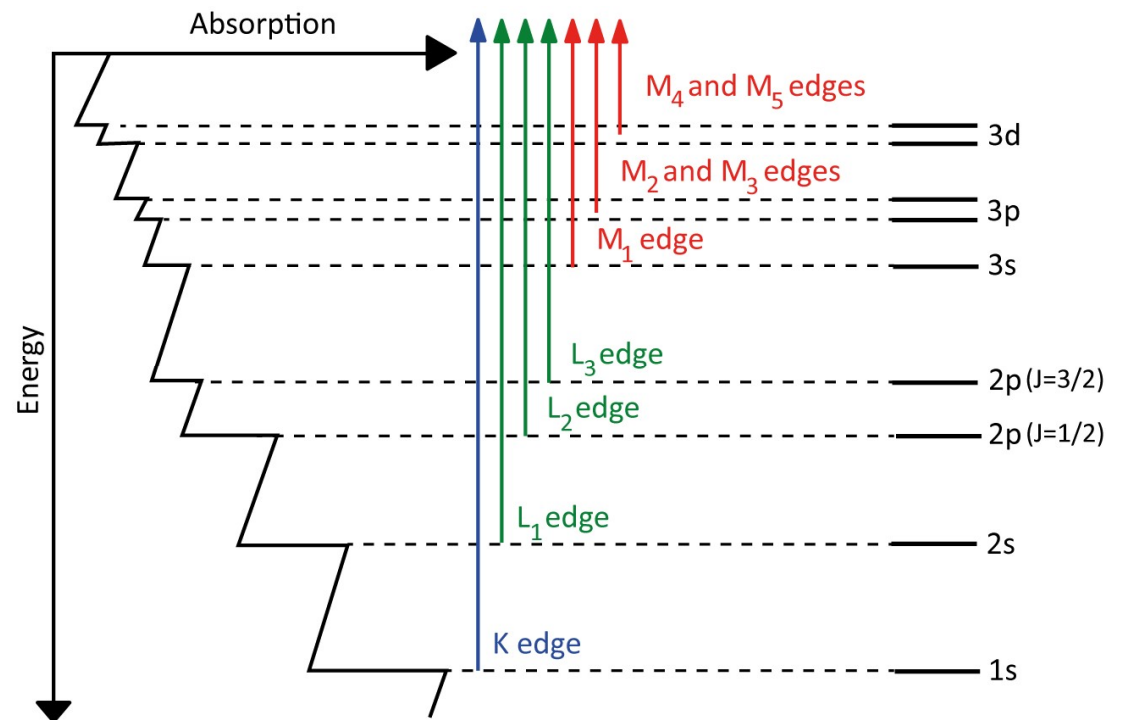
X-ray absorption

Given a specific wavelenght, each element has a defined absorption coefficient.

Absorption coefficients decrease with energy of the incident radiation, but their behavior is not continuous.

Absorption edges correspond to electron transitions between core atomic levels.

Absorption correction factor for diffraction intensities (at a specific wavelenght).

At the absorption edge, the atomic scattering factor has an additional imaginary component...
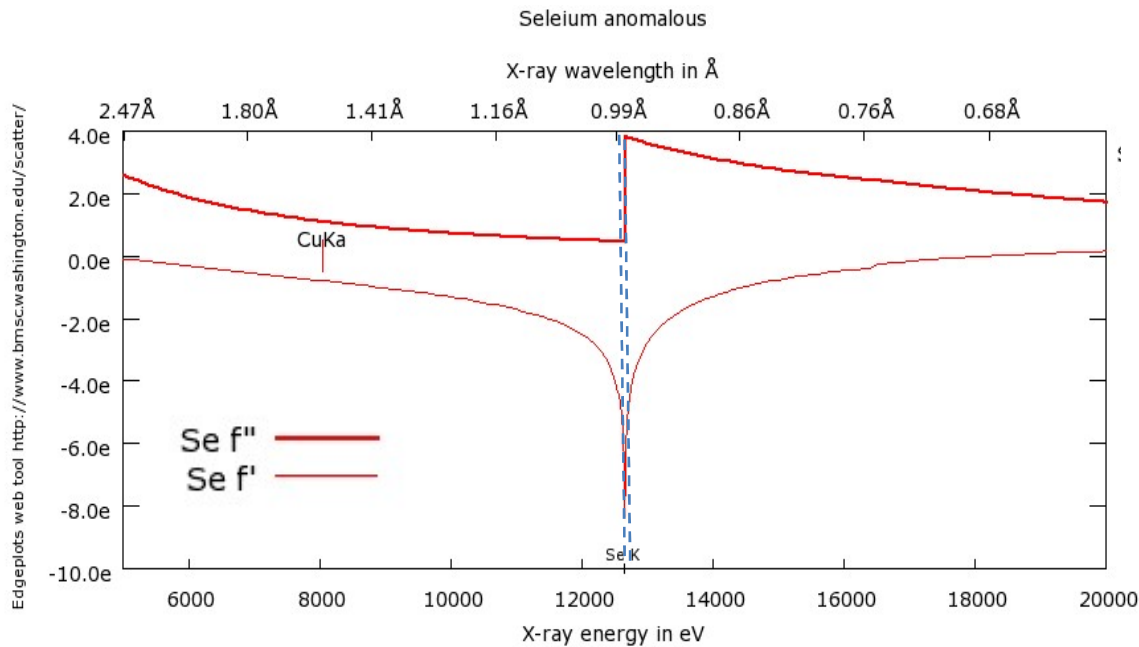
Anomalous scattering

Atomic scattering factor:
$$f(\theta, \lambda) = f_0(\theta) + f'(\lambda) + if''(\lambda)$$

dispersive term

absorption, imaginary term

Wavelenght dependent contributions (but independent from θ).

Absorption contribution breaks Friedel's law.

At the absorption edge:

$$I_{hkl} \neq I_{\bar{h}\bar{k}\bar{l}}$$

Elements with edges in the typical energy range (5-15 keV) for crystallographic experiments:

K edge: from Mn to Kr

L edge: from I to Pb

M edge: U

Anomalous scattering is exploited for the experimental phasing of diffraction data, in presence of a heavy atom.