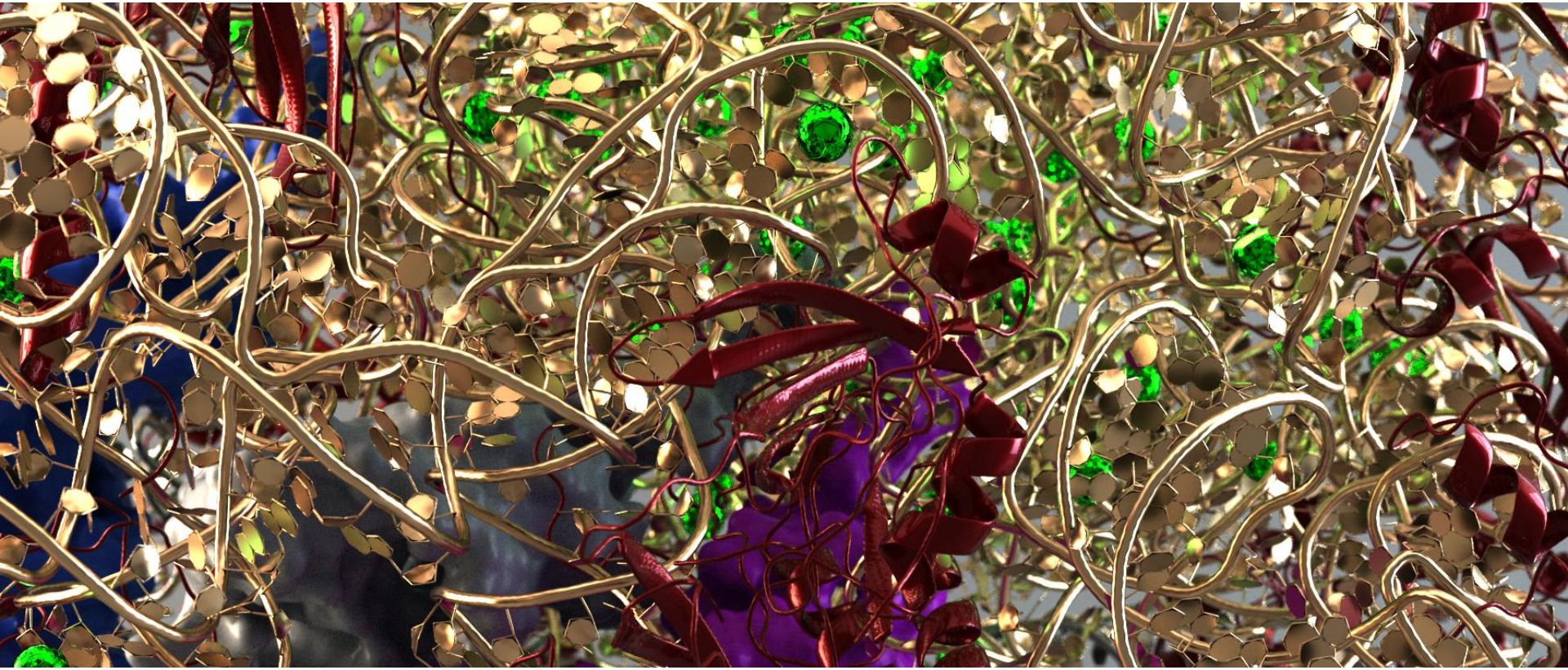
Basic Diffraction Theory



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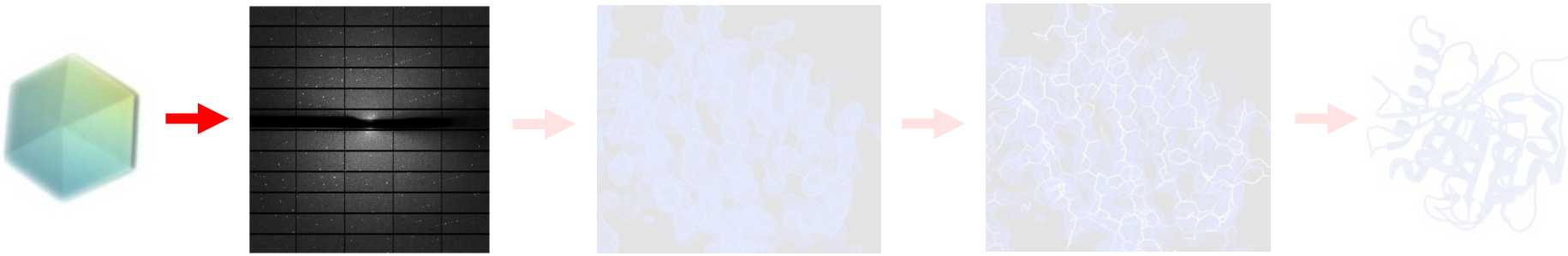
X-ray crystallography experiment



Crystal

Diffraction pattern

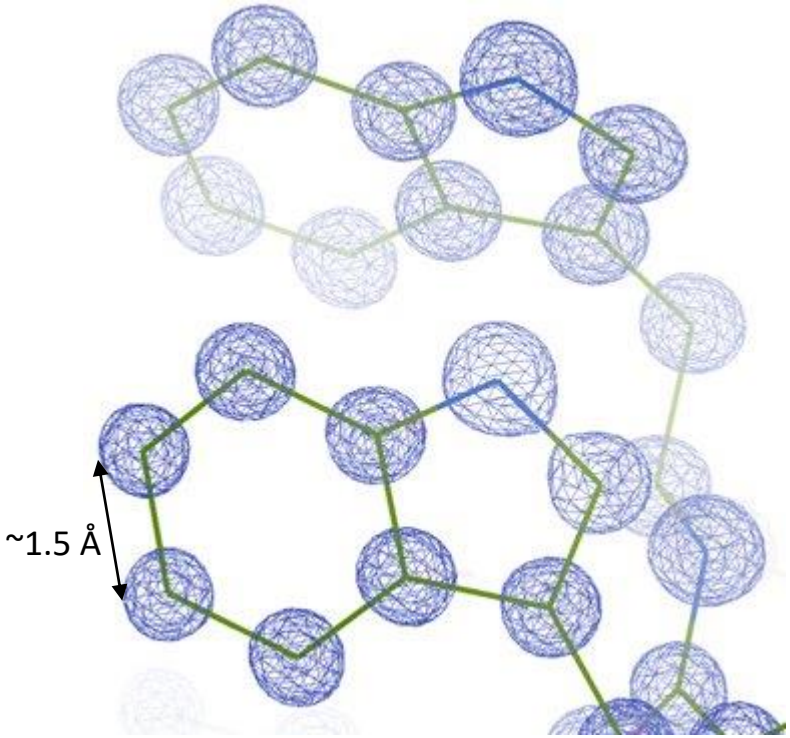
Electron density maps

Model building & refinement

Final model

- Why do we need X-rays?
- Why do we need crystals?
- How are X-rays diffracted by crystals?

Why can't we see atoms with visible light?

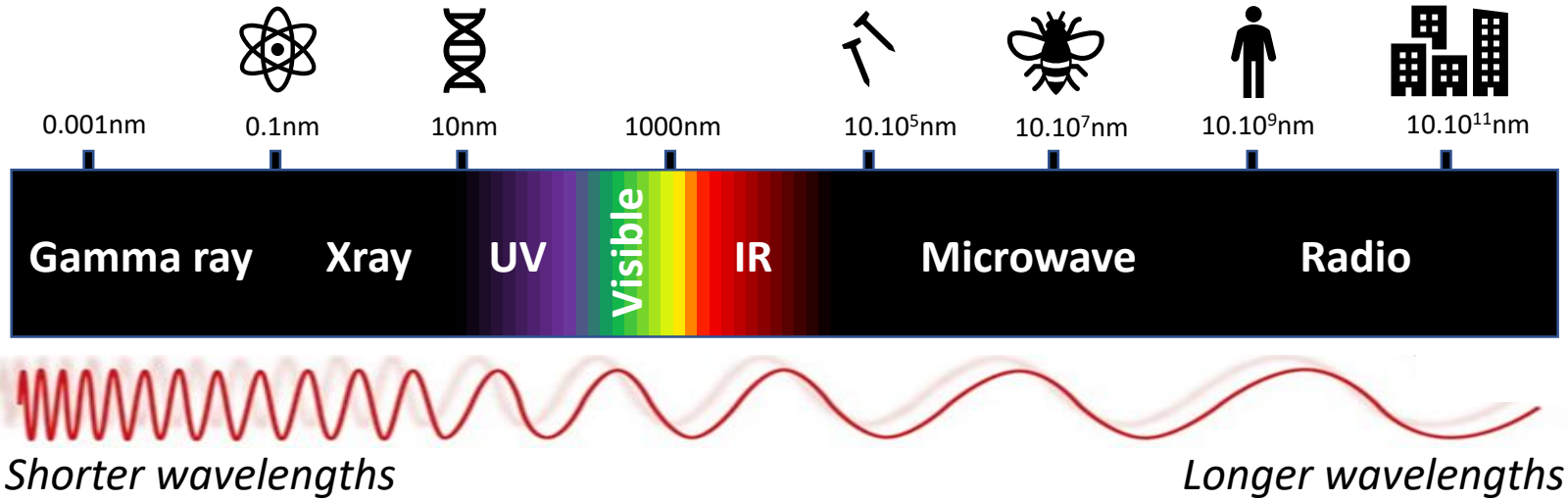


1 Å = 0.1 nm = 10^{-10} m

$$r = \frac{\lambda}{2 \cdot NA}$$

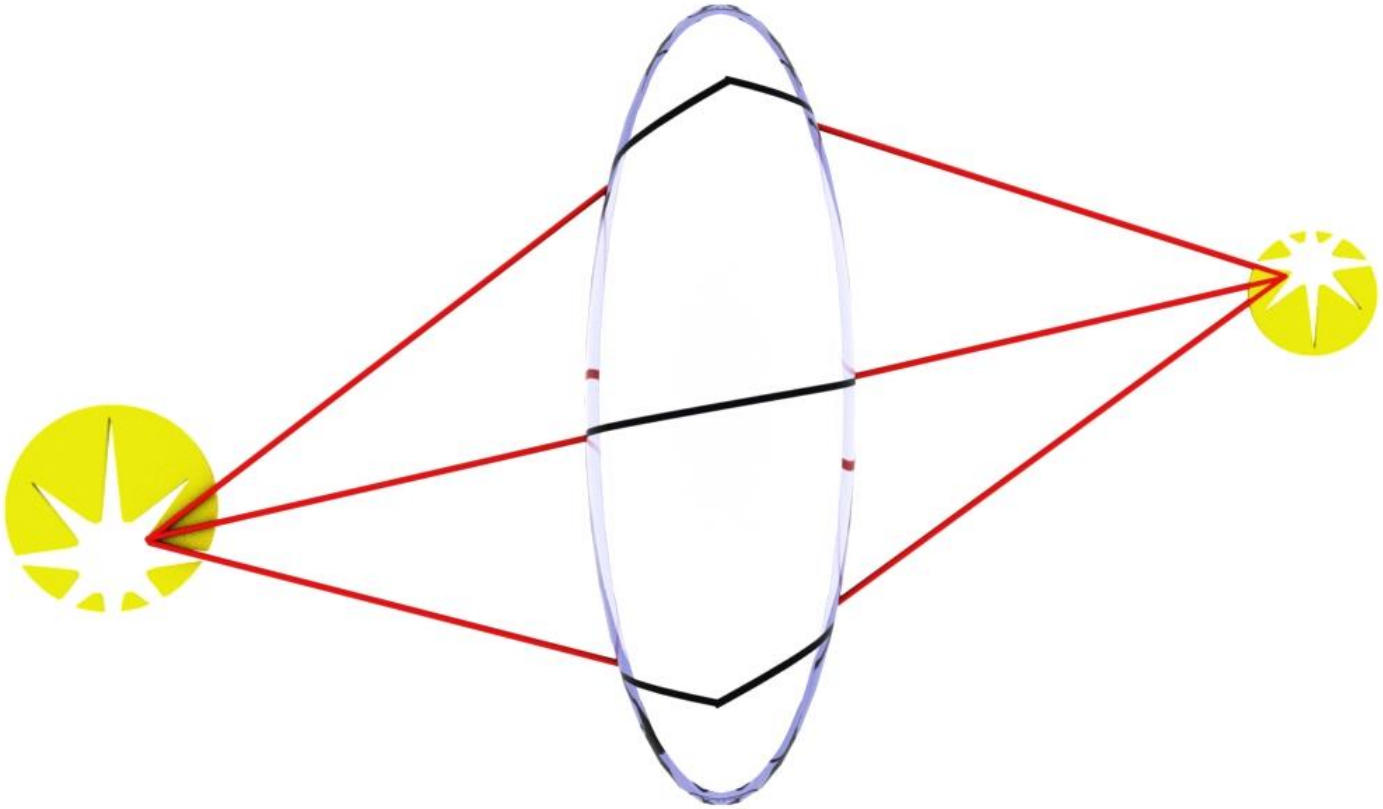
r *is the minimum distance between resolvable points.*
λ *is the wavelength of light*
NA *is the numerical aperture*

We can't see objects that are much smaller than the wavelength (λ) of the light that is being used.



- The wavelength for visible light is measured in 100s of nm, while atoms are separated by distances of the order of 0.1 nm.
- Looking at the electromagnetic spectrum, X-rays are the best suited.
- X-rays are penetrating radiations and can provide a truly 3D image, on contrary to visible light.

Light arriving on one point of the image comes from one point on the object



Object Lens Image

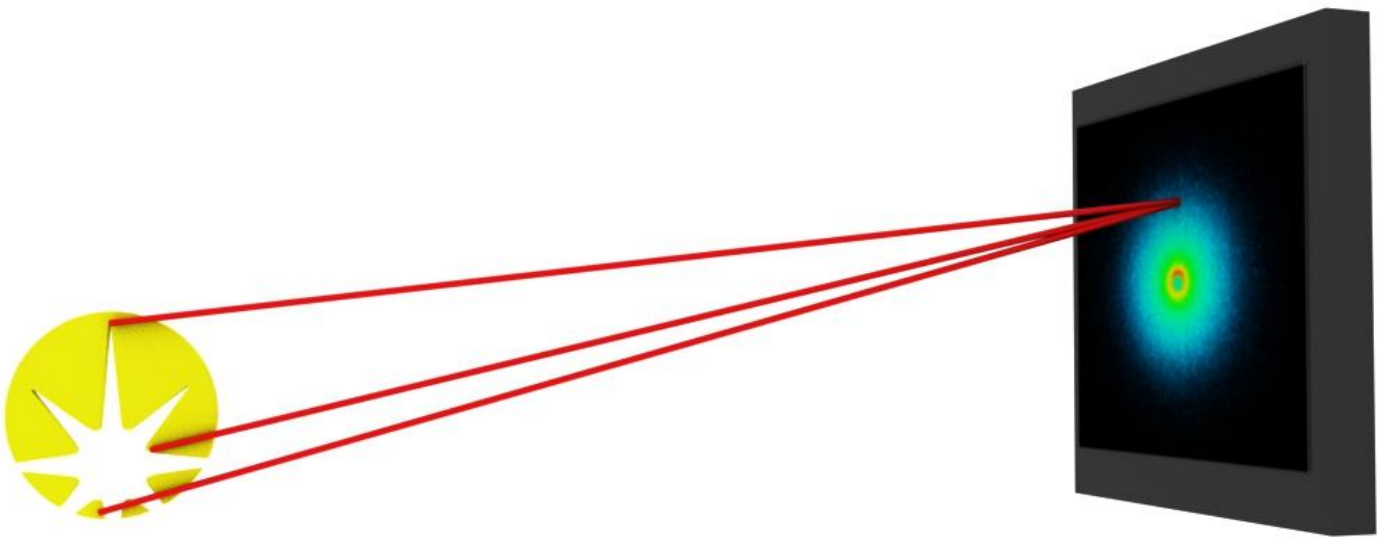
We can't build an X-ray microscope to look at molecules:

- X-ray lenses don’t exist. If they did, they would need tolerances smaller than the distance between two atoms.

- X-rays have refractive index close to 1 so their path does not change much when entering a material. The focal lengths for these lenses become impractically long.

Zone plates can focus X-rays to form an image but resolution is limited to ~ 30-50 nm.

Without a lens, light arriving on one point of the image comes from all points on the object.

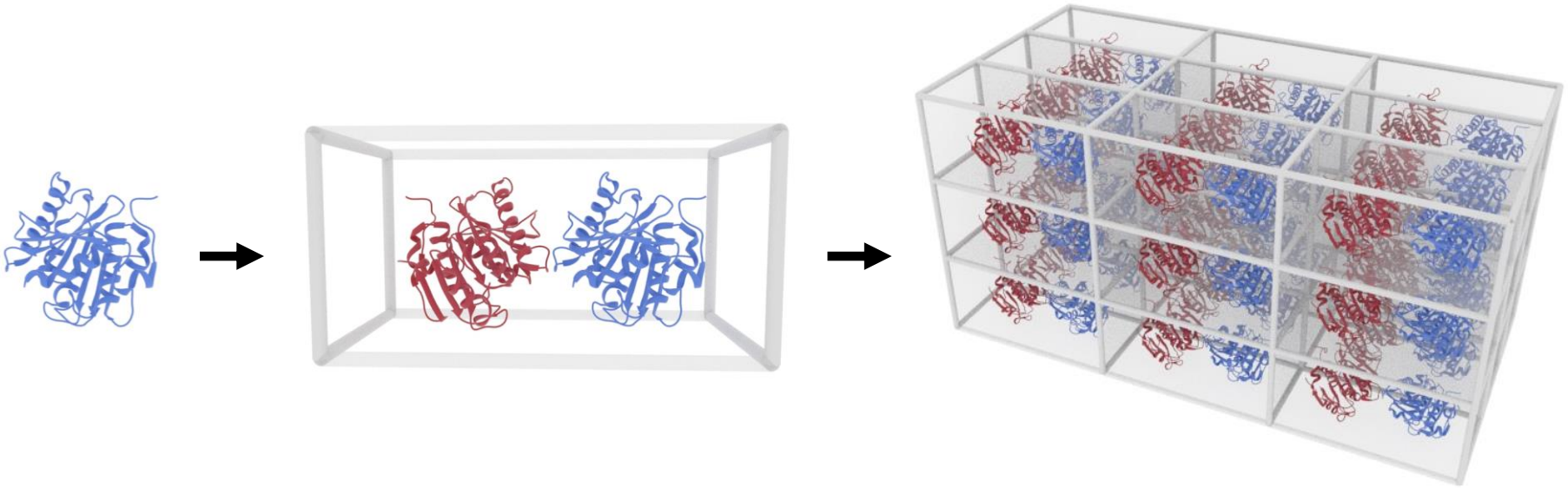


Object

Diffraction spectra

Why do we need crystals?

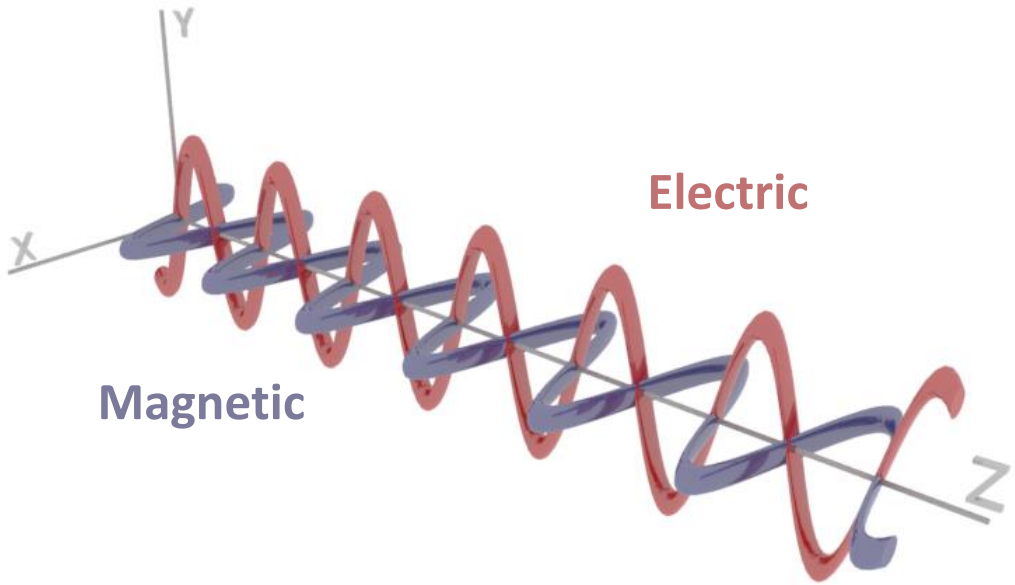
- Diffraction from one molecule is too weak.
- Crystals are made up of identical building blocks called unit-cells.
- Multiple unit-cells constitute a 3-dimensional translation lattice.
- A crystals acts as a signal amplifier and are particularly suited for X-ray diffraction (λ ~ atomic spacing).



- Why do we need X-rays?
- Why do we need crystals?
- How are X-rays diffracted by crystals?

Electromagnetic waves

- X-rays (and visible light) are one type of electromagnetic radiations, they can also be called electromagnetic waves, light or photons (particle without mass).
- Electromagnetic waves consist of 2 waves oscillating perpendicular to one another at the speed of light: magnetic and electric components.



Electromagnetic waves

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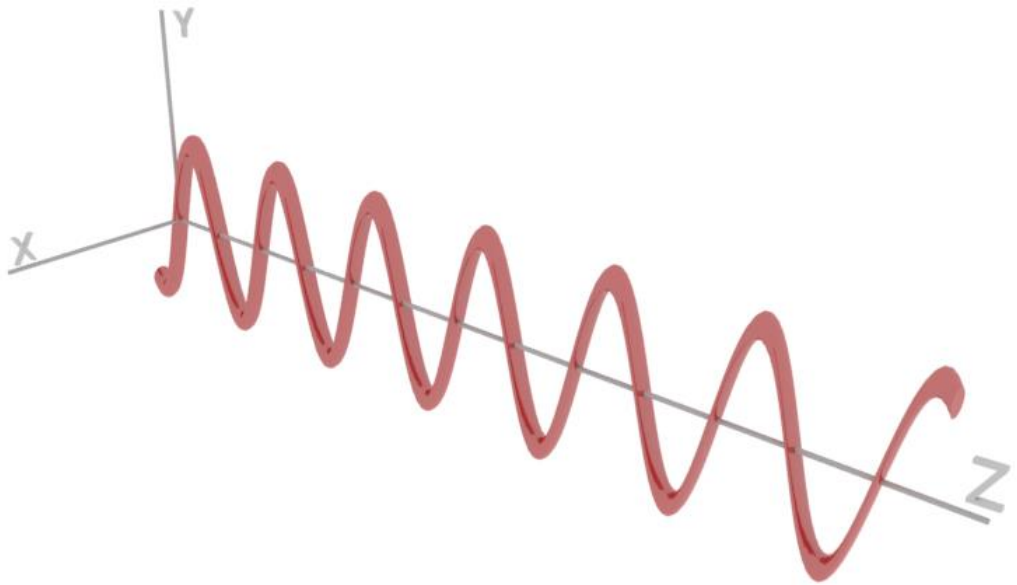
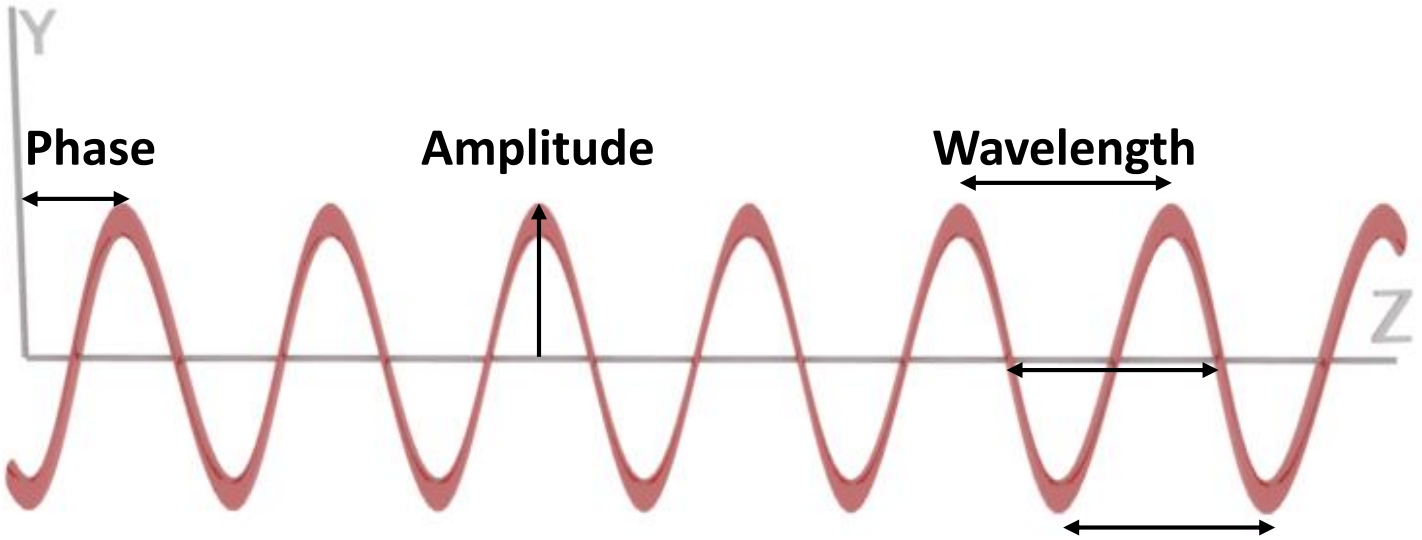
- Electromagnetic waves consist of 2 waves oscillating perpendicular to one another at the speed of light: magnetic and electric components.
- For simplification, electromagnetic waves are often represented only by their electric component (most important one for our experiment).

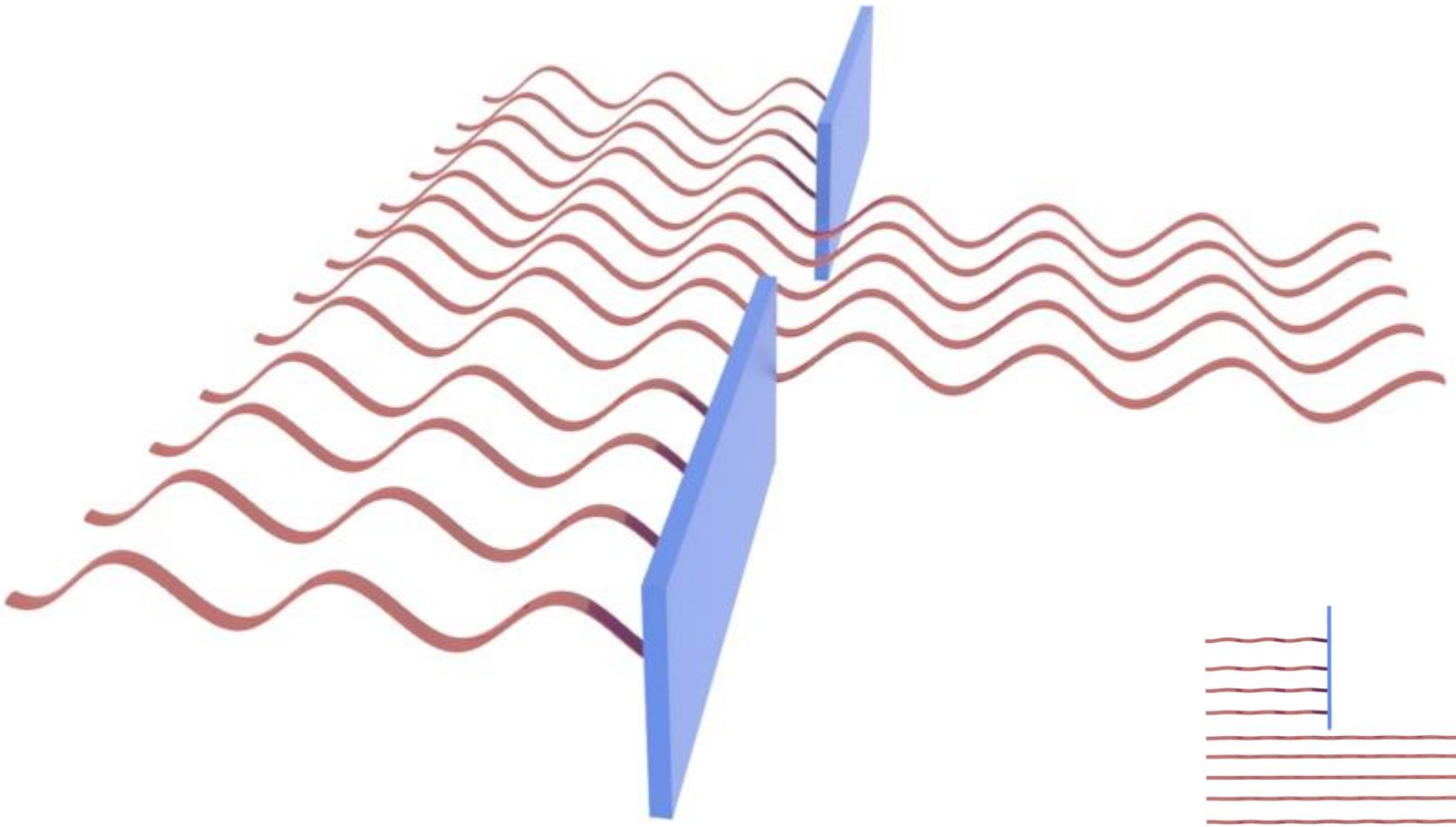


Electromagnetic waves



- A wave can be defined by its wavelength, amplitude and phase.
- In XRC experiments, we usually use monochromatic X-rays, so the wavelength (λ) is known and fixed.

Slit experiment

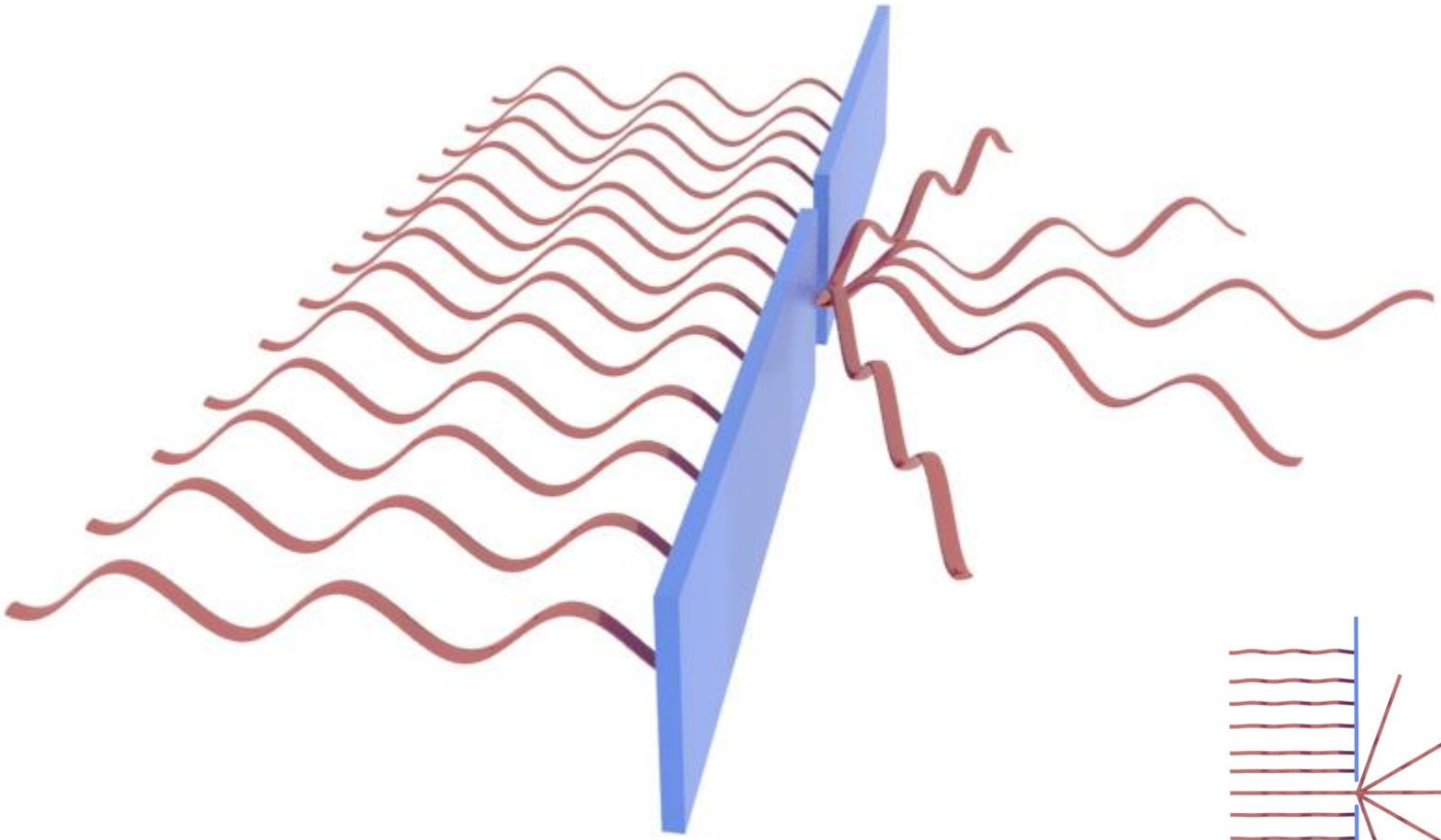


Top view

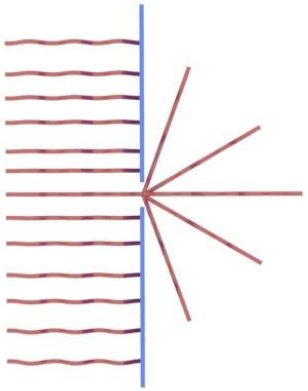
Slit width >> λ

Slit experiment

Diffraction is the spreading out of waves as they pass through an aperture or around objects.

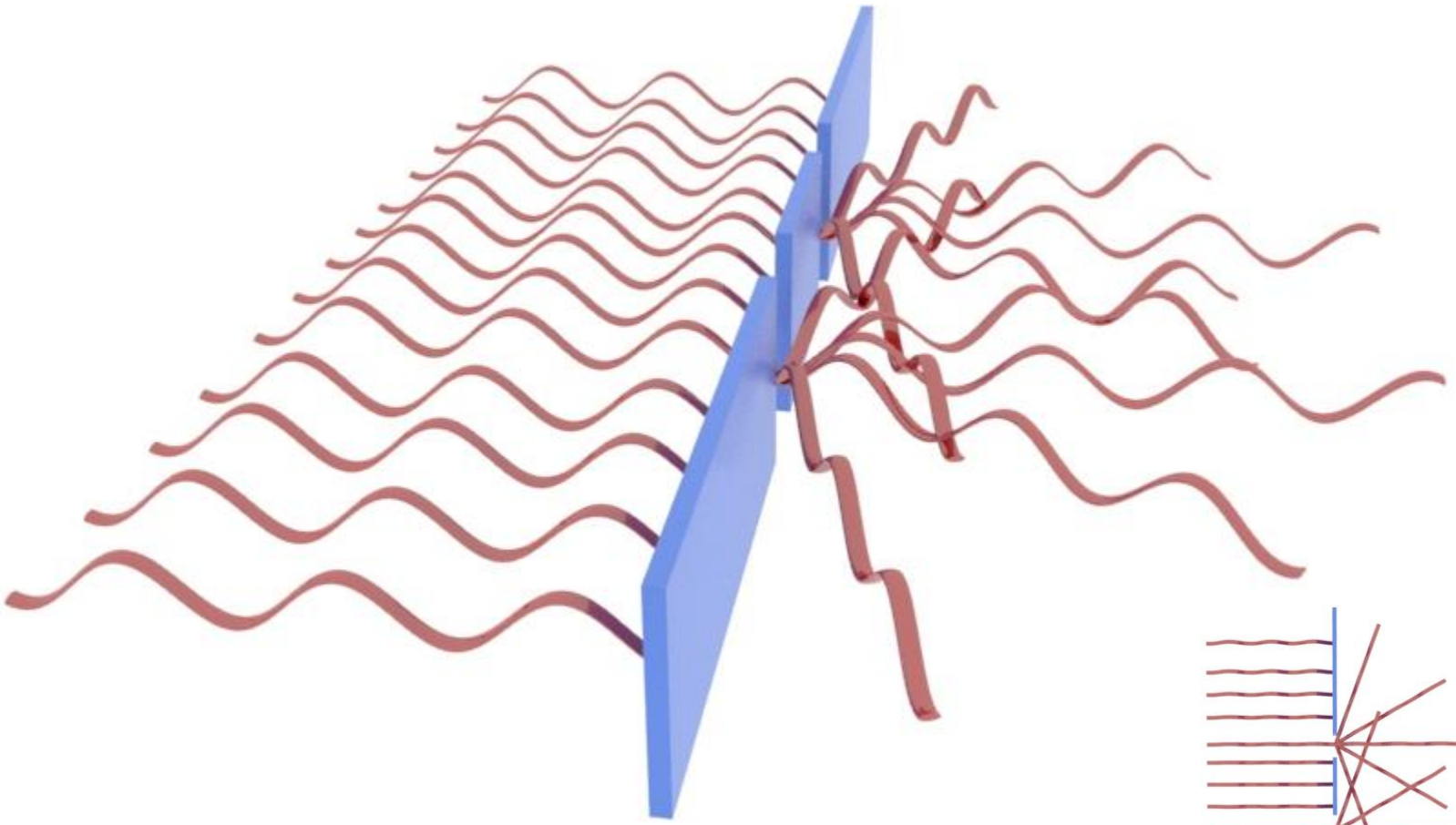


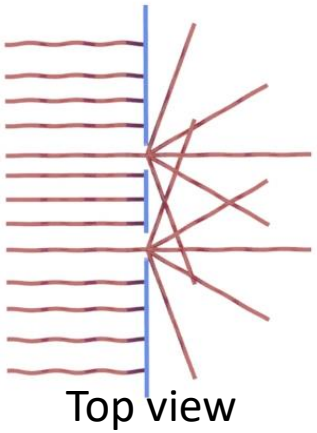
Slit width ~ λ



Top view

Slit experiment

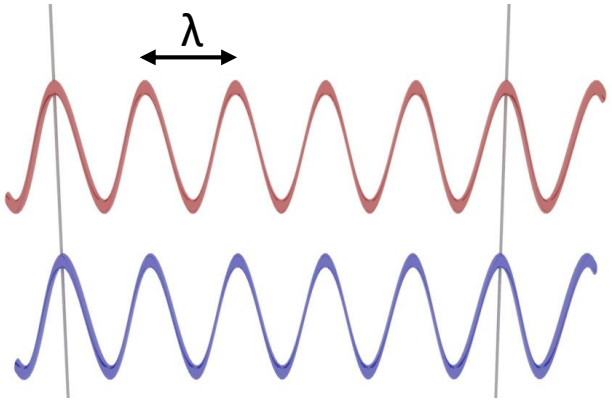




Top view

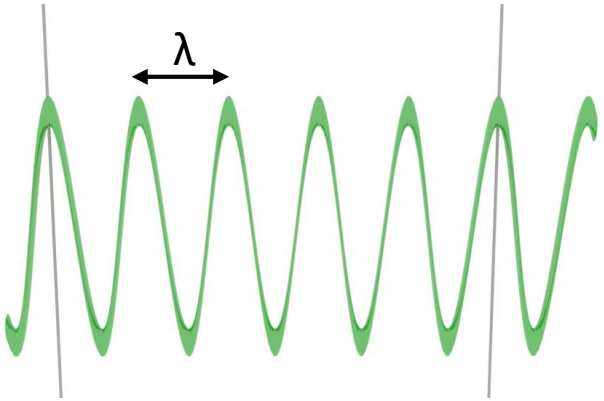
Slit width ~ λ

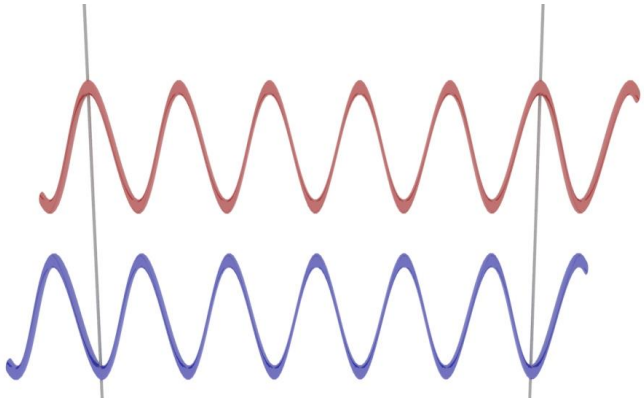
Wave interference



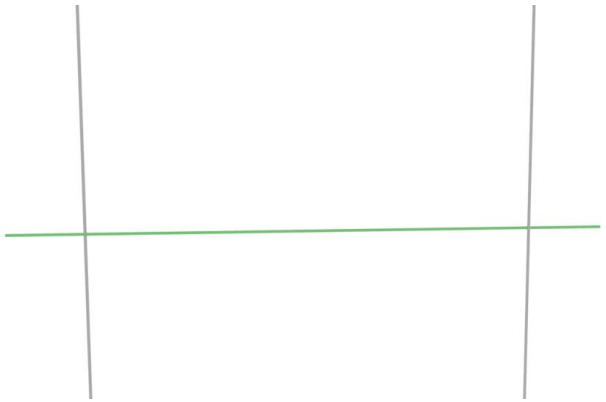
In phase

Constructive interference



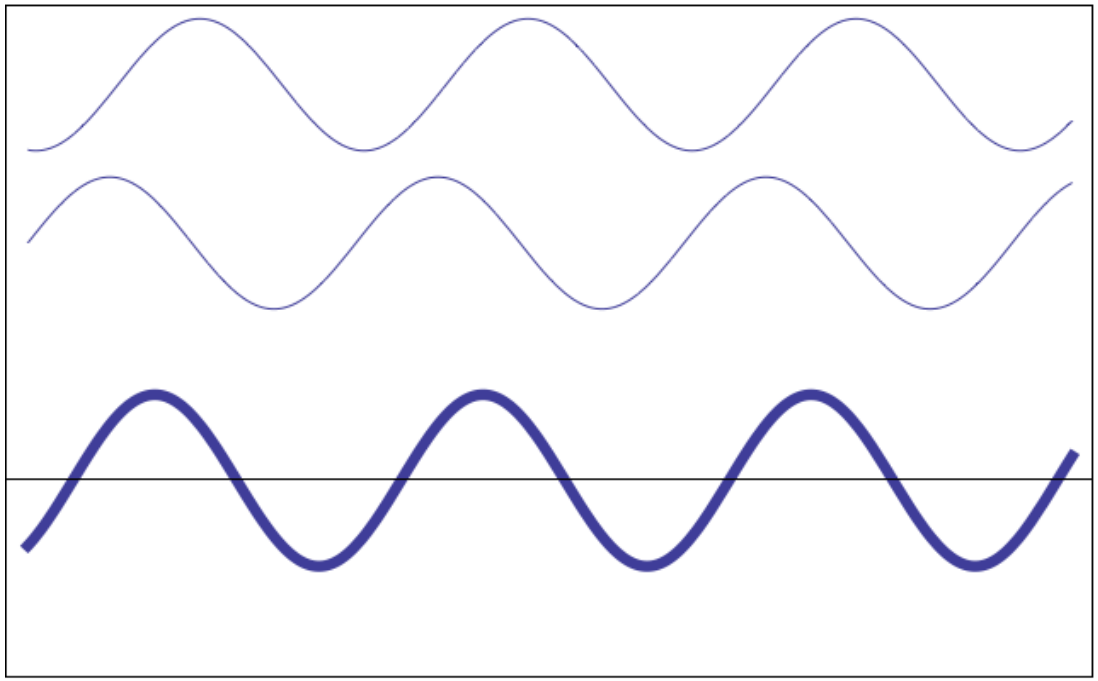


Out of phase of λ/2



Destructive interference

Wave interference

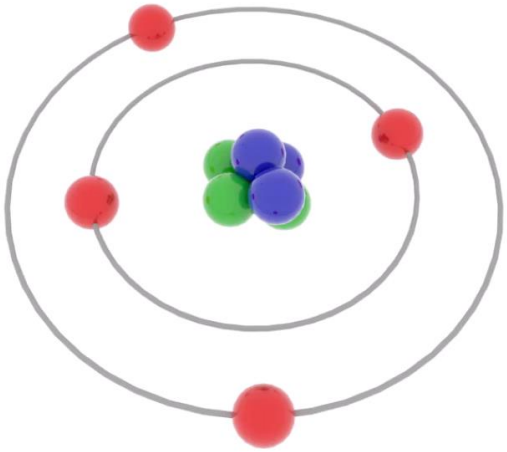


https://www.acs.psu.edu/drussell/Demos/superposition/superposition.html

Wave interference

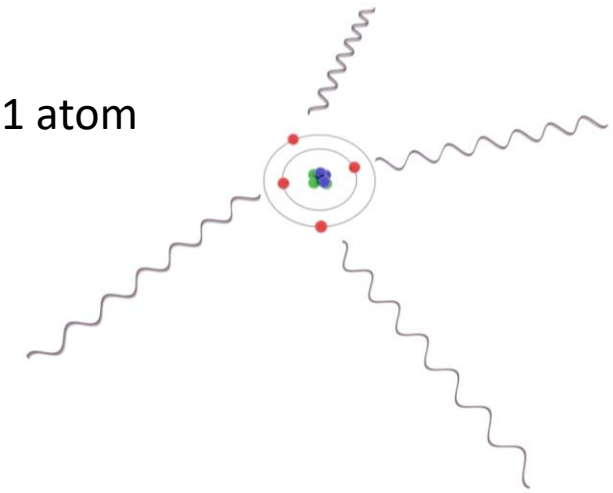
Interference of water waves

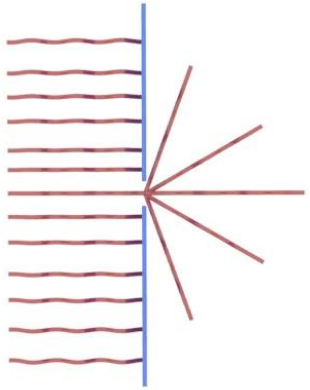
https://www.youtube.com/watch?v=Iuv6hY6zsd0&list=PLDvVtGPo3ANw8upOKjs_FrkE8iqRrAVnT&index=1



- When X-rays interact with electrons, they set the electron oscillating with the X-ray wavelength (excited state).
- To return to its unexcited state, the oscillating electron radiate X-rays with the same wavelength, in all directions (elastic scattering, Thomson scattering).
- Electrons become an X-ray source.

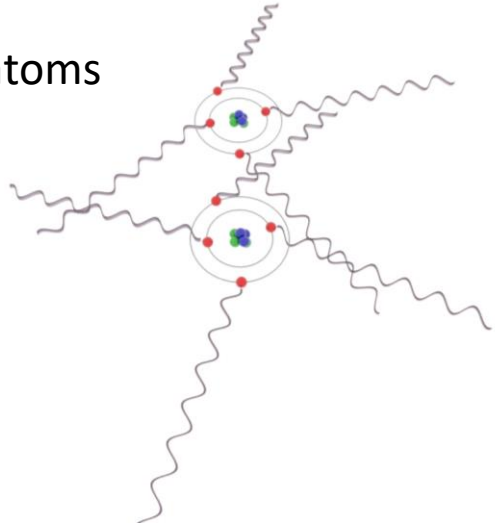
1 atom

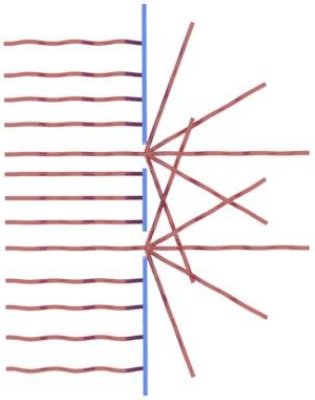




Diffraction

2 atoms





Diffraction
and interference

Crystals are regular arrays of electrons, that behave similarly to slits, they will radiate X-rays in all directions with the same wavelength but different amplitude and phases.

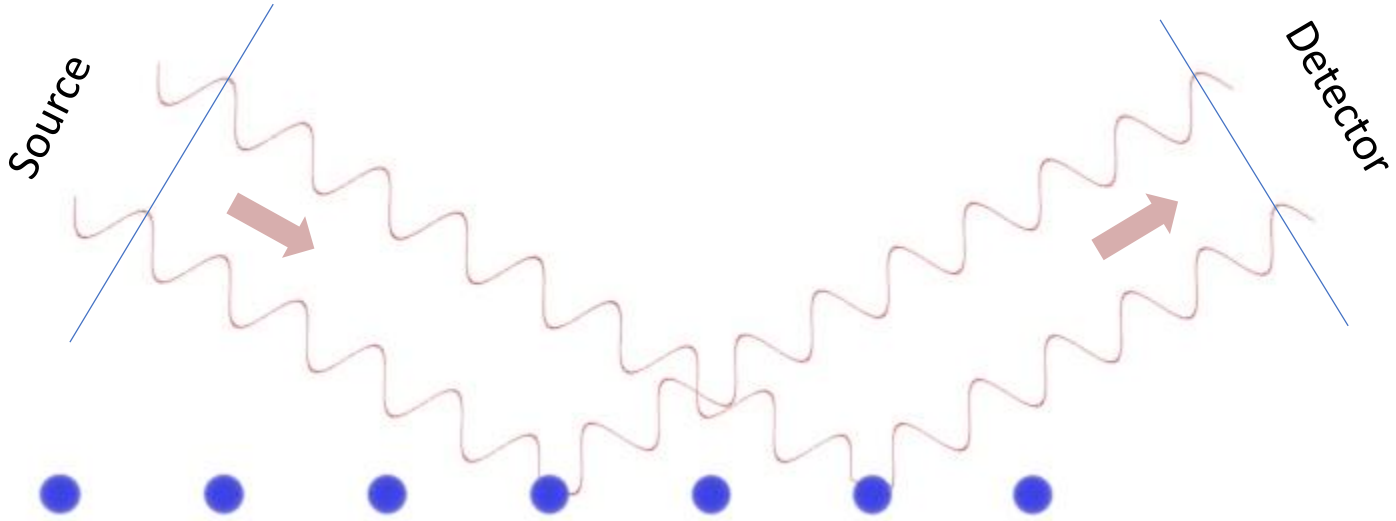
Waves in phase

If we shine monochromatic X-ray source on a crystal, two waves are in phase when:

- They travel the same distance.
  - Direct beam
  - Single plane

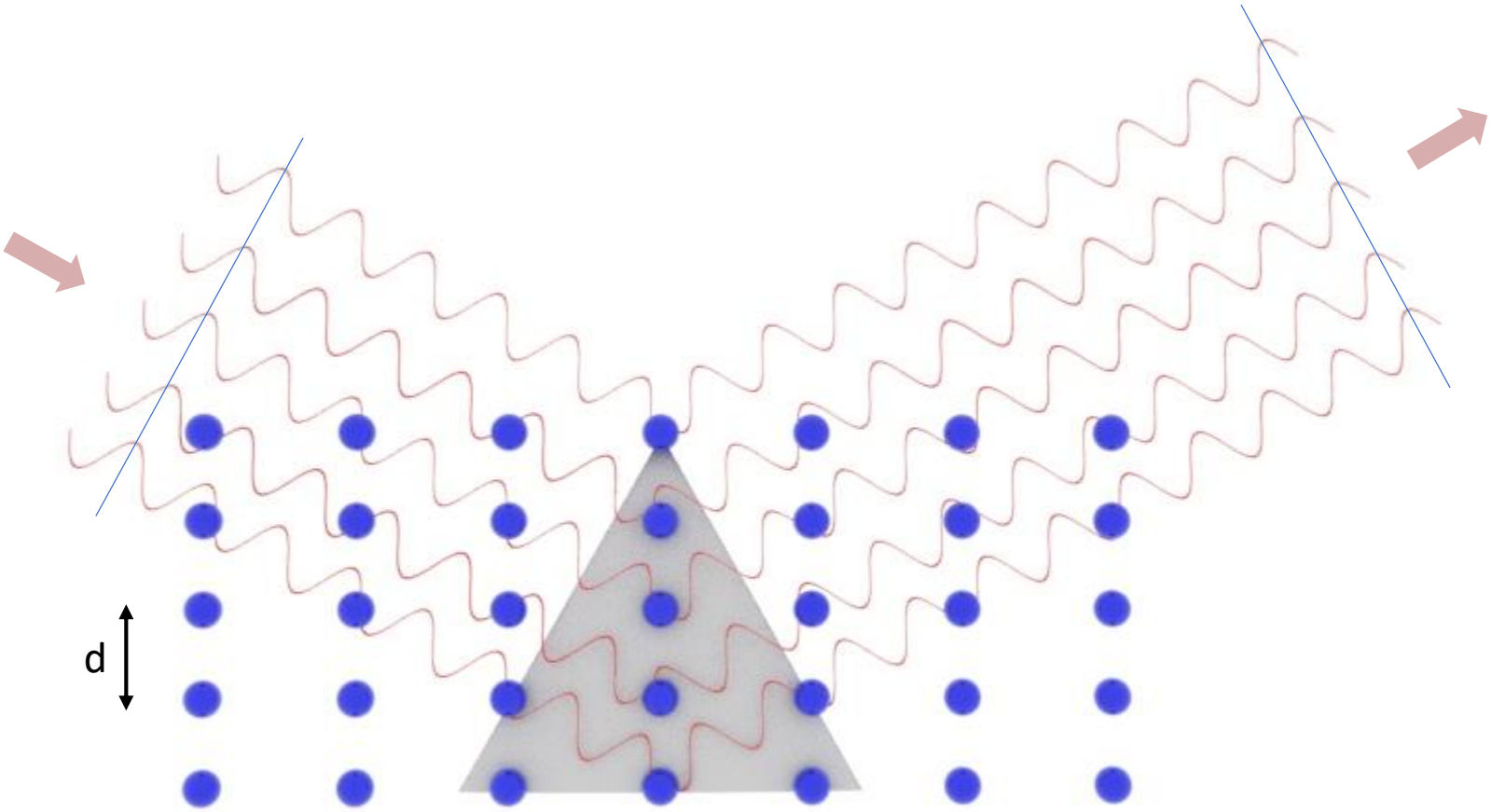
- The difference between the path lengths is equal to an integer multiple of the wavelength.

Waves in phase



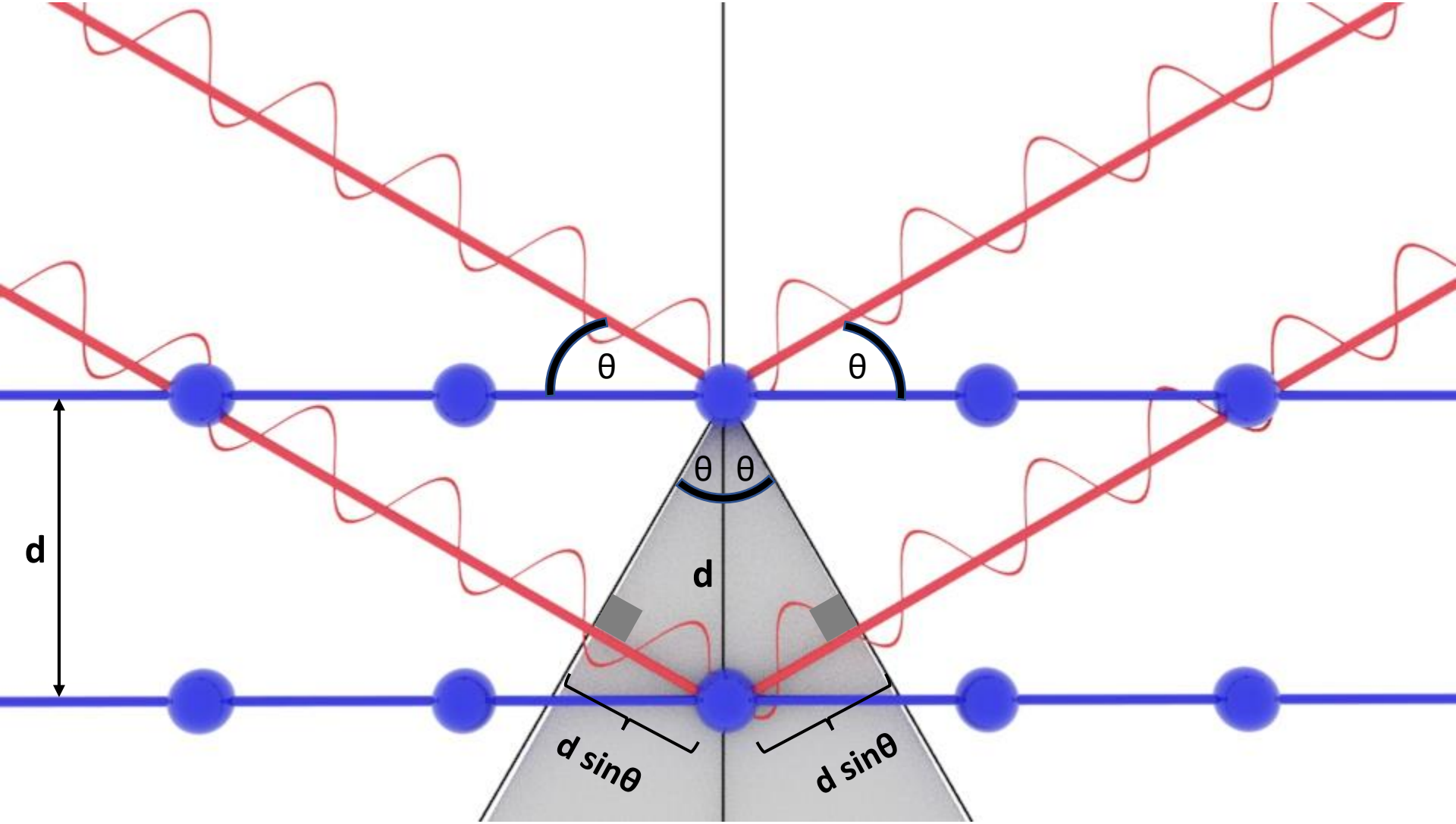
When their path length is the same.

Waves in phase



When their path length differ by an integer number of wavelength.

Waves in phase



The extra path travelled by the wave is (d.sin θ + d.sinθ).

Waves in phase

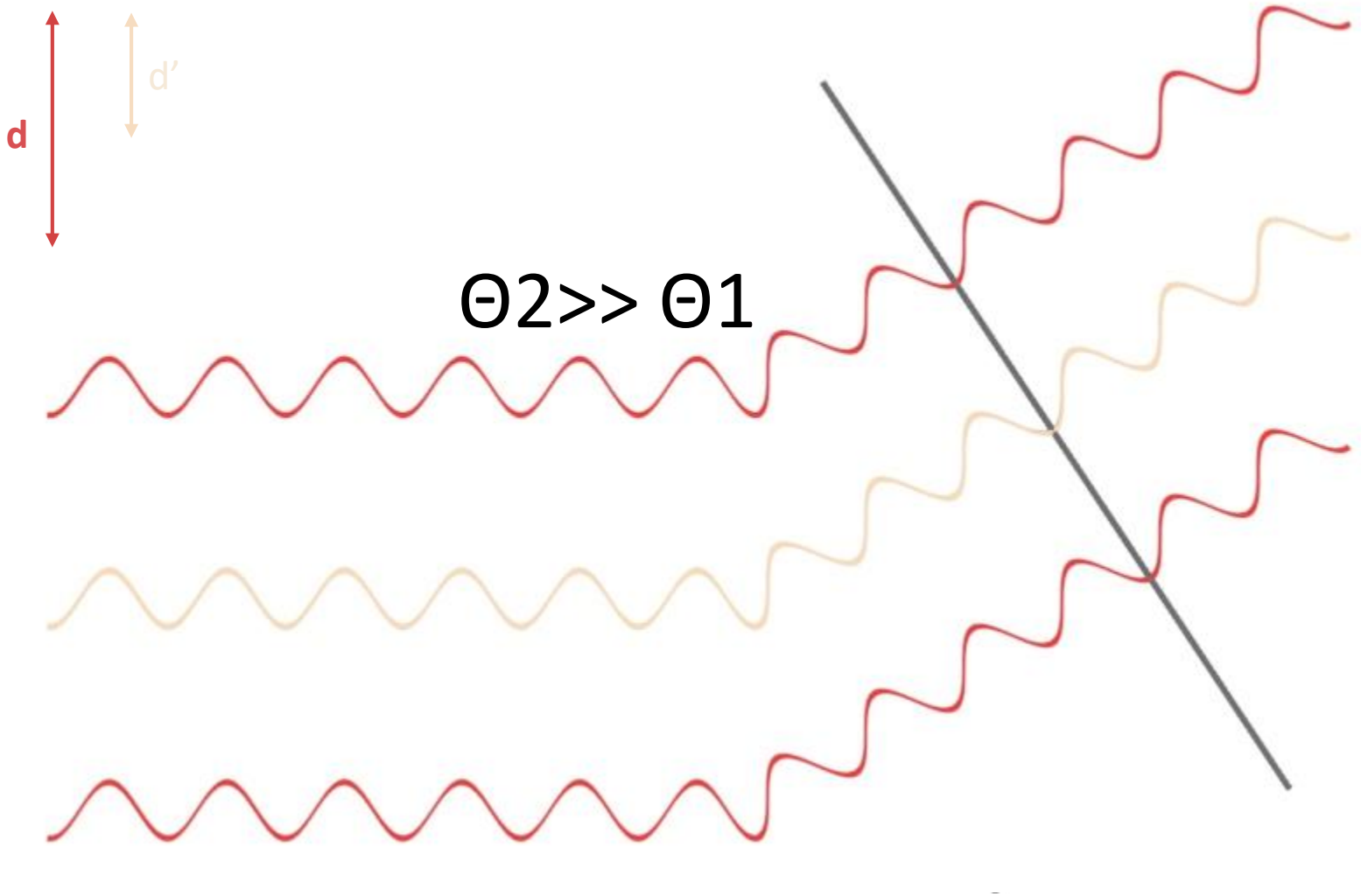
- In order for the waves to interfere constructively, the differences in the travel path must be equal to integer multiples of the wavelength.
- When this constructive interference occurs, a diffracted beam of X-rays will leave the crystal at an angle equal to that of the incident beam.

$$n\lambda = 2d\sin\theta$$

λ is the wavelength of the radiation used,
d is the inter-planar spacing involved,
θ is the angle between the incident (or diffracted) ray and the crystal planes,
n is an integer, referred to as the order of diffraction.

- Because Bragg's planes behaves like 'mirrors', the diffracted X-rays form a diffraction spot on the detector, this is also called: a reflection.
- Since we know, n, λ and θ, we can find d the distance between planes and start to get some information about interatomic distances.

Waves in phase



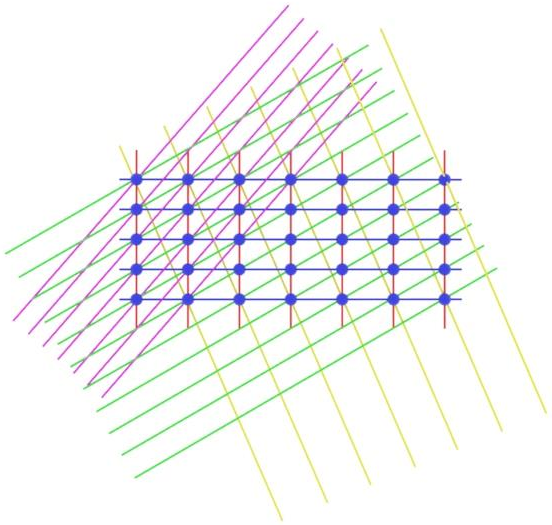
The smaller the spacing between planes, the larger the diffraction angles are.

Miller indices

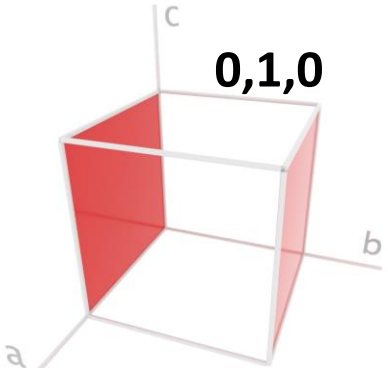
- We need to define the planes of atoms responsible for constructive interferences.

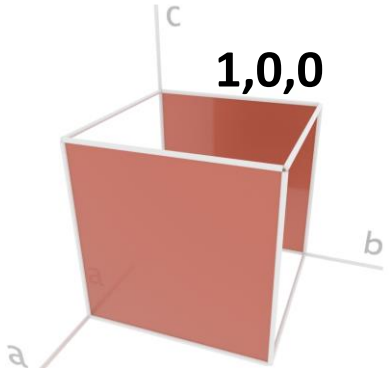
- A family of lattice/Bragg planes is defined by 3 integers *h*, *k*, *l*, called the *Miller indices*.

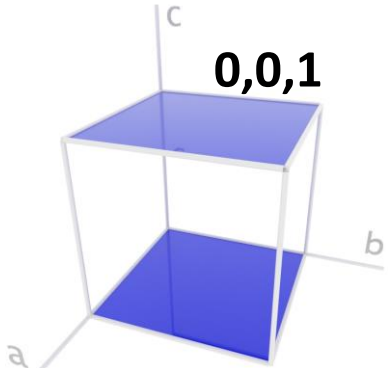
- The orientation of the lattice planes is described in term of their intercept on the axes a, b and c.

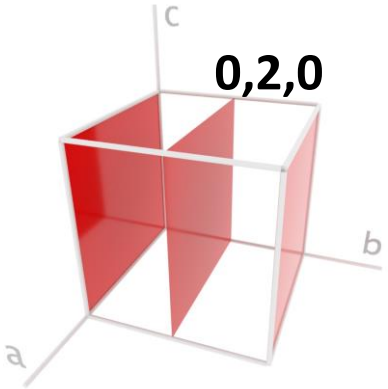


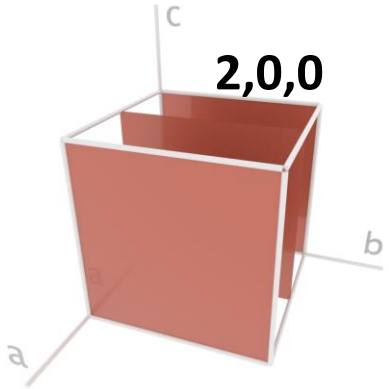
Miller indices

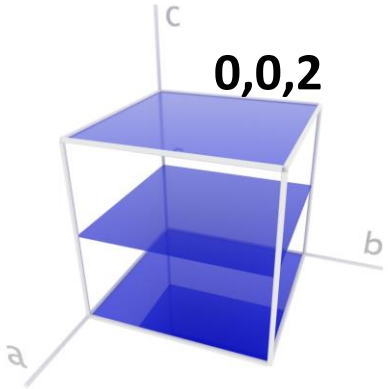


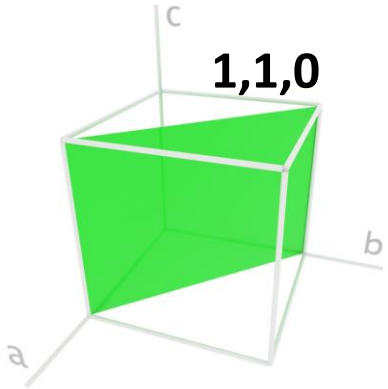


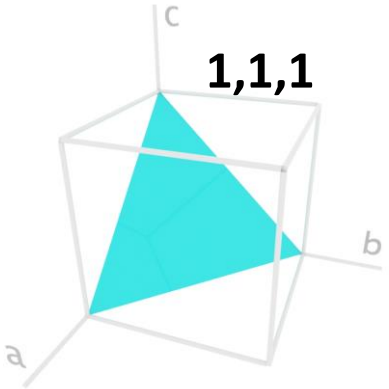




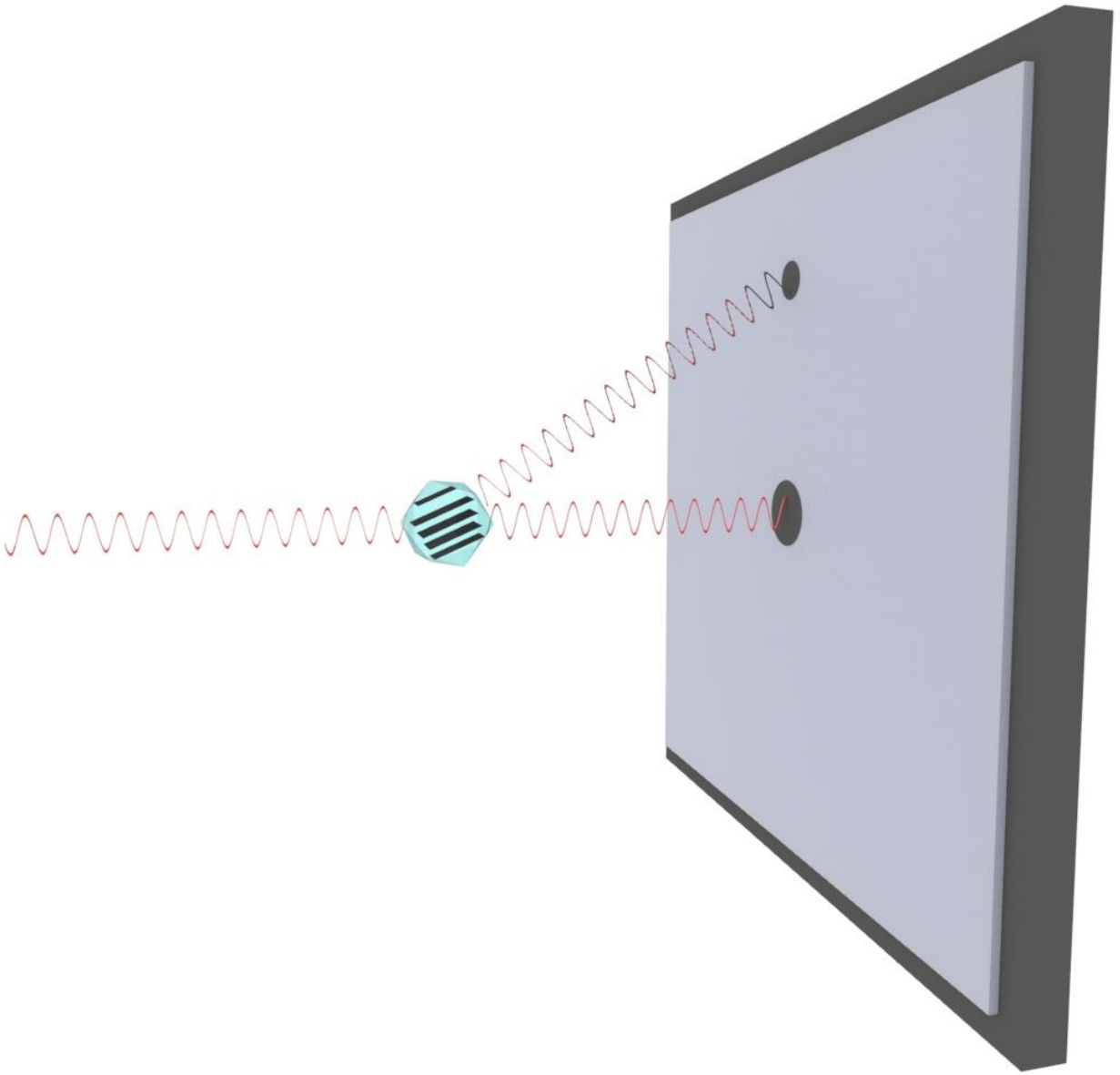








Miller indices



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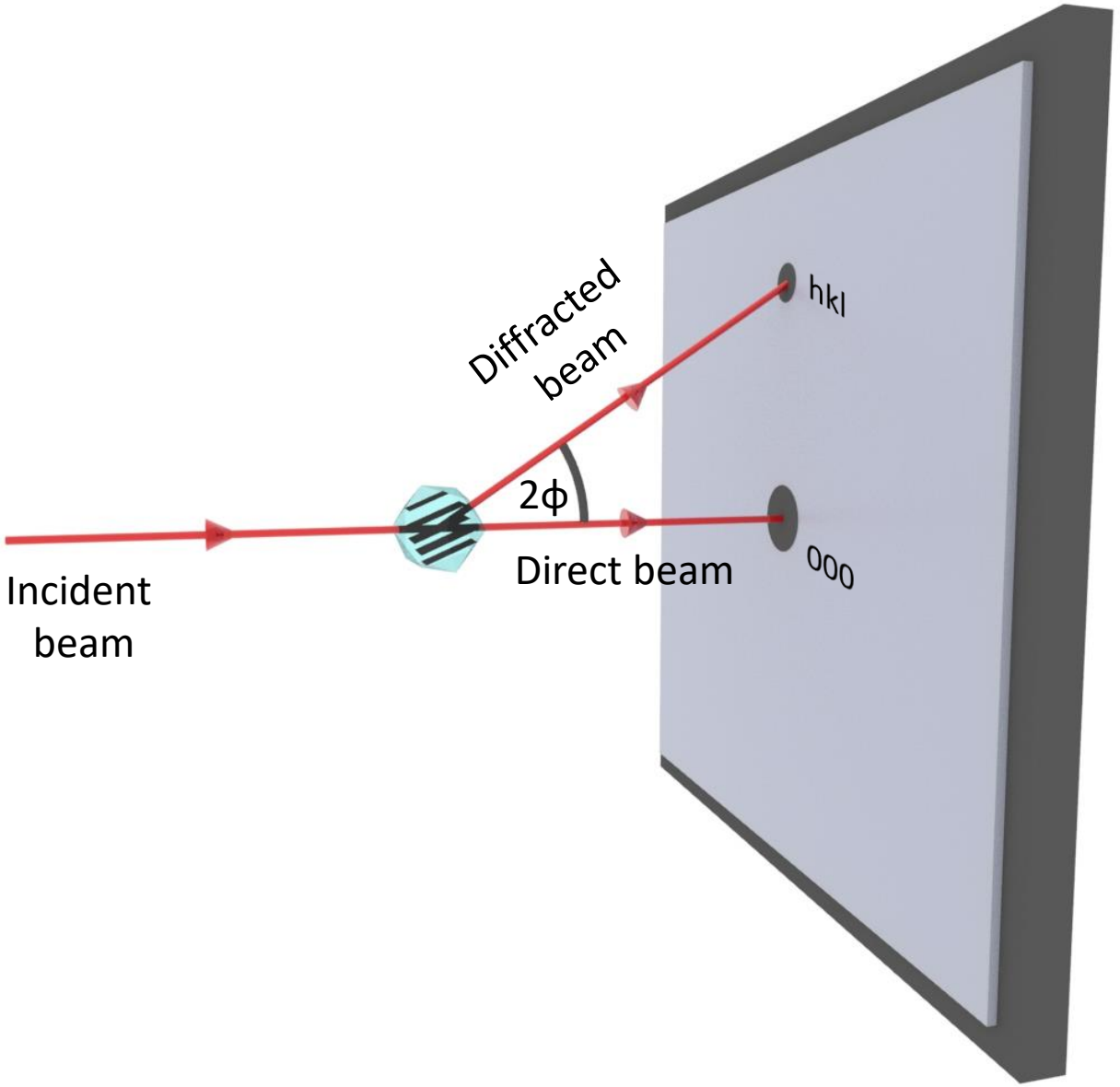


Reciprocal lattice

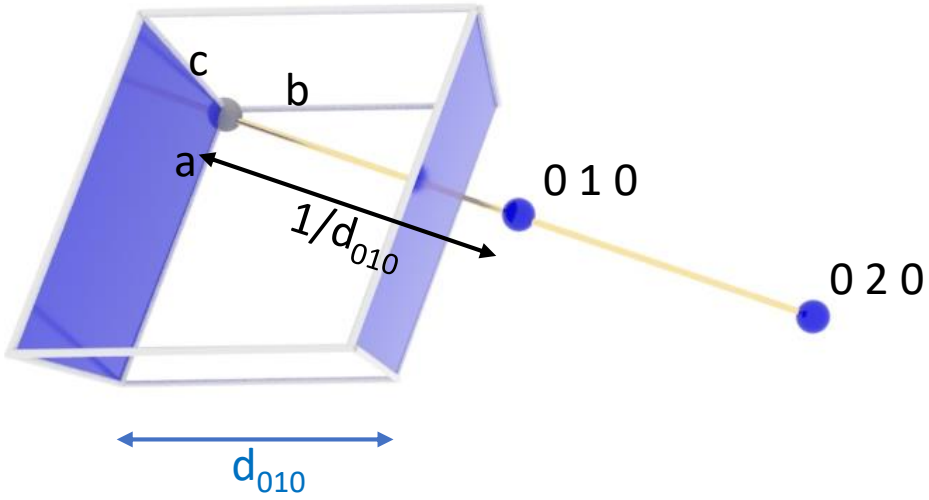
- Because of the reciprocal nature of d spacings and θ from Bragg's Law, the pattern of the diffraction we observe can be related to the crystal lattice by a mathematical construct called the reciprocal lattice.

- For each lattice plan in the real space, we can construct a point in the reciprocal lattice.

    1. We define the origin in the crystal lattice.
    2. We select a set lattice planes (h,k,l), and draw a vector with:
        - a length $1/d_{hkl}$
        - a direction normal to the set of lattice planes (h,k,l)

Reciprocal lattice

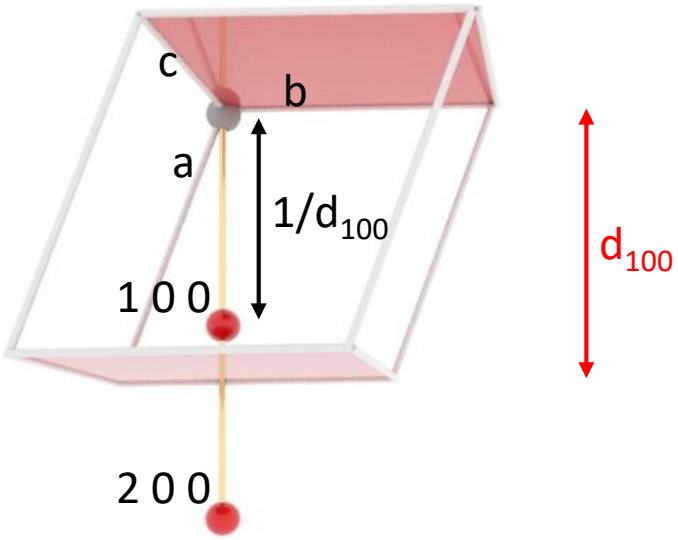
Planes: 0 1 0



Not to scale

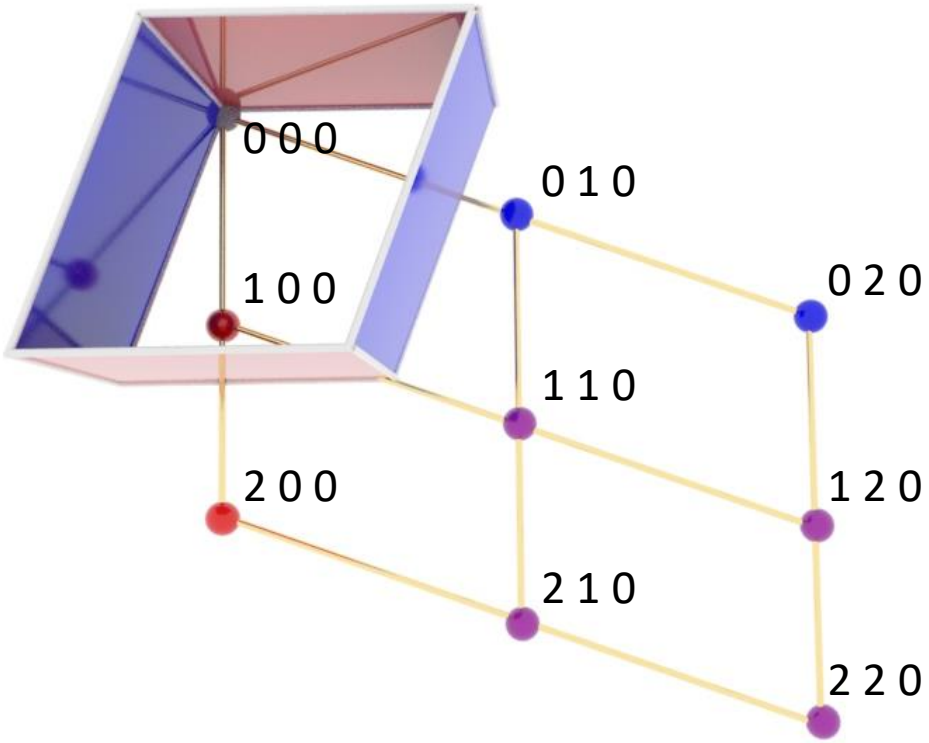
Reciprocal lattice

Planes: 1 0 0



Not to scale

Reciprocal lattice



Not to scale

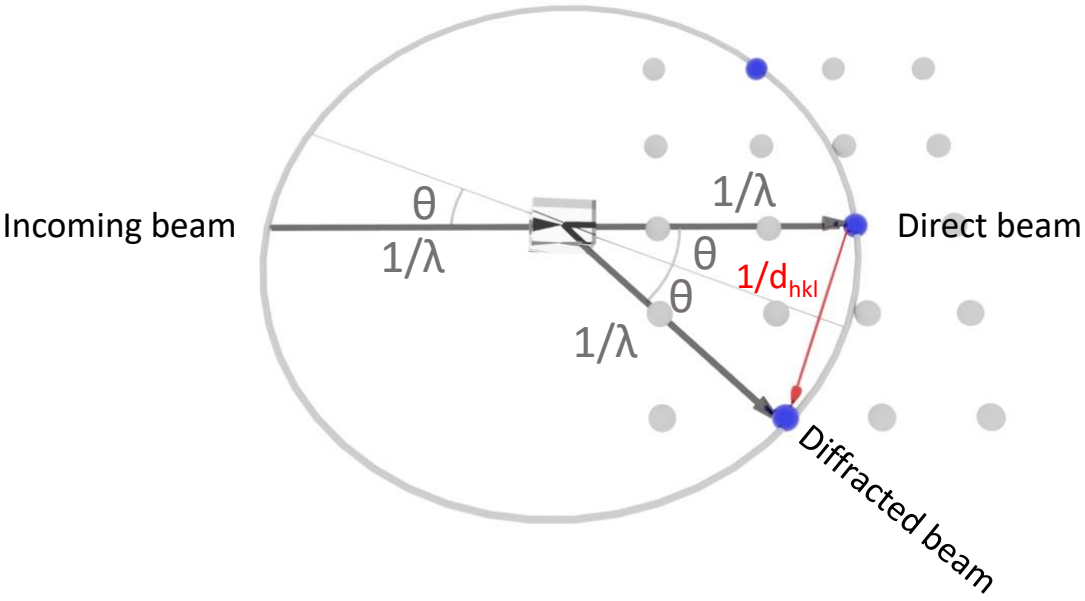
Ewald sphere

- Geometrical construction to visualise which Bragg planes are in the correct orientation to diffract.

- We define:
  - A sphere of radius = $1/\lambda$
  - The origin of the crystal is at the centre of the Ewald sphere,
  - The origin of reciprocal space is at the point where the incoming X-ray beam exits the Ewald sphere.
  - The vector S between the exit of the direct beam and the exit of the diffracted ray.

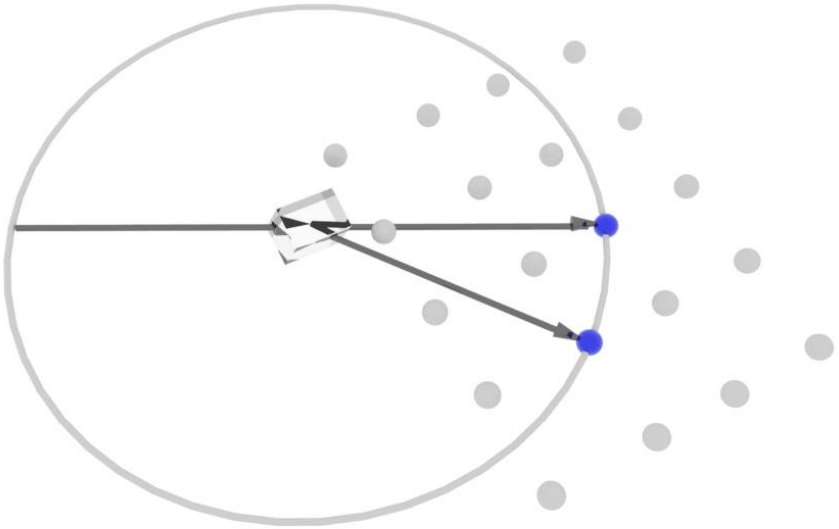
Ewald sphere

- If a set of planes is in the diffracting condition, the corresponding reciprocal space vector has to end on the surface of the Ewald sphere.



- Conversely, if the direct beam does not strike the planes with the correct angle θ, the reciprocal space vector will not be on the surface of the Ewald sphere.

Ewald sphere

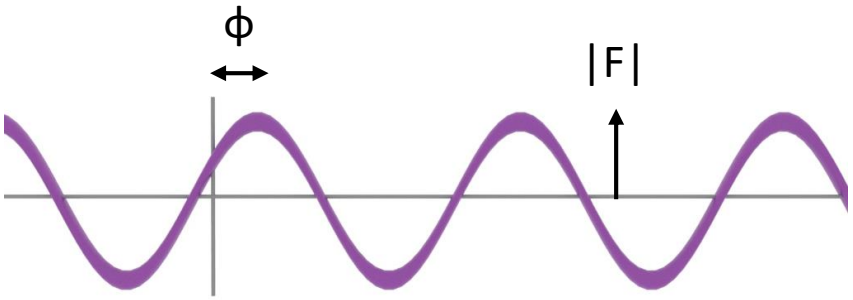


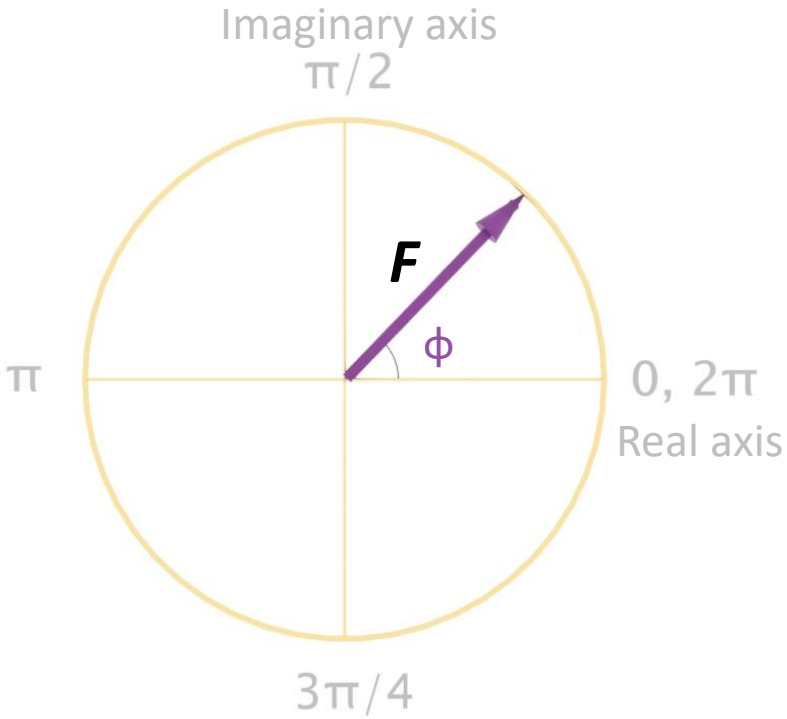
By observing the spacing and pattern of reflections on the diffraction pattern, we can determine the lengths and angles of the unit cells as well as some information on the space group.

So how do we find what is inside the unit cell?

Argand diagram

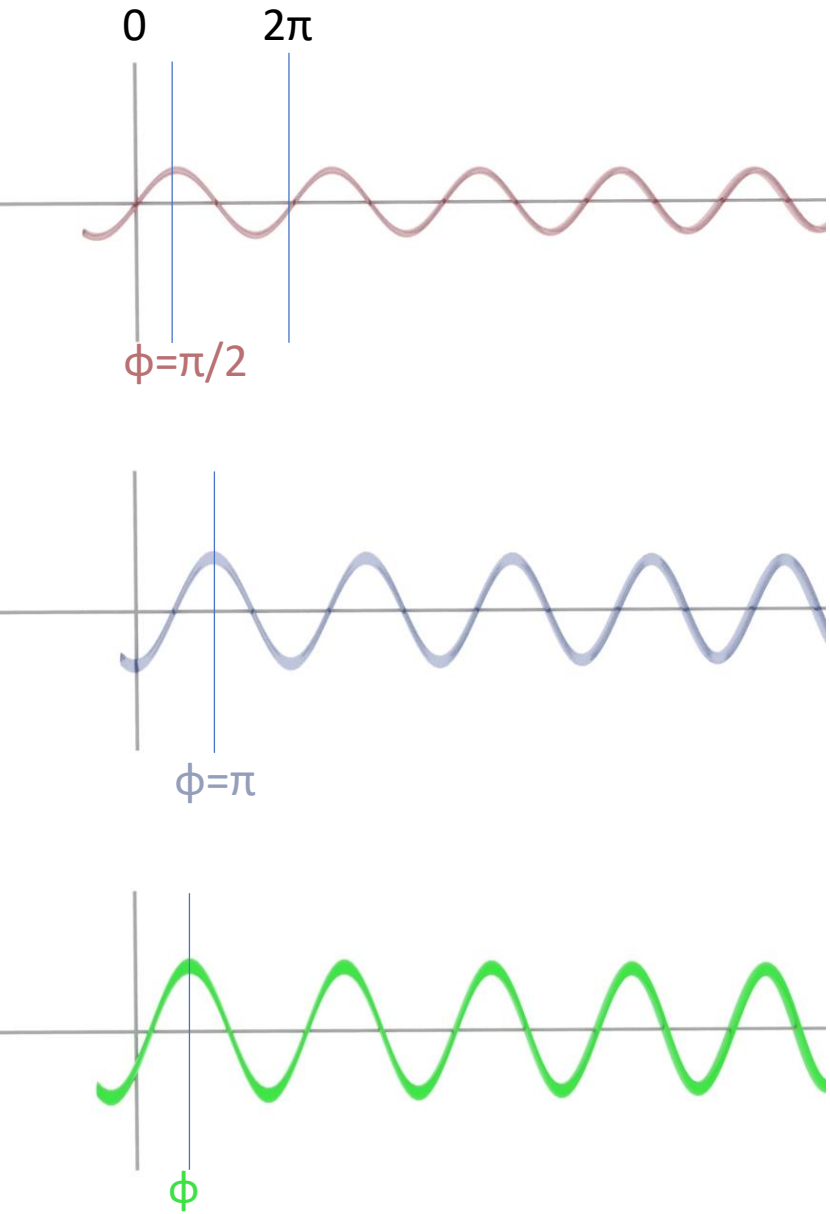
- Y axis imaginary component and x axis: real component.
- Waves (F and ϕ) are represented by vectors.
- Easier way to add waves.

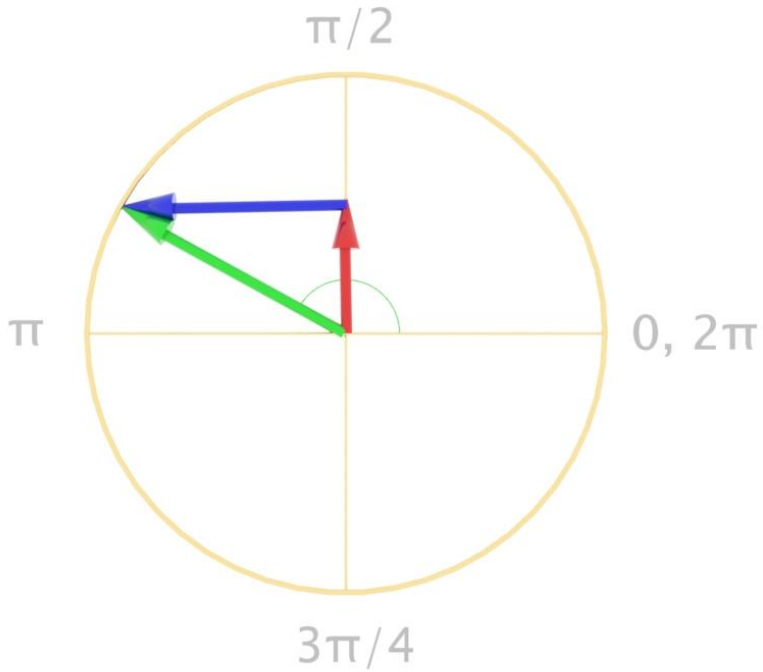




$$F = |F|.(\cos(\phi t)+i.\sin(\phi\, t)) = |F|.e^{i\phi}$$

Argand diagram

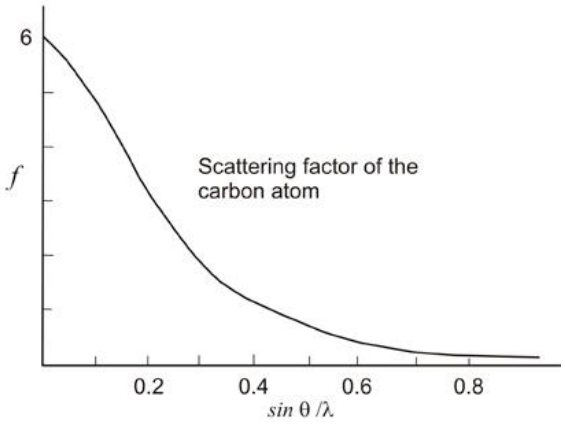




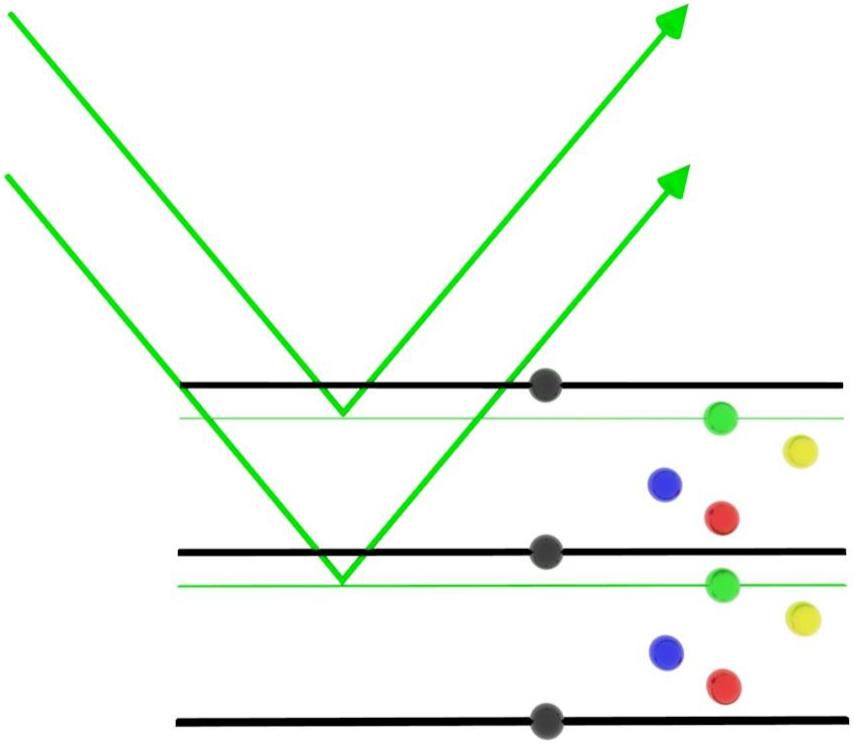
Atomic scattering factors

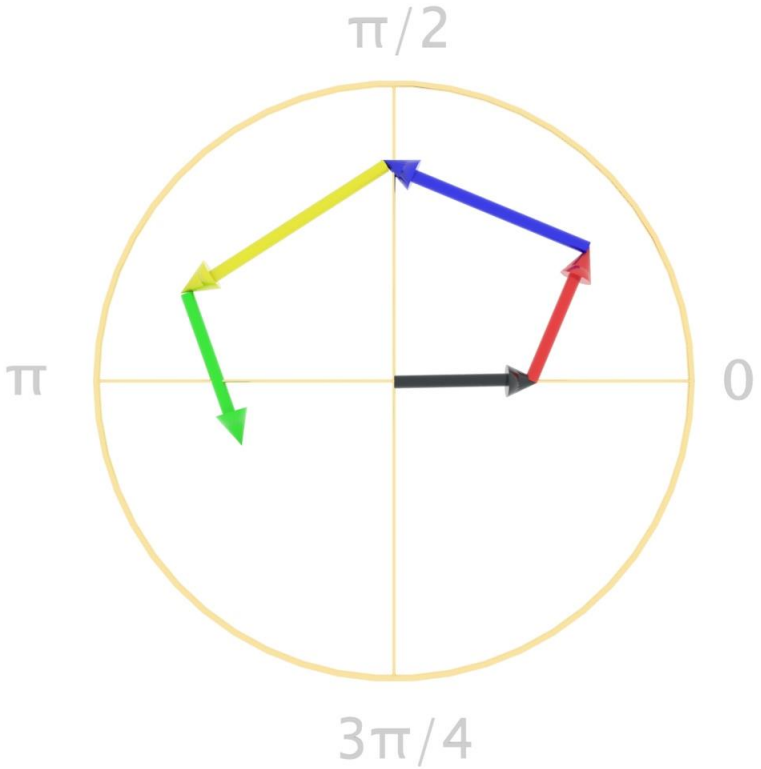
The individual atomic components (f_j) are called atomic scattering factors.

- Provide a measure of how efficiently an atom scatters X-rays compared to an electron.
- Depend on nature of atom, direction of scattering, and X-ray wavelength.
- Listed as a function of sin(θ)/λ for each atom in the International Tables.
- Maximum value of f_j is Z_j, the number of electrons of the j^{th} atom
- The atomic scattering factor is independent of the position of the atom in the unit cell.



Structure factors

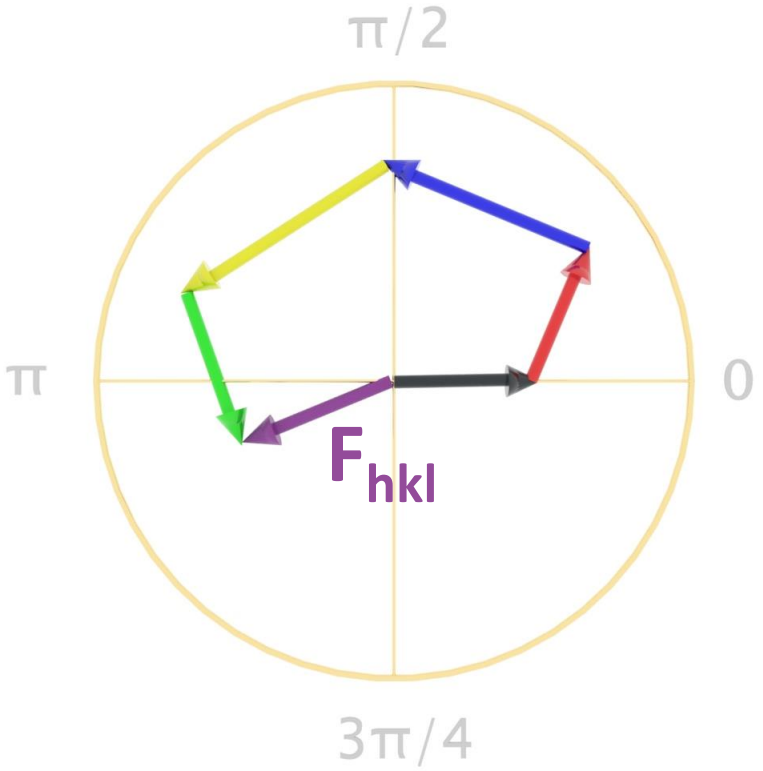




Structure factors

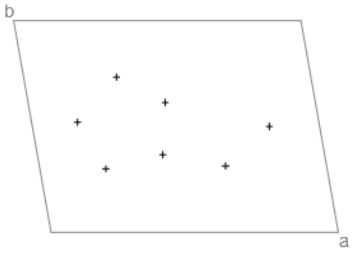
- The total scattering F_{hkl} is the vector sum of the individual atomic scattering vectors.

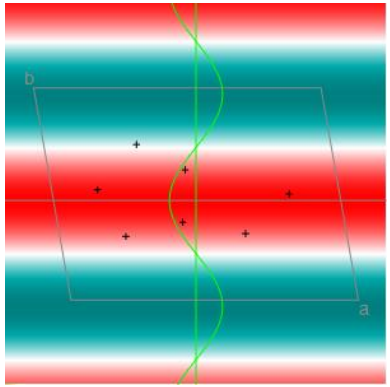
- F_{hkl} is called the structure factor because it is dependant on the structure of atoms in the unit cell.



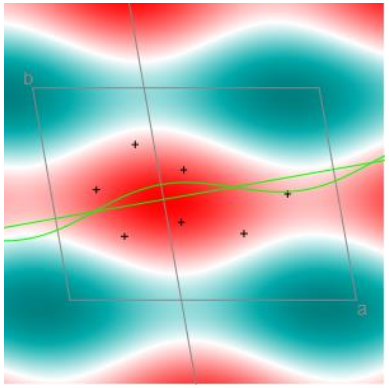
- The structure factor F_{hkl} is a mathematical function describing the amplitude and phase of a wave diffracted from crystal lattice planes h,k,l by the n atoms contained in the unit cell.

Atoms in a unit cell, structure factors and electron density.

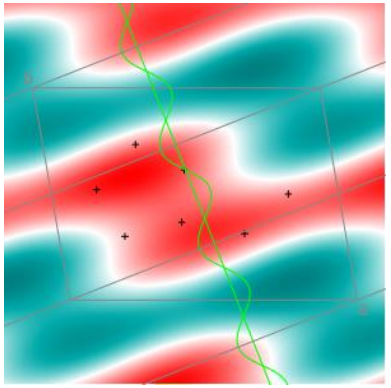




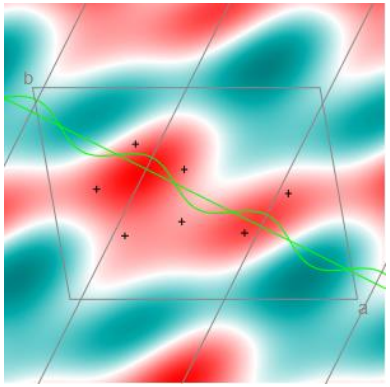
(0,1)



(1,0)



(-1,2)



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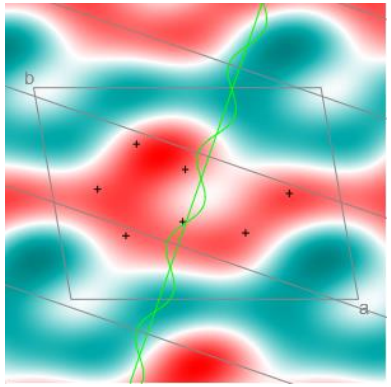
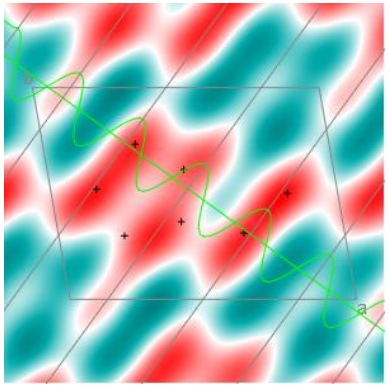
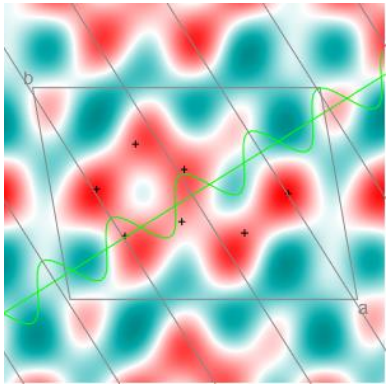


(1,2)



(3,-2)



(3,1)

http://www.ysbl.york.ac.uk/~cowtan/sfapplet/sftut3.html

$$\boldsymbol{F}(\boldsymbol{h},\boldsymbol{k},\boldsymbol{l}) = V \int_{x=0}^{1}\int_{y=0}^{1}\int_{z=0}^{1} \rho(x,y,z).\exp\left[2\pi i(hx+ky+lz)\right] dxdydz$$

Wave — Periodic function — FT

Structure factor equation

Every atom in the unit cell contribute to a every structure factor F_{hkl}.

$$\rho(x,y,z) = \frac{1}{V}\sum_h \sum_k \sum_l \left|F(h,k,l)\right| \exp\left[-2\pi i(hx+ky+lz)+i\alpha(h,k,l)\right]$$

Periodic function — Wave — FS

Electron density equation

Every F_{hkl} contribute to every atom in the unit cell.

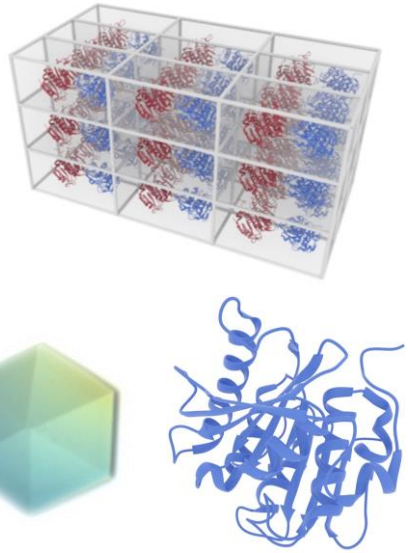
Fourier transform and synthesis

- The decomposition of a periodic function *(electron density)* into sine waves *(structure factors)* is called a Fourier transformation.
    - The structure factor equation is a Fourier transform.
    - *Data collection*

- The construction of a periodic function *(electron density)* by the summation of sine waves *(structure factors)* is called a Fourier synthesis.
    - The electron density equation is a Fourier synthesis
    - *Structure solution*

Fourier transform and synthesis

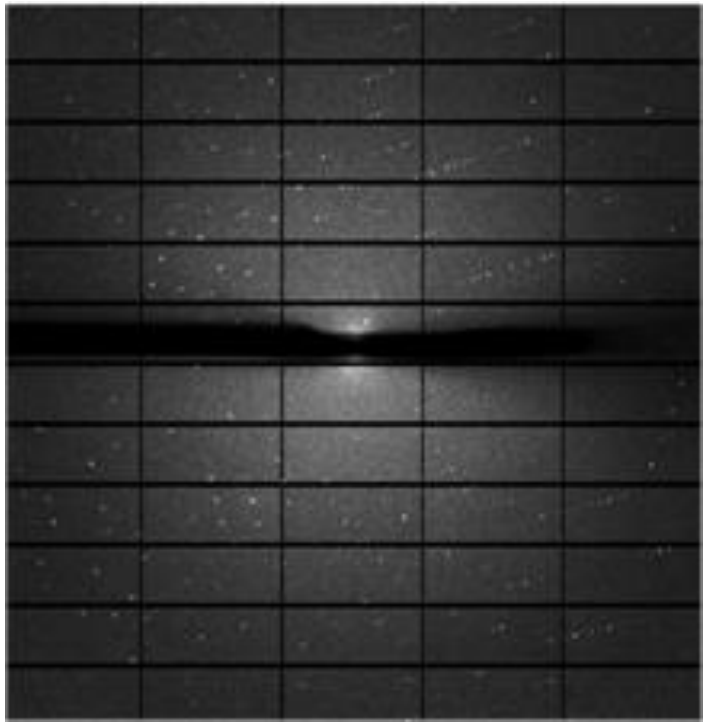
Real Space



Fourier
Transformation

Fourier
Synthesis

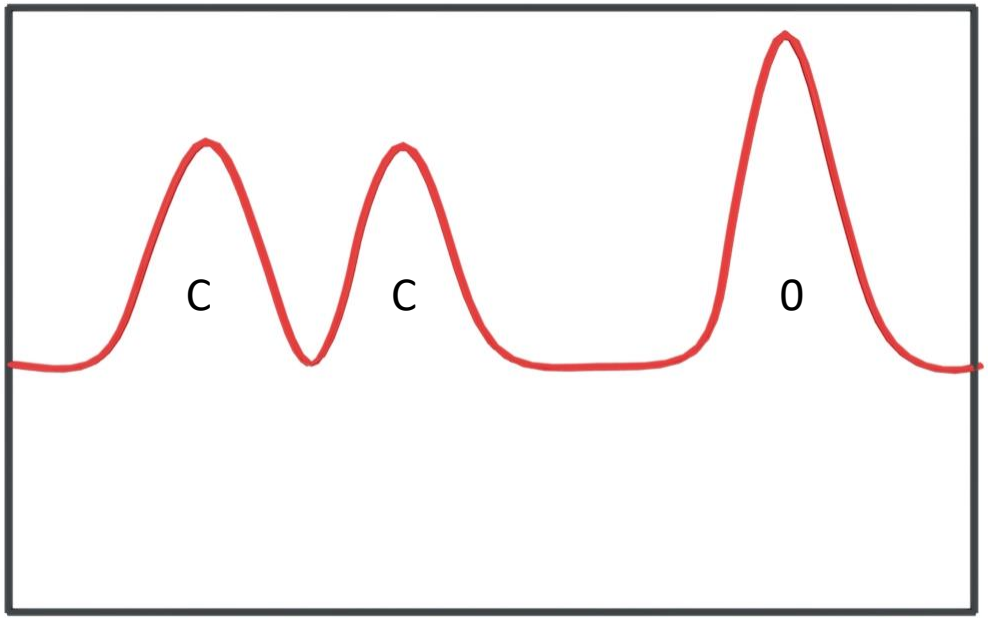
Reciprocal Space



Electron density

Structure factors

Fourier transform and synthesis

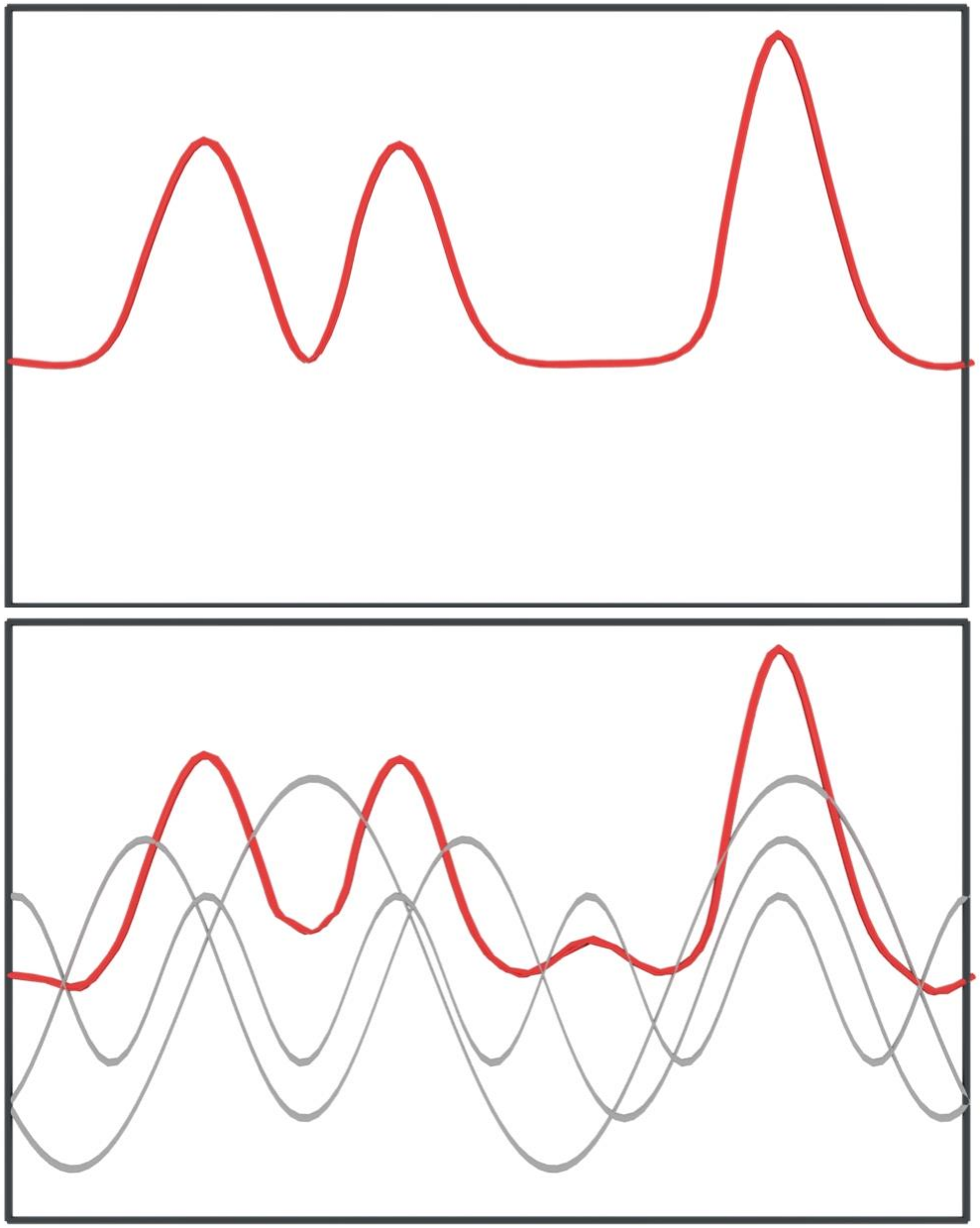


- Consider an imaginary one-dimensional crystal with 3 atoms in the unit cell. The electron density in the unit cell looks like above.

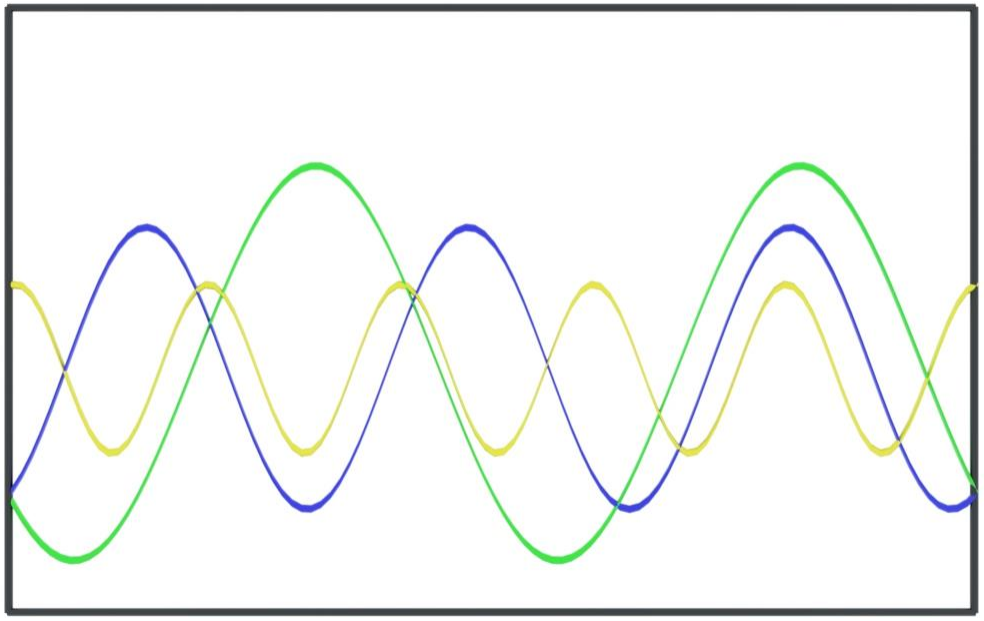
- We will represent this function in terms of sine waves with different frequency.

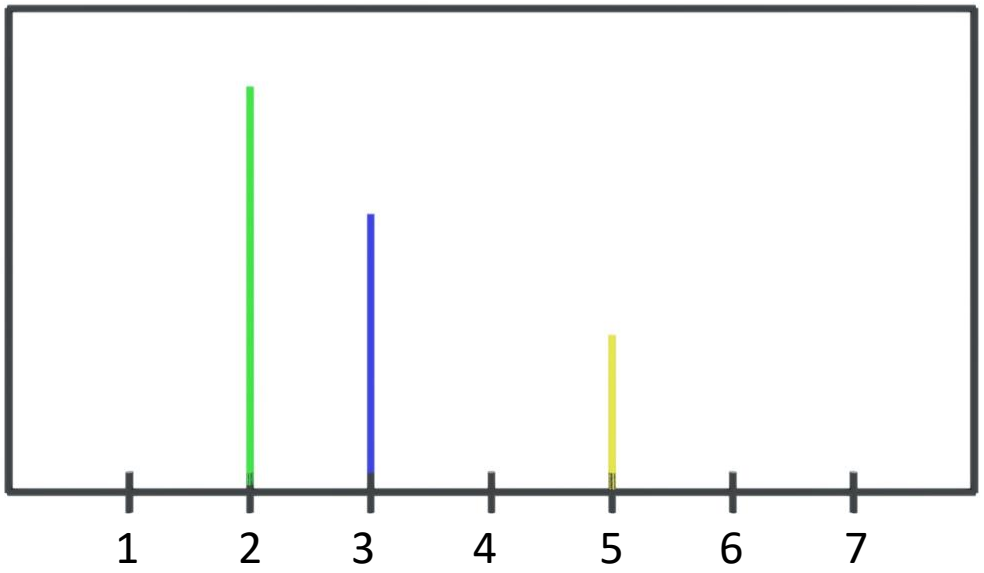
Adapted from http://www.ysbl.york.ac.uk/~cowtan/fourier/ftheory.html

Fourier transform and synthesis



Fourier transform and synthesis





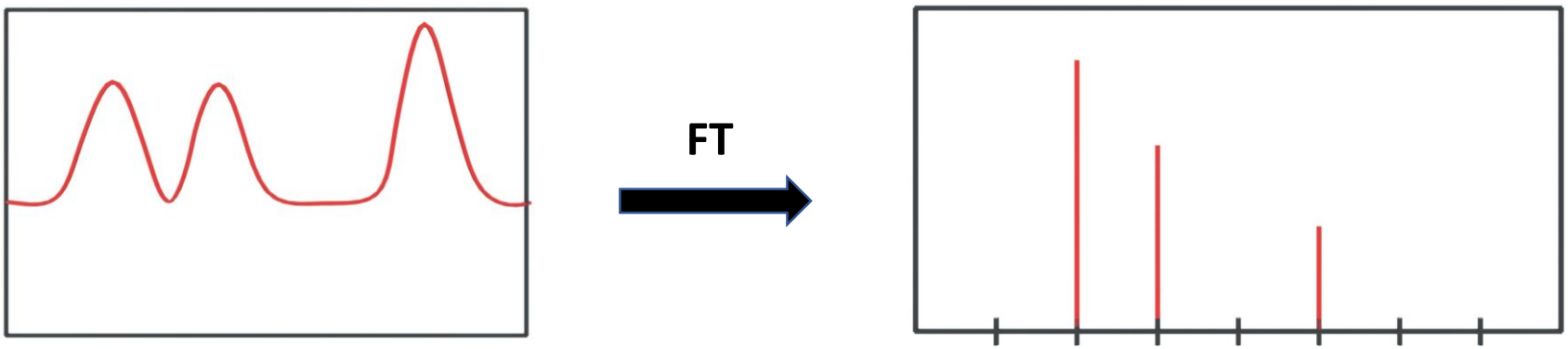
The complete set of components that are necessary to describe a periodic function is called a Fourier series.

Freq = 2

Freq = 3

Freq = 5

Fourier transform and synthesis



The Fourier Transform tells us what mixture of sine-waves is required to make up any function.

Diffraction pattern:

- Position of reflections gives information about unit cell dimensions and translational symmetry elements.

- The amplitude |F| of a particular structure factor indicates the extent to which the electron density is concentrated on planes parallel to the Bragg planes.

- The phase indicates the position of planes of high electron density relative to the Bragg planes.

Thank you for you attention!

Vocabulary

PDB: Protein Data Bank

Diffraction refers to various phenomena that occur when a wave encounters an obstacle or a slit. It is defined as the bending of waves around the corners of an obstacle or through an aperture into the region of geometrical shadow of the obstacle/aperture.

Refraction: the change in direction of a wave passing from one medium to another.

Scattering: changes of direction suffered by the incident radiation.

Dispersion: the phenomenon that causes the separation of a wave into components of varying frequency

Crystallography is the science that examines the arrangement of atoms in crystalline solids.

A **crystal** is a solid material whose constituents are arranged in a highly ordered structure, forming a crystal lattice that extends in all directions.

A **synchrotron** accelerates electrons in vacuum to extremely high energy, close to the speed of light. These fast-moving electrons produce very bright light, called synchrotron light.