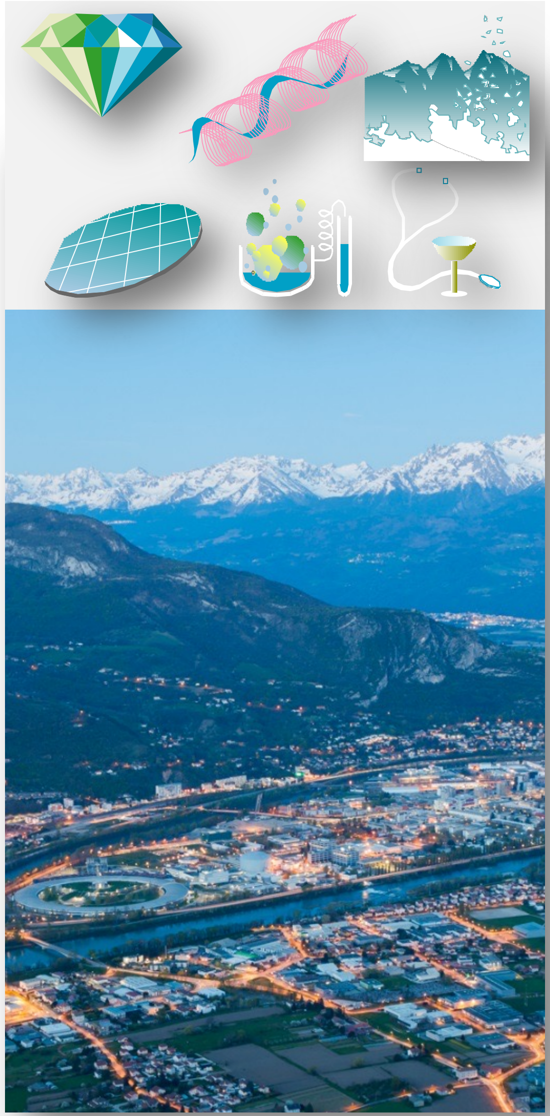
X-rays and their interaction with matter

Luigi Paolasini

European Synchrotron Radition Facility
paolasini@esrf.eu

OUTLINES

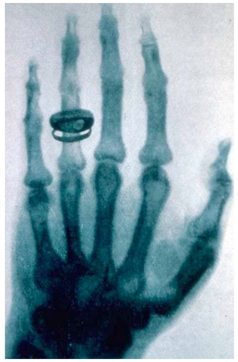


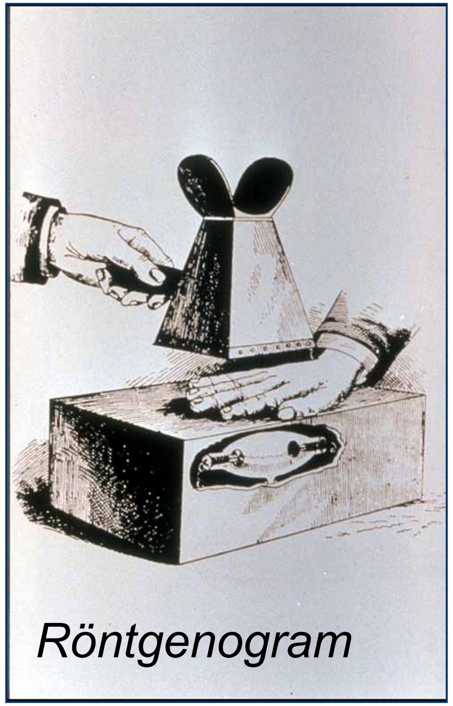
"X-rays and their interaction with matter"

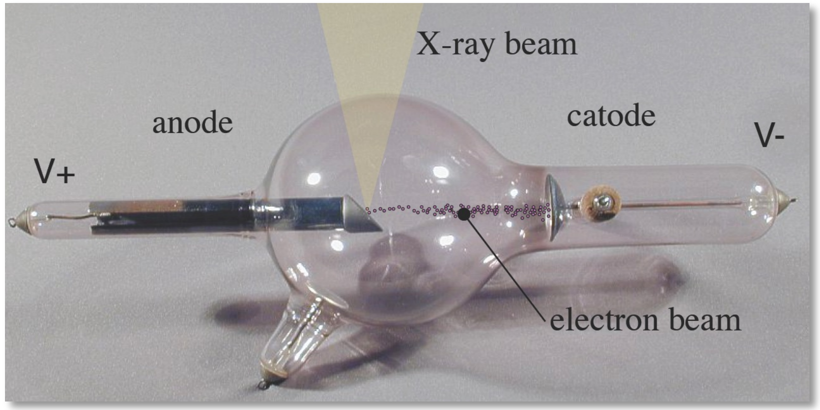
- Waves and photons
- Elastic and inelastic scattering
- Absorption spectroscopies
- Optical properties

X-RAY DISCOVERY: W.C. RÖNTGEN, 1895

Röntgen discovered a penetrating form of electromagnetic radiation able to pass through the human body: the X-rays.
X-rays are produced by collision of electrons with a metal target (kinetic energy loss, “bremstralung”)



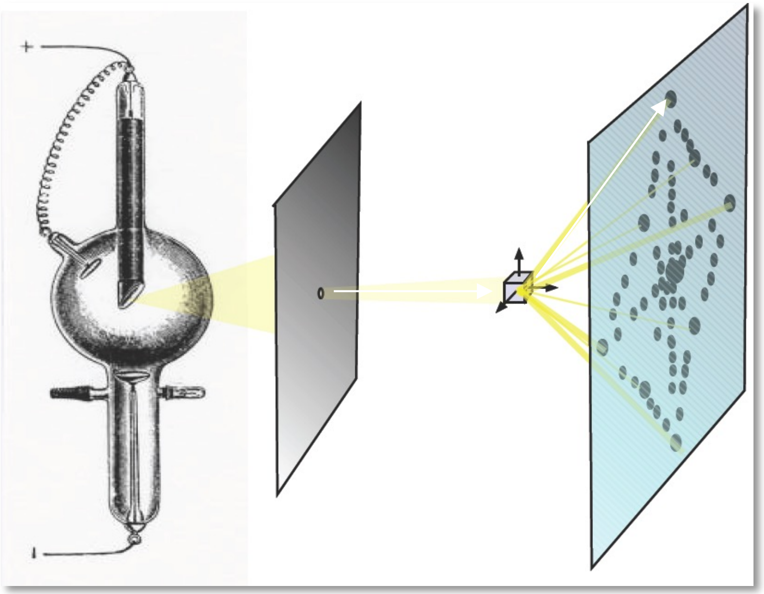


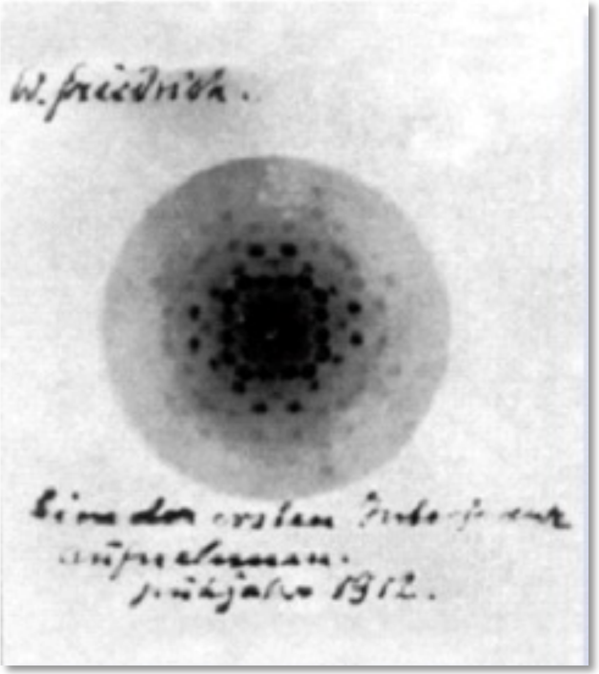


CRYSTAL DIFFRACTION: MAX VON LAUE, 1912

X-rays are electromagnetic waves:

- The x-ray wavelengths are comparable with the interatomic distances and molecular bonds.
- Typical interference x-ray patterns when pass through a periodic arrangement of atoms, like in a crystal, and reveal their crystallographic symmetries.



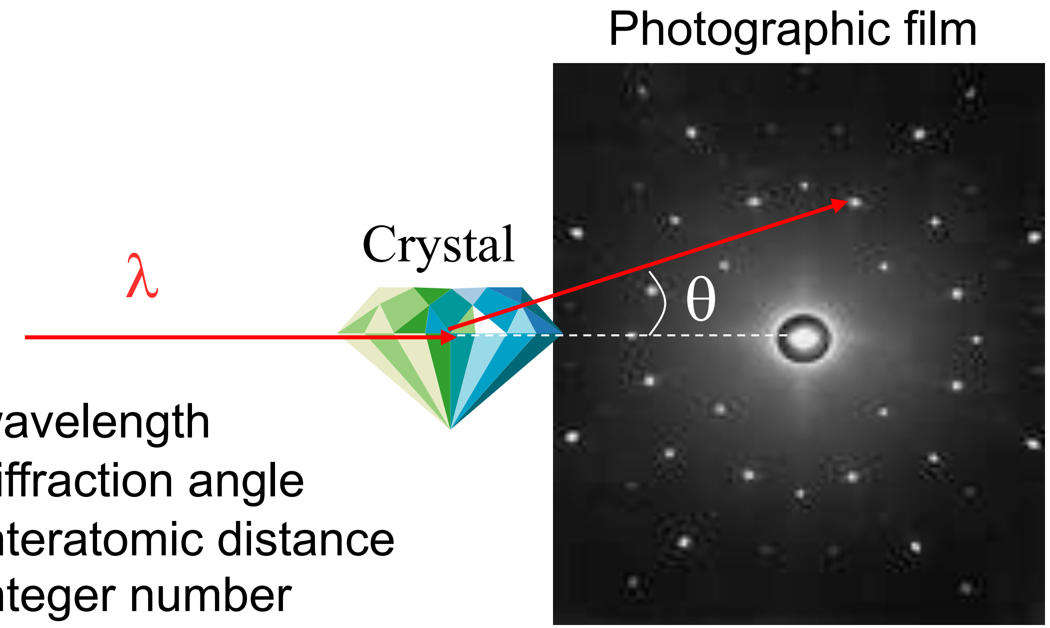


THEORY OF X-RAYS DIFFRACTION: BRAGG LAW, 1913

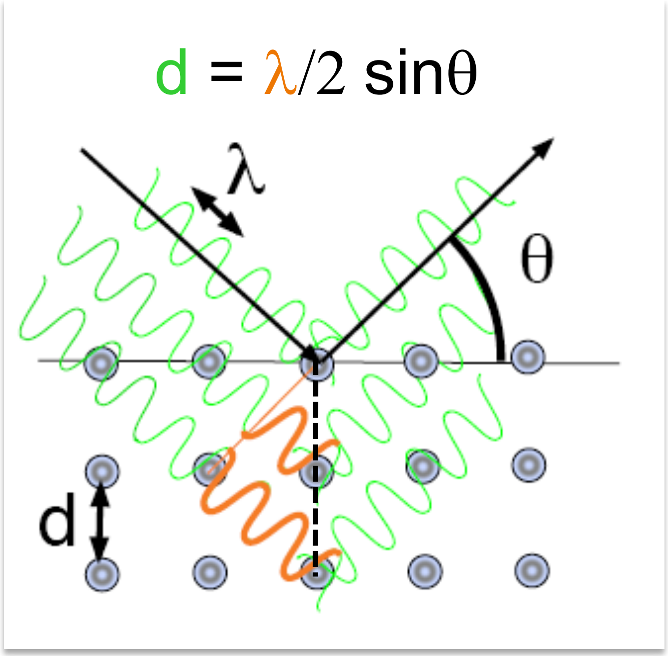
The interference X-ray pattern contains the signature of the periodic arrangement of atoms in a crystals.

The Bragg's law define the relation between interatomic distances d and scattering angle θ

Bragg Law: $2d \sin\theta = n\lambda$



λ : wavelength
θ : diffraction angle
d : interatomic distance
n : integer number

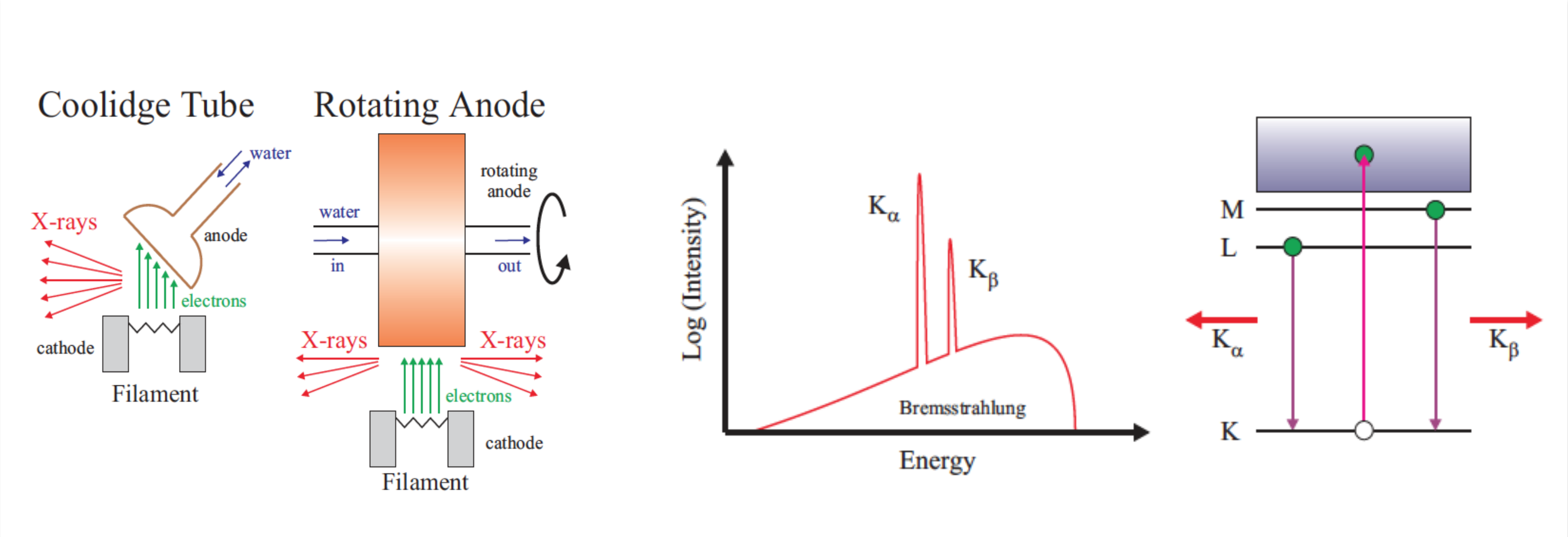


FROM COOLIDGE TUBE TO ROTATING ANODE.

W.D. Coolidge's tube from General Electric developed in 1912 served as the standard X-ray tube for many decades until the advent of rotating anode generators.

The X-ray spectrum has two distinct components:

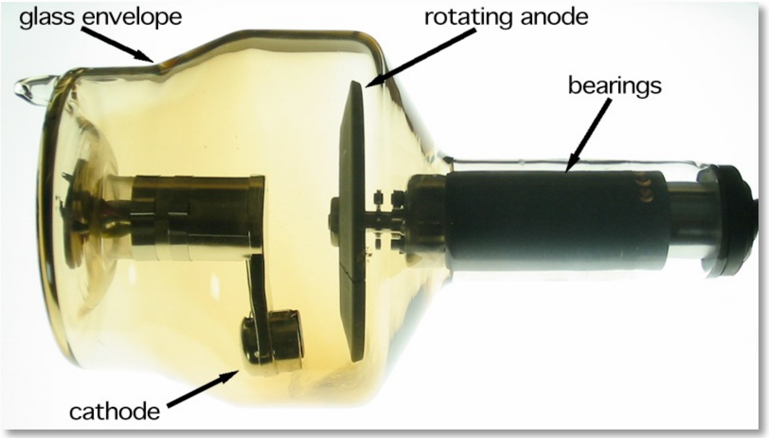
- Bremsstrahlung radiation : a continuous component
- Sharp radiations with a characteristic energy emission K_α and K_β of the metal target.
- Only 1% of the incident energy is emitted in the form of x-rays

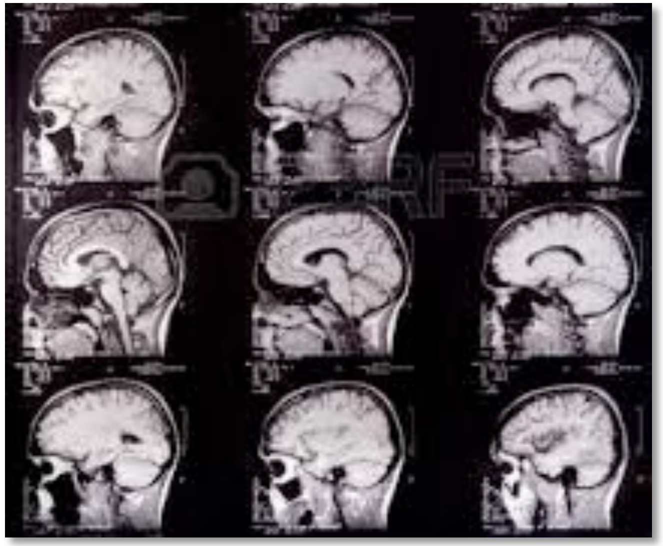


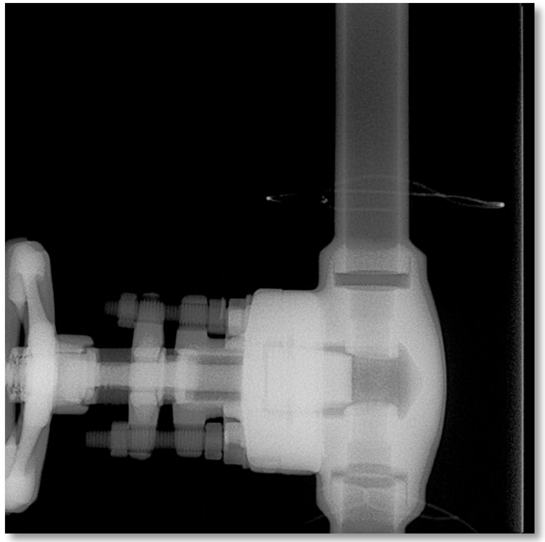
X-RAY TUBES: ROTATING ANODE

Today powerful x-rays sources can be obtained by rotating anode x-ray tubes.

X-ray tubes are also used in CAT scanners, airport luggage scanners, X-ray crystallography, and for industrial inspection.

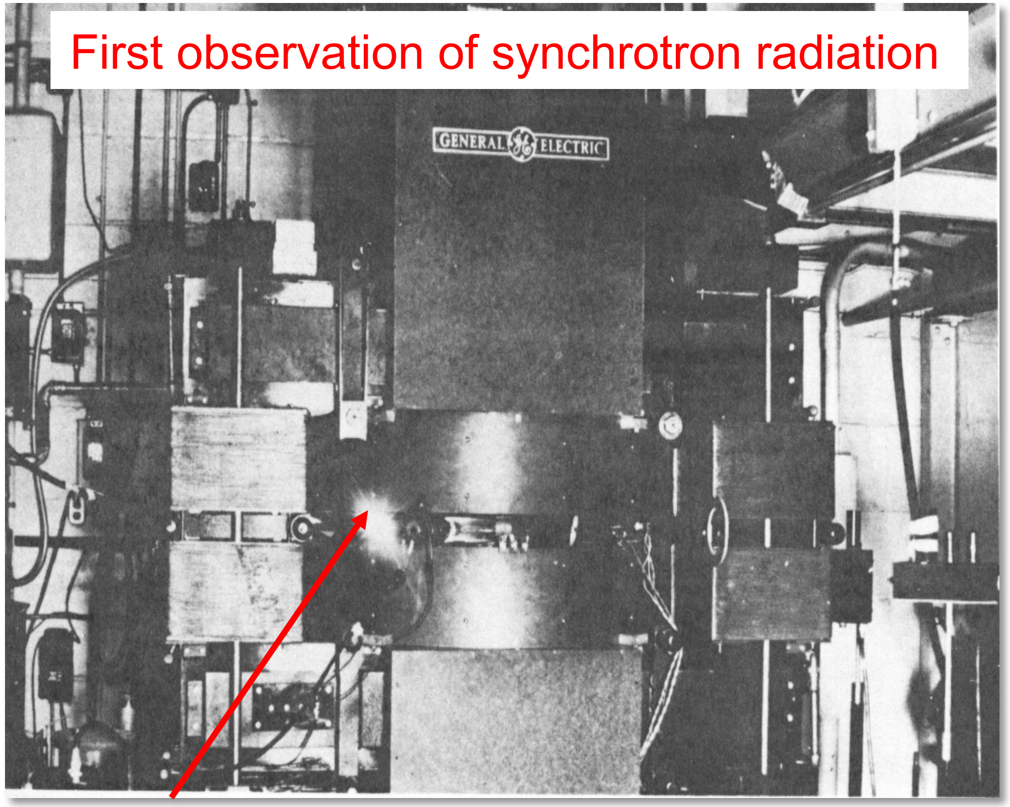






DISCOVERY OF SYNCROTRON RADIATION : GENERAL ELECTRIC 1947

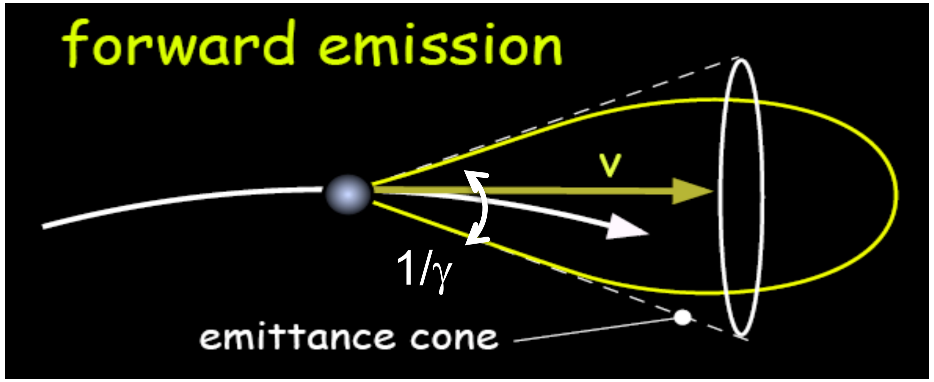
Electromagnetic radiation emitted when **charge particles** moving at ultra-relativistic energies are forced to change direction under the action of a magnetic field.



Visible light emission discovered in a 70-MeV betatron at General Electric in 1947.

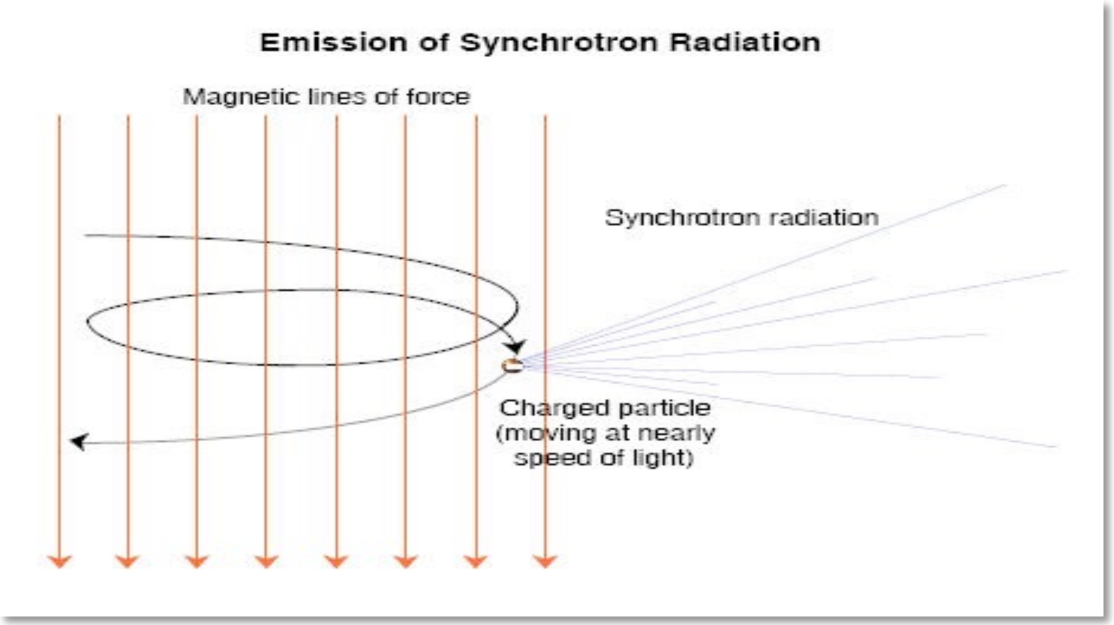
$E >> m_e c^2 \sim 0.511$ MeV

$\gamma = E/m_e c^2 >> 1$
$\gamma \sim 1957$ E[GeV]



Synchrotron emission

Most of the radiation of our galaxy is composed by synchrotron radiation.



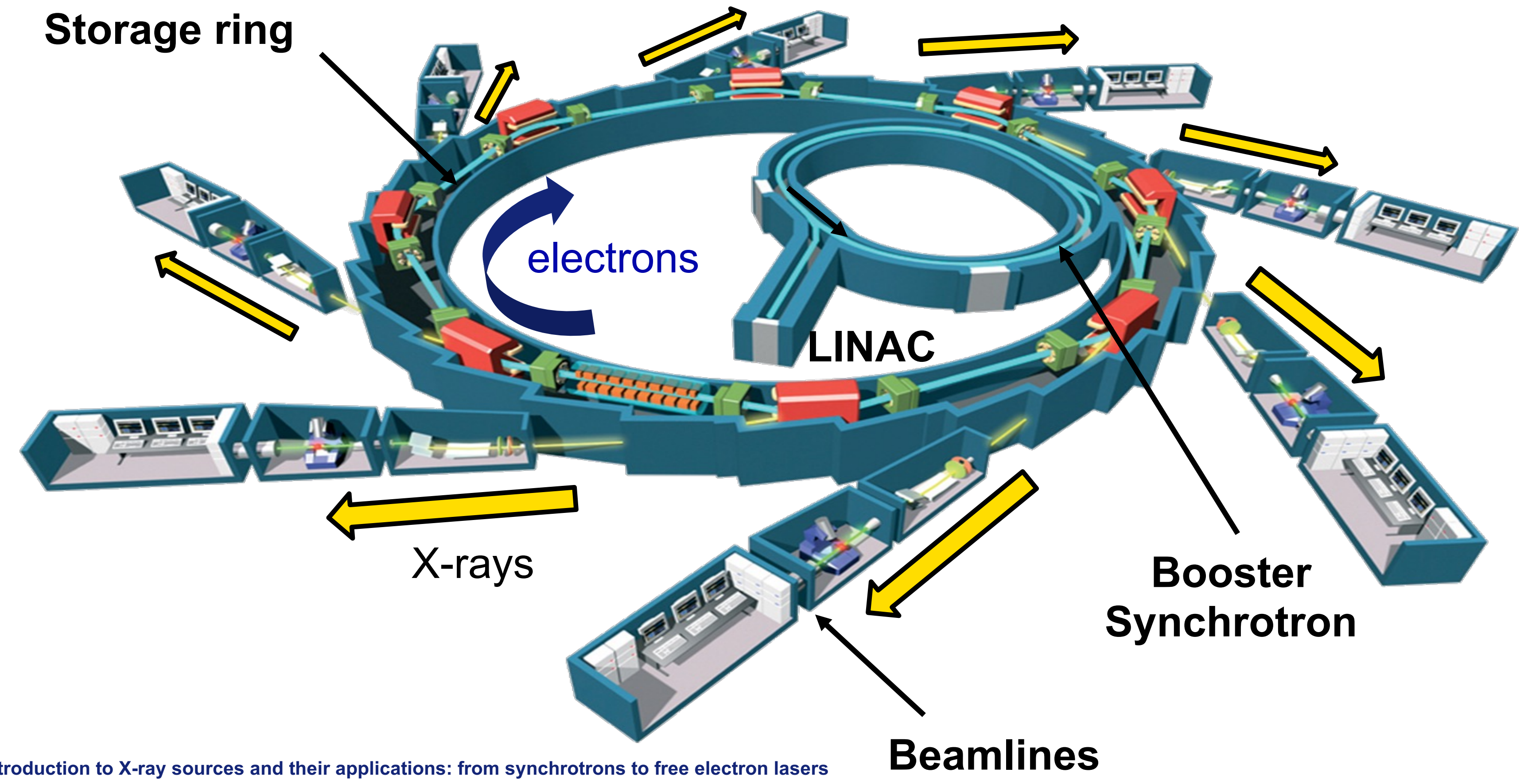
Synchrotron light was first detected in a jet emitted by M87 in 1956 by Geoffrey R. Burbidge.

Crab nebula

Gas emission (red) and synchrotron light (blu) produced by high energy electrons in the magnetic field of a neutron star (Crab nebula)

THE SYNCHROTRON RADIATION FACILITY

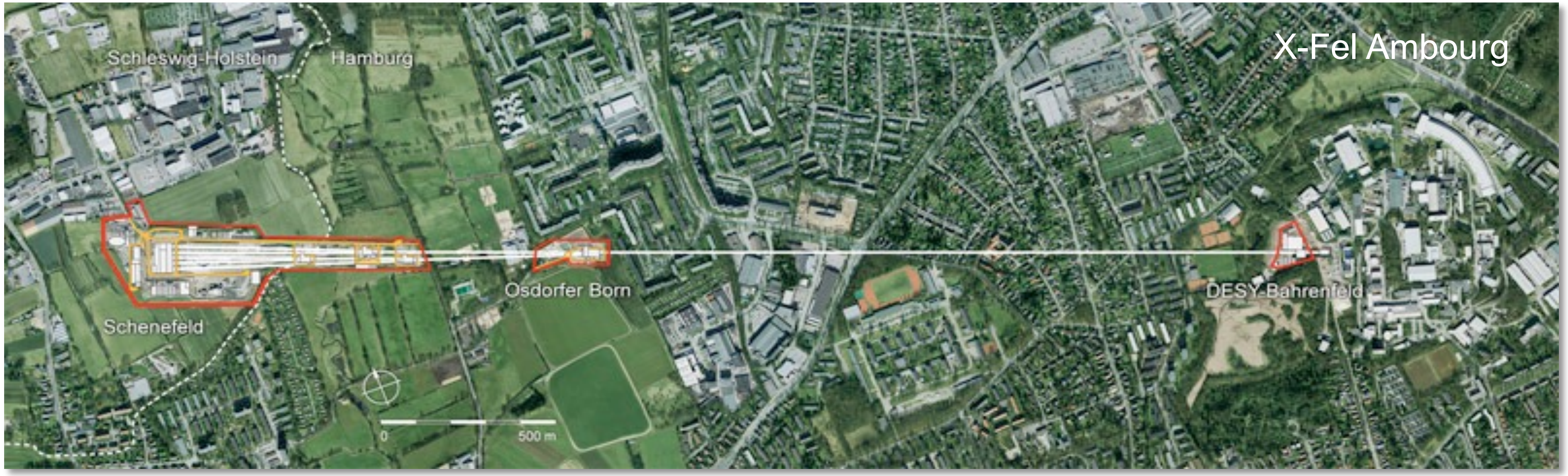
The Synchrotron is a “storage ring” where the **electrons** are first accelerated by a booster at high energies and then constrained on a circular orbit.
X-rays are produced by the insertion devices (bending magnets or undulators) and then used in the different beamlines located in the tangent of electron trajectory



X-RAYS LARGE SCALE FACILITIES

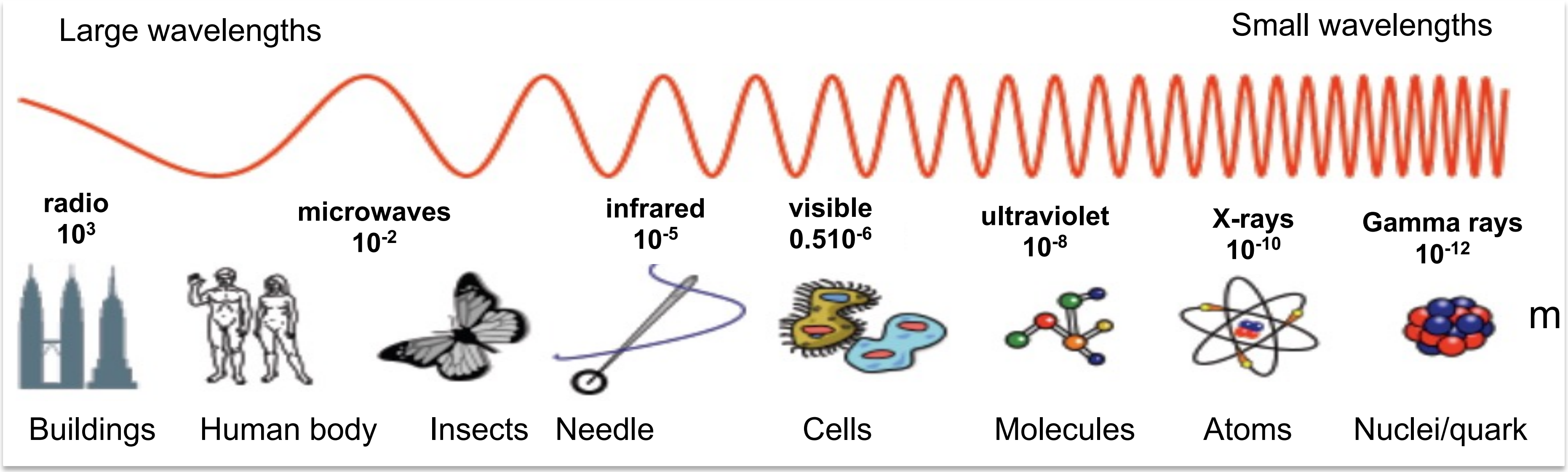
SYNCHROTRONS :
the electrons circulate in a close orbit

FREE ELECTRON LASERs:
the electrons travel in linear accelerators



X-RAYS ARE ELECTROMAGNETIC WAVES

Wavelenght : $\lambda = 2\pi/k = c/\ \nu$ Energy : $h\nu = \mathcal{E}$ Planck's constant : h

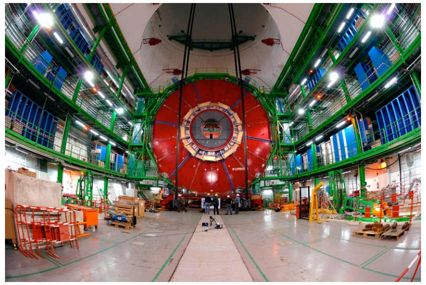



Radio waves


Radar


Microscopes


Synchrotrons


Large accellerators

X-RAYS LENGTH SCALES

ULTRA SMALL

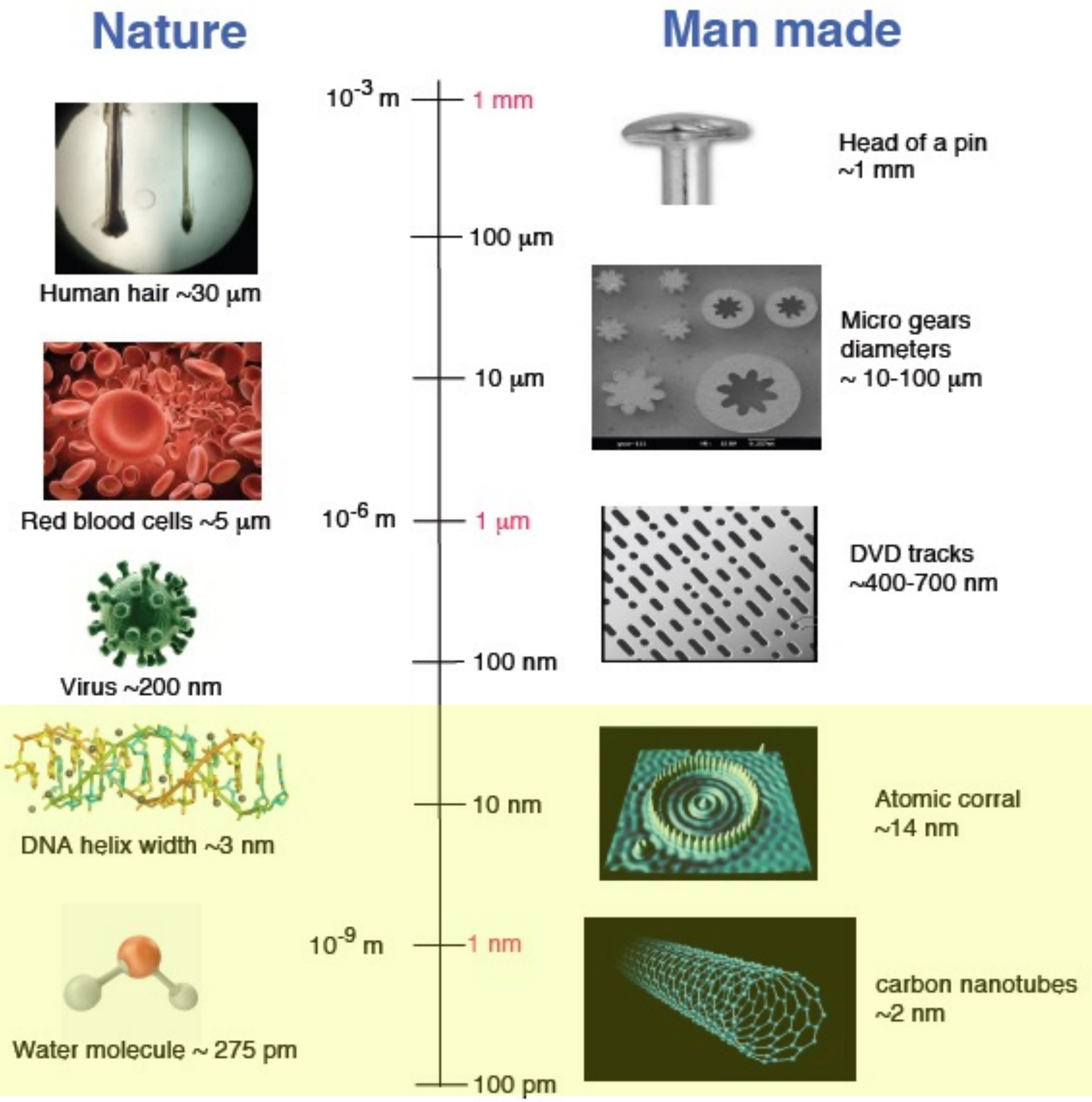
$$\mathcal{E}[\text{keV}] = \frac{hc}{\lambda} = \frac{12.398}{\lambda[\text{Å}]}$$

Planck's constant h = 4.135 x 10^{15} eV s

ex. 1 Å = 0.1 nm @ 12.398 keV

Hard X-rays
1.2 MeV - 2.5 keV ~ 0.001÷ 0.5 [nm]

Soft X-rays
2.5 keV - 100 eV ~0.5 ÷ 12 [nm]



X-RAYS TIMESCALES

ULTRA FAST

10keV X-rays

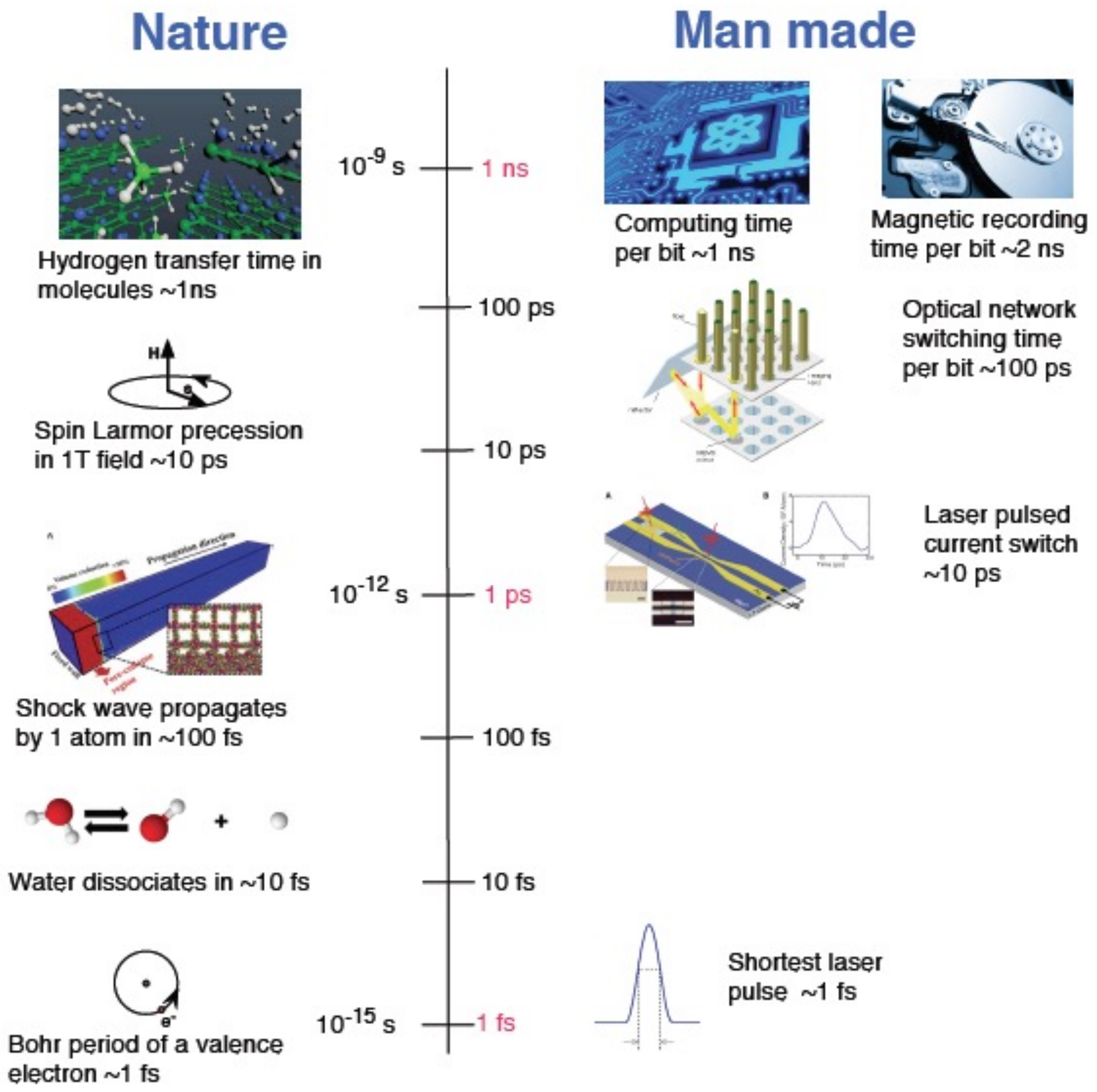
2.4 x 10^{18} Hz = 2.4 exa Hz

T = 41 x 10^{-3} fs = 41 attosecond

λ = 12.5 nm = 1.25 Å

Pulse duration ESRF
20 ps

Pulse duration X-FEL (theory)
4.5 fs



ELECTROMAGNETIC WAVES AND MAXWELL EQUATIONS

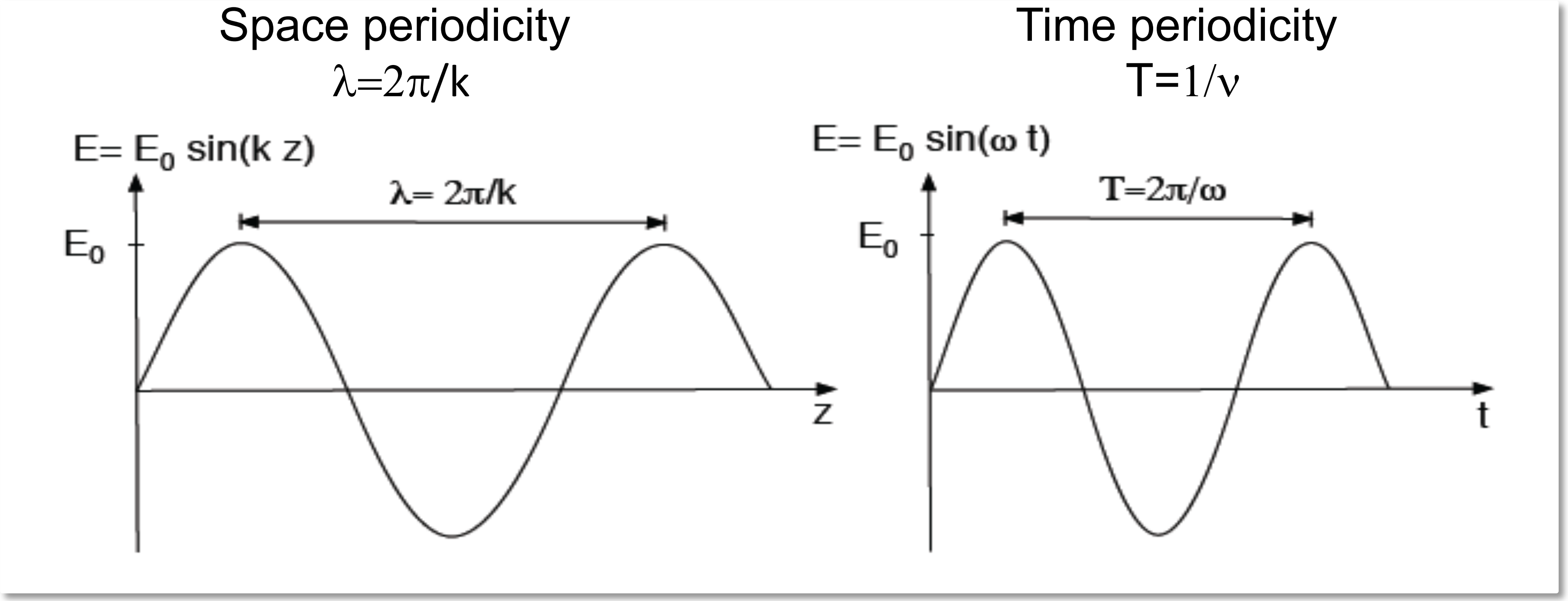
The electromagnetic field generated by the electrons is described by the electric **E** and magnetic **B** in term of scalar Φ and vector **A** potential:

$$\vec{B} = \nabla \times \vec{A}$$
$$\vec{E} = -\nabla\Phi - \frac{1}{c}\frac{\partial \vec{A}}{\partial t}$$

$$\mathbf{A} = \mathbf{A}_0 e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}$$ Vector potential

Transverse EM waves

$$\mathbf{E} = \mathbf{E}_0 e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}$$
$$\mathbf{B} = \mathbf{B}_0 e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}$$

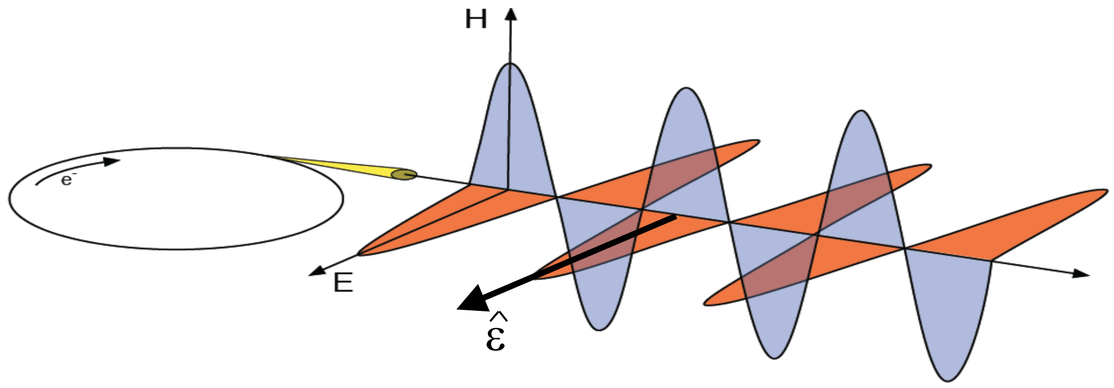


X-RAYS POLARISATIONS

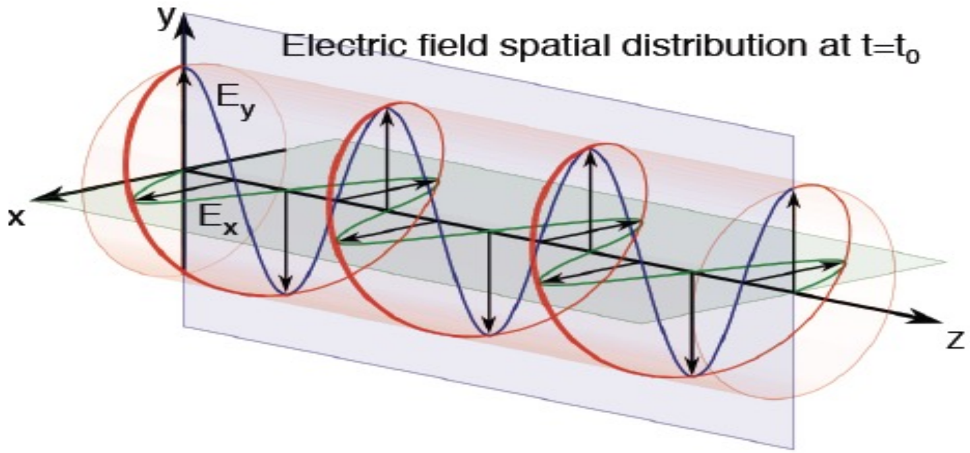
- The X-rays delivered by the insertion devices (bending magnets or undulators) are **transverse polarized** electromagnetic waves
- The polarization vector ε is parallel to the electric field **E**.
- Some particular insertion devices can also deliver circular polarization (ex. helical undulators, phase plates)

Linear transverse EM wave

$$\vec{\mathbf{E}}(\vec{\mathbf{r}}, t) \quad = \quad \hat{\epsilon} E_0 e^{i(\vec{\mathbf{k}}\cdot\vec{\mathbf{r}}-\omega t)}$$

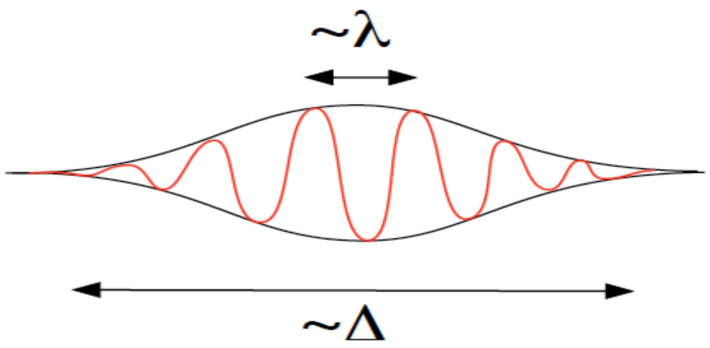


Circular transverse EM wave



WAVE - PARTICLE DUALITY

Description of the behaviour of a quantum-scale objects.

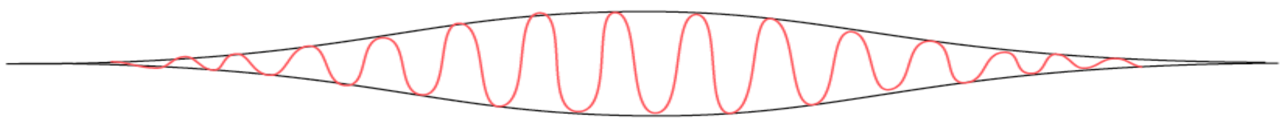


Heisenberg uncertainly principle:

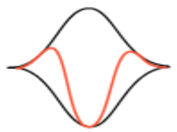
Cannot define both Δ and λ to an arbitrary accuracy

Oscillations → wave
Envelope → particle localization

Wave: Δ>>λ



particle: Δ<<λ



Decreasing Δ to define better the position, but we lose information on λ

Energy: $E = h\nu = \hbar\omega$

Momentum: $p=h/\lambda = \hbar k$

where
h= Planck's constant
ν=frequency
k=wavevector

WAVES AND PHOTONS : QUANTUM MECHANICS ASSUMPTIONS

(i) Particles are represented mathematically by a wavefunction, $\psi(\underline{r})$

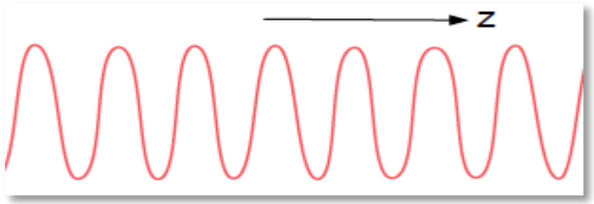
(ii) Probability of finding a particle in a (infinitesimal) volume dV is $|\psi(\underline{r})|^2 dV$

Infinite plane wave (spatial part):

$\psi(\underline{z}) = e^{ikz} = \cos(kz) + i \sin(kz)$

$|\psi|^2 = \psi\psi^* = e^{ikz}e^{-ikz} = 1$

1 particle per unit volume everywhere!

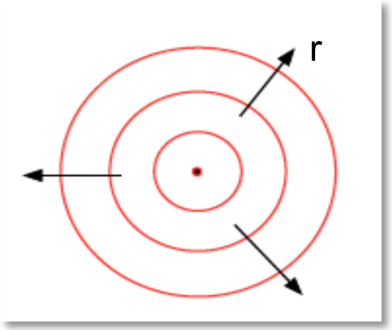


Spherical wave:

$\psi(\underline{r}) = b/r \, e^{ikr}$

$|\psi(\underline{r})|^2 = \psi\psi^* = b^2/r^2$

Density of particles falls as $1/r^2$



Flux of particles

I = No. of particles incident normally on unit area per second =

= particle density x velocity

$= |\psi|^2 \times v = |\psi|^2 \; \hbar k/m \qquad (m^{-2} s^{-1})$

TOTAL SCATTERING CROSS SECTION

Total cross section: Effective area viewed by scattering particles!

$$\sigma = \frac{\text{Total no. particles scattered in all the directions per second}}{\text{Incident flux}}$$

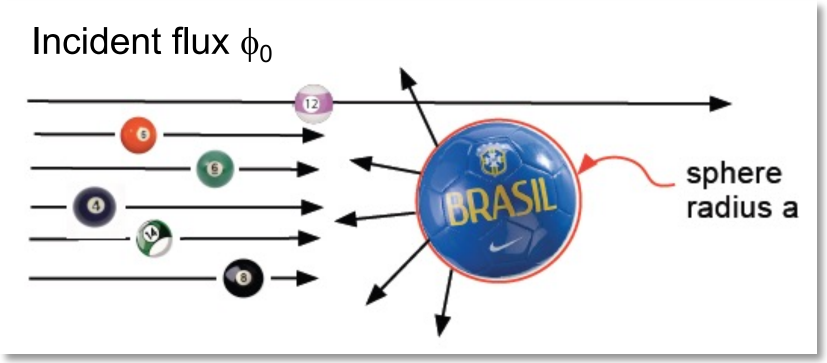
Classical case:

no. particles scattered per second = $\phi_0 \times \pi a^2$

$\sigma = \pi a^2$

n. Particles x unit area x sec.

Cross-sectional area of sphere



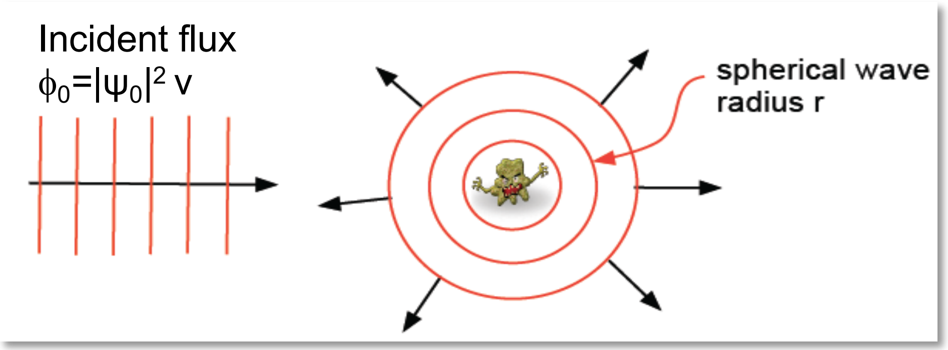
Quantum case:

Incident wave	$\psi_0 = e^{ikz}$
Incident flux	$\phi_0=\vert\psi_0\vert^2\, v = v$
Scattered wave	$\psi_{sc} = b/r\, e^{ikr}$
Scattered flux	$\phi_{sc}=\vert\psi_{sc}\vert^2\, v = b^2 v/r^2$

no. particles scattered per second = $\phi_{sc} \times 4\pi r^2$

$\sigma = 4\pi b^2$

b= scattering length



DIFFERENTIAL SCATTERING CROSS SECTION

Definition:

$$\frac{d\sigma}{d\Omega} = \frac{\text{Number of particles scattered into solid angle } d\Omega \text{ per sec.}}{\text{incident flux} \times d\Omega}$$

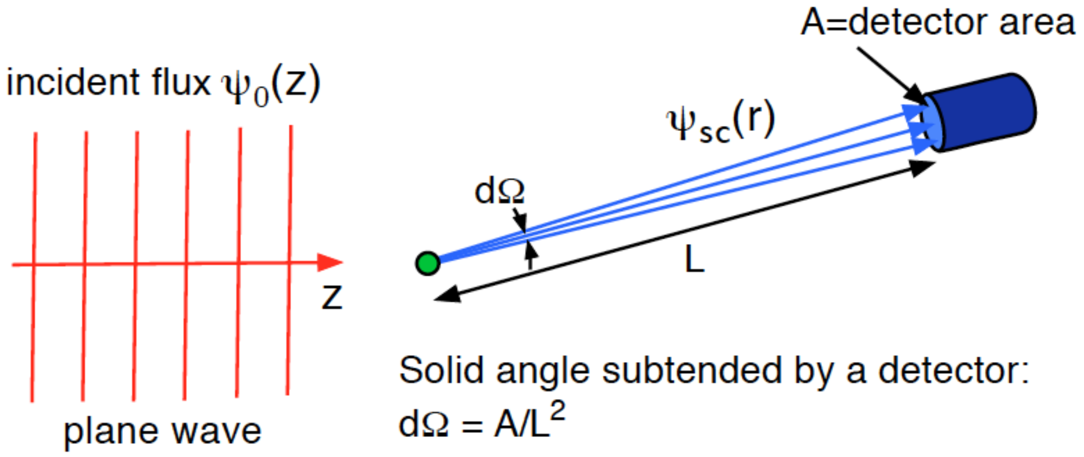
Solid angle subtended by the detector:

$$\Delta\Omega = A/L^2$$

No. particles detected per sec.:

$d\sigma/d\Omega = (|\psi_{sc}|^2 v \;\; x\, A) / (|\psi_0|^2 v\, d\Omega)$

$|\psi_{sc}|^2 = b^2/L^2$ Detector area



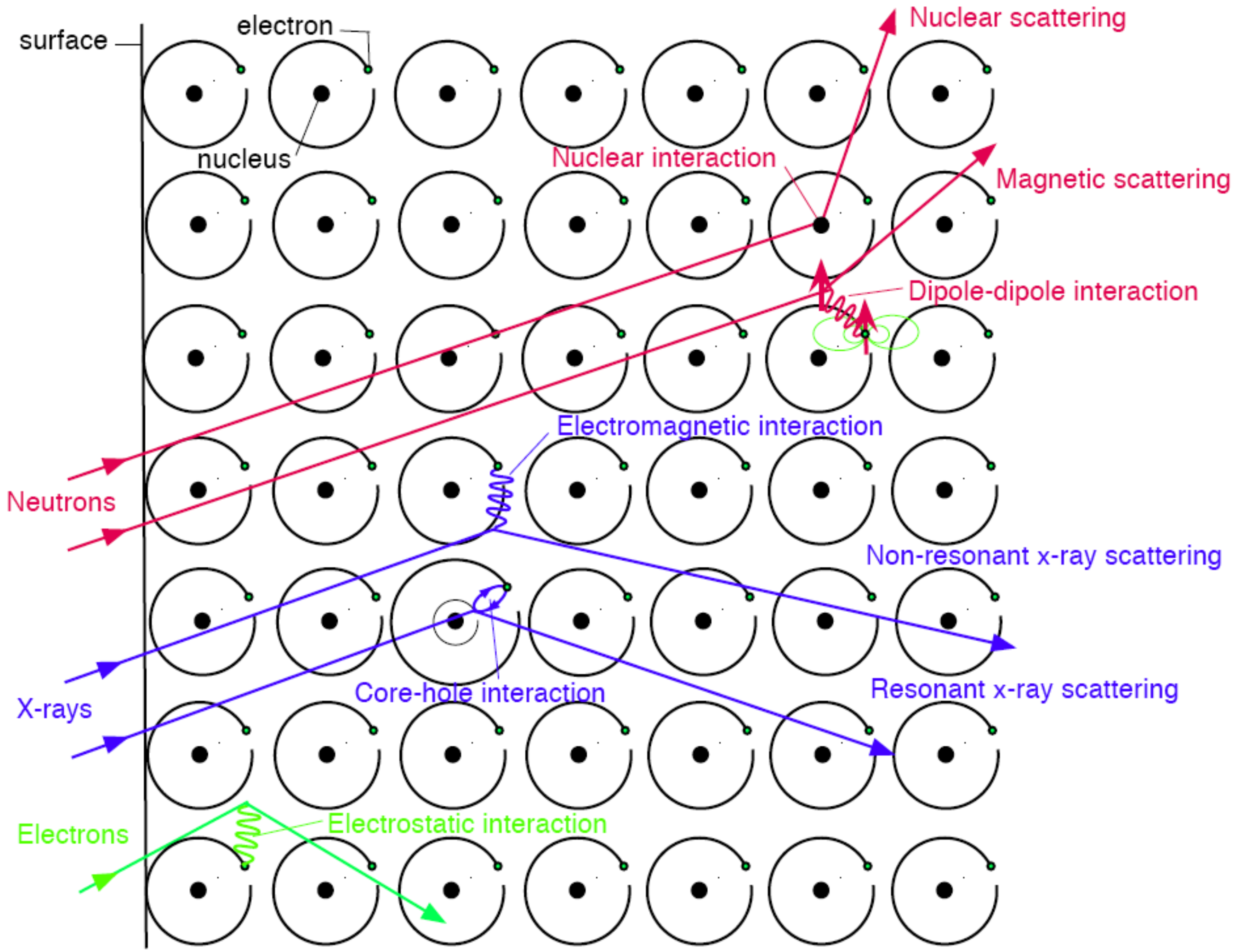
$$\frac{d\sigma}{d\Omega} = \frac{|\psi_{sc}|^2}{|\psi_0|^2} L^2 = b^2 = \frac{\sigma}{4\pi}$$

(barns/steradian)   1 barn=10^{-28} m^2

Notice that ψ_{sc} is a spherical wave $|\psi_{sc}|^2 = b^2/L^2$

SCATTERING PROBES AND INTERACTION POTENTIALS

The scattering length **b** depends from the type of interaction potential with the scattering probes

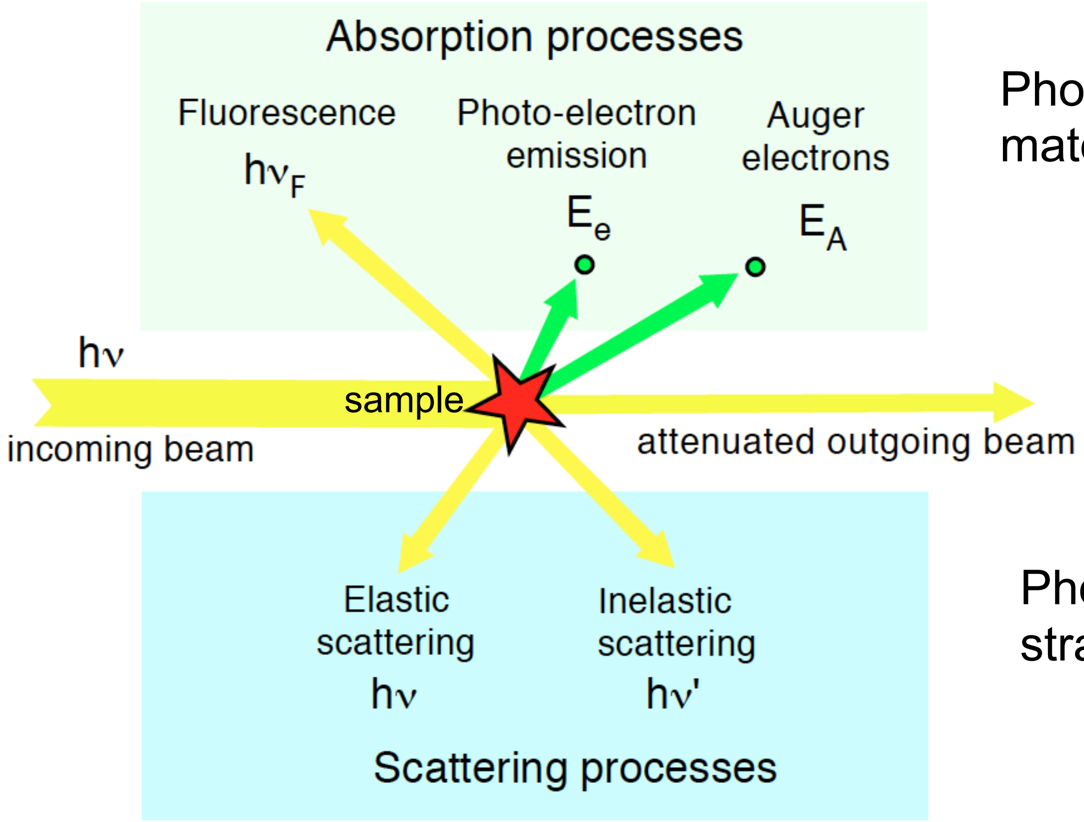


Neutrons:
Nuclear and magnetic interaction

X-rays:
Electromagnetic and core-hole interactions

Electrons:
Electrostatic interaction

X-RAY MATTER INTERACTION



Photons are totally absorbed by the material

Photons are deviated by their straight direction

Photon absorption/emission : Excitation with or without emission of electrons

Photon scattering :

Elastic coherent	=> Thomson
Inelastic incoherent	=> Compton
Resonant	=> elastic or inelastic

X-RAY ELASTIC SCATTERING BY A FREE ELECTRON

- The incident electric field E_{in} forces the motion of the electron : Lorentz's Force **F=qE**
- **Re-radiation** of a spherical wave E_{rad}

Radiated spherical field E_{rad} at observer position R:

- proportional to the electron acceleration

- anti-phase with respect E_{in}

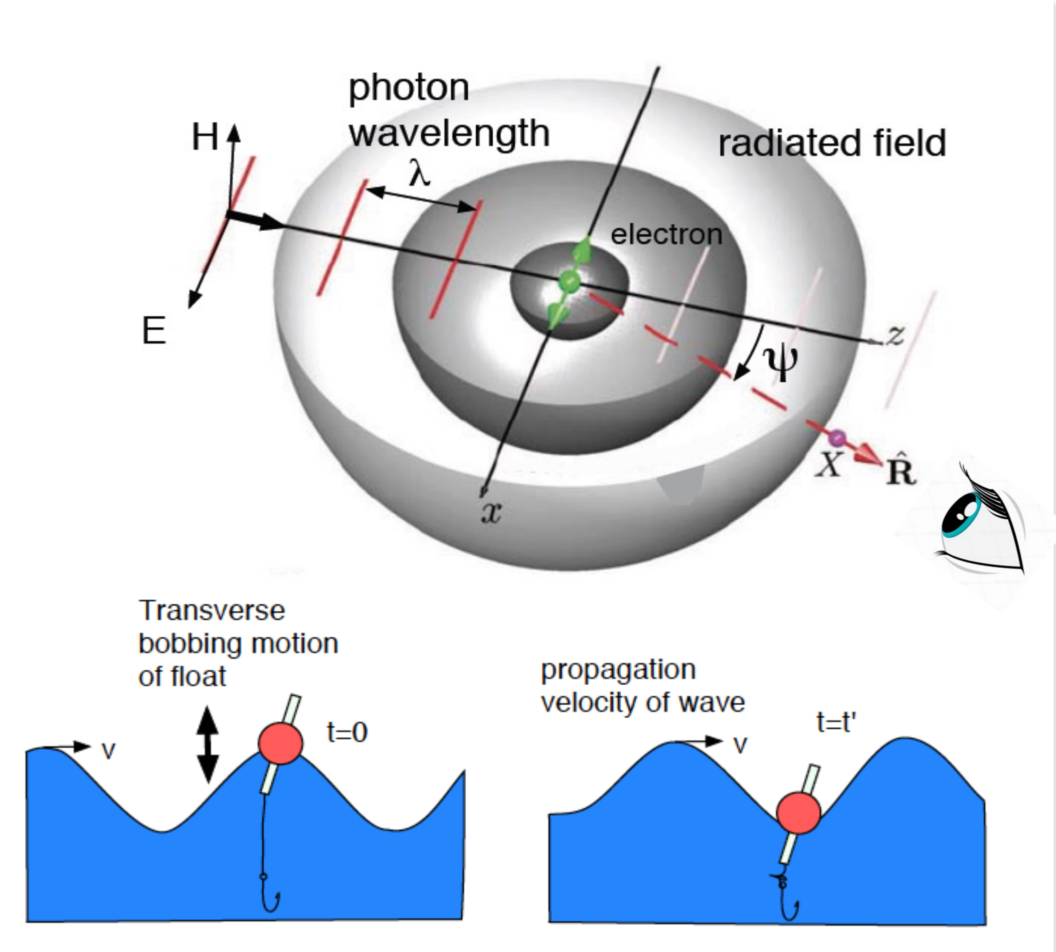
- decreases with cos(ψ)

$$\frac{E_{rad}(R,t)}{E_{in}} = -\left(\frac{e^2}{4\pi\epsilon_0 mc^2}\right)\frac{e^{ikR}}{R}\cos\psi$$

Thomson scattering length:

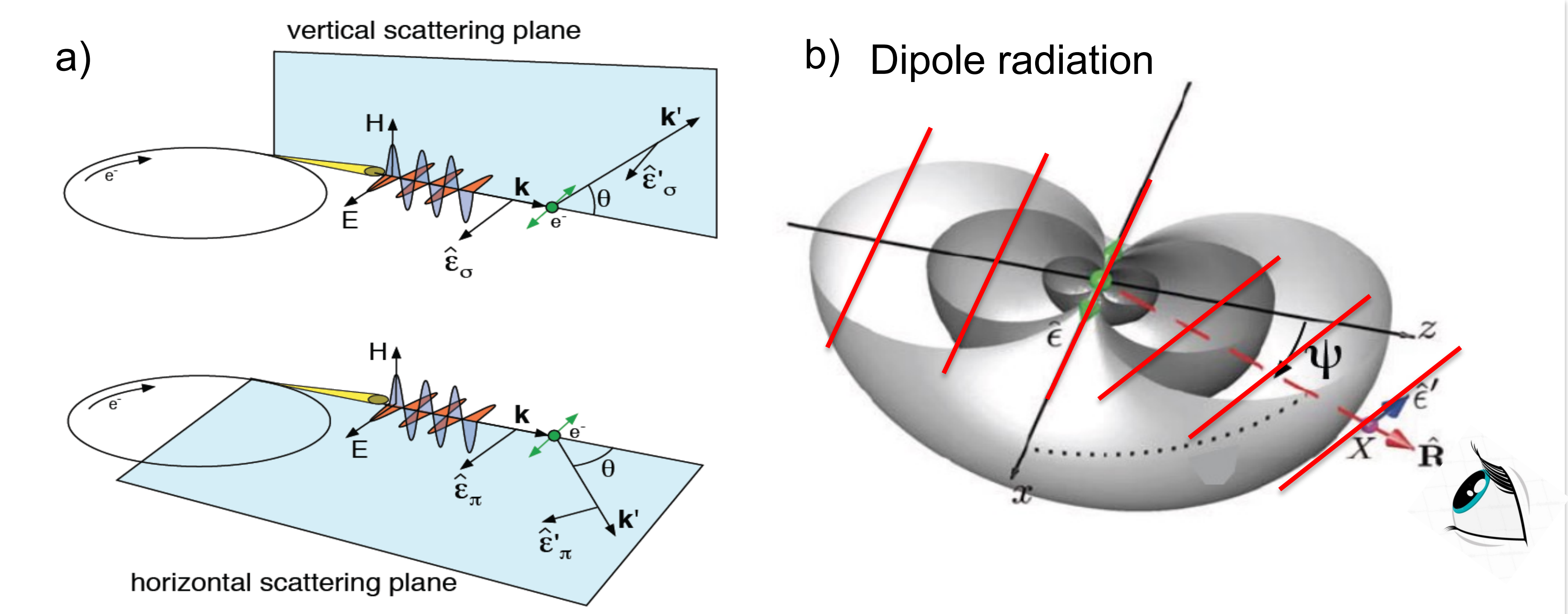
$$r_0 = \left(\frac{e^2}{4\pi\epsilon_0 mc^2}\right) = 2.82 \times 10^{-5}\ \text{Å}$$

(Classical electron radius)



The differential cross section for the Thomson scattering depends from the incident and scattered photon polarizations

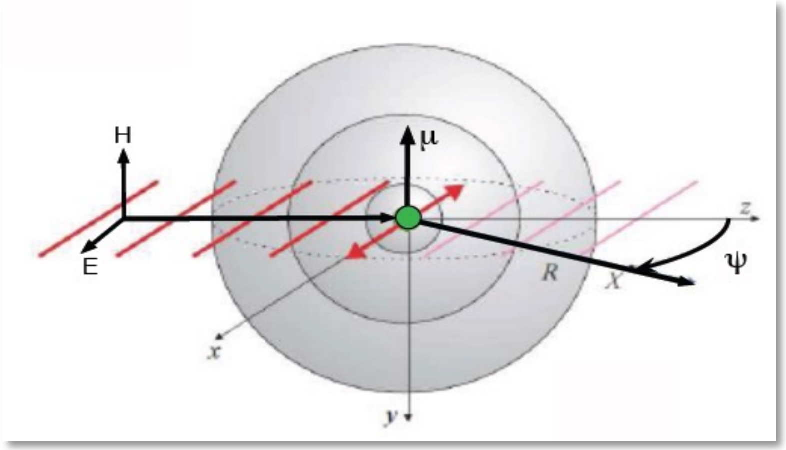
$$\left(\frac{d\sigma}{d\Omega}\right) = r_0^2 \left|\hat{\varepsilon}\cdot\hat{\varepsilon}'\right|^2 \quad P = \left|\hat{\varepsilon}\cdot\hat{\varepsilon}'\right|^2 = \begin{cases} 1 & \text{synchrotron: vertical scattering plane} \\ \cos^2\psi & \text{synchrotron: horizontal scattering plane} \\ \frac{1}{2}\left(1+\cos^2\psi\right) & \text{unpolarized source} \end{cases}$$

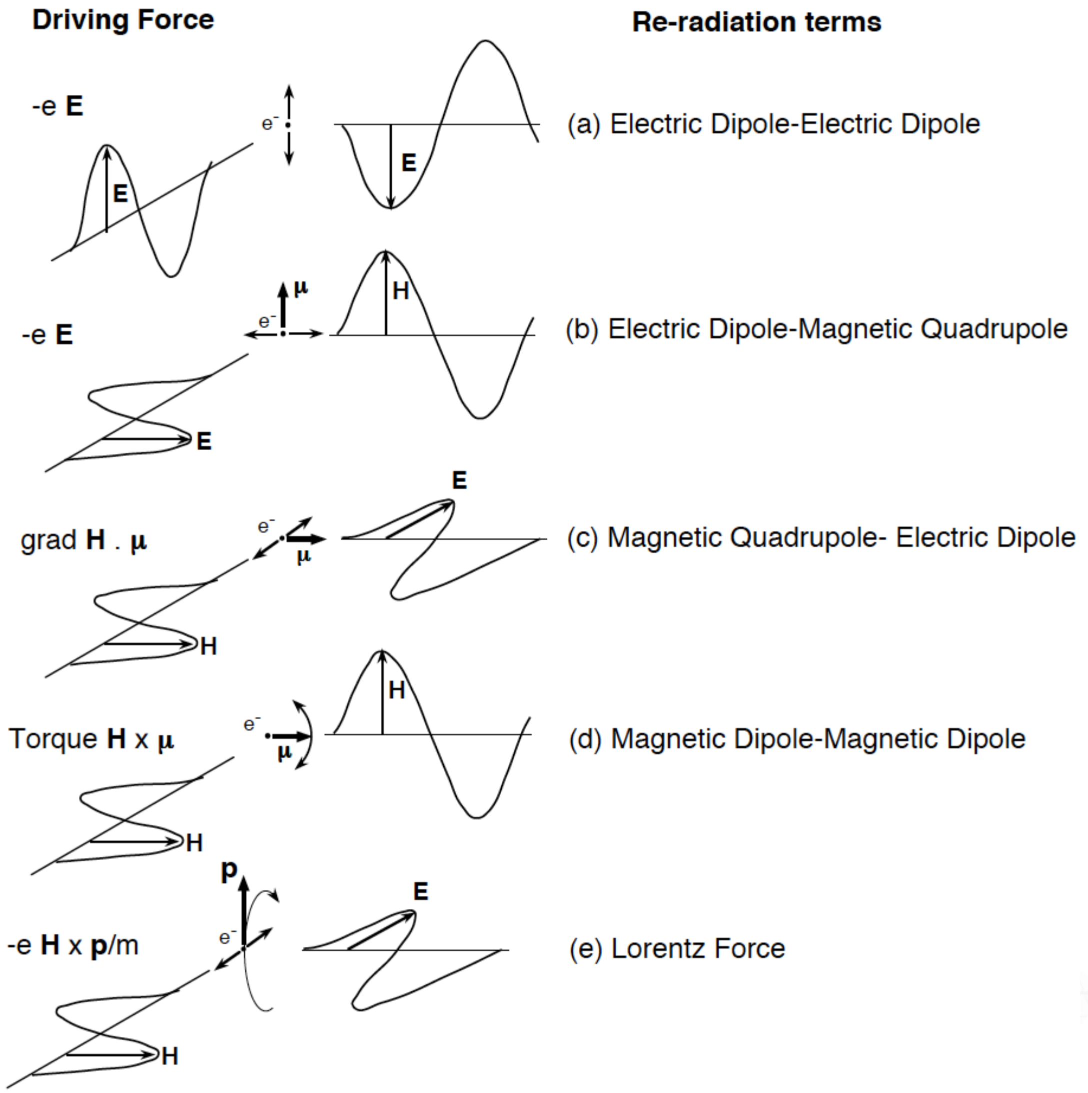


MAGNETIC SCATTERING BY A FREE ELECTRON

The magnetic scattering amplitudes are very weak because proportional to the relativistic factor E/mc^2

Both the **H** magnetic and the electric **E** field interact with the charge and magnetic moments of the electron



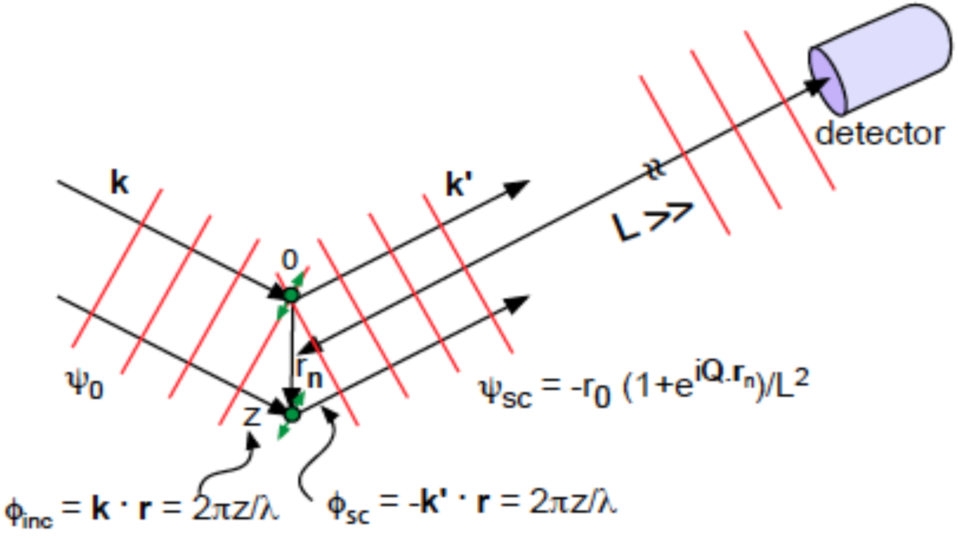


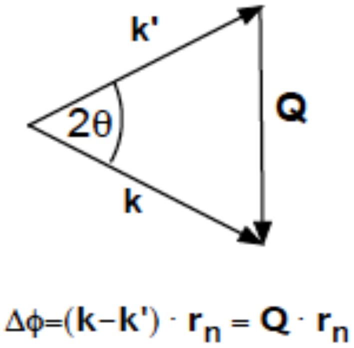
from: *de Bergevin and Brunel (Acta Cryst, 1981)*

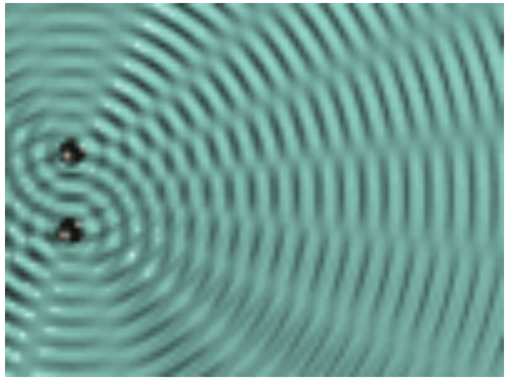
THOMSON SCATTERING BY TWO FREE ELECTRONS

– Interference between scattered X-rays observed in the direction **k**’ and at large distances (far field limit), with |**k**|= |**k’**|= 2π/λ.

– The phase difference between the two scattered X-rays is Δϕ=(**k**-**k**’) · **r** = **Q** · **r**







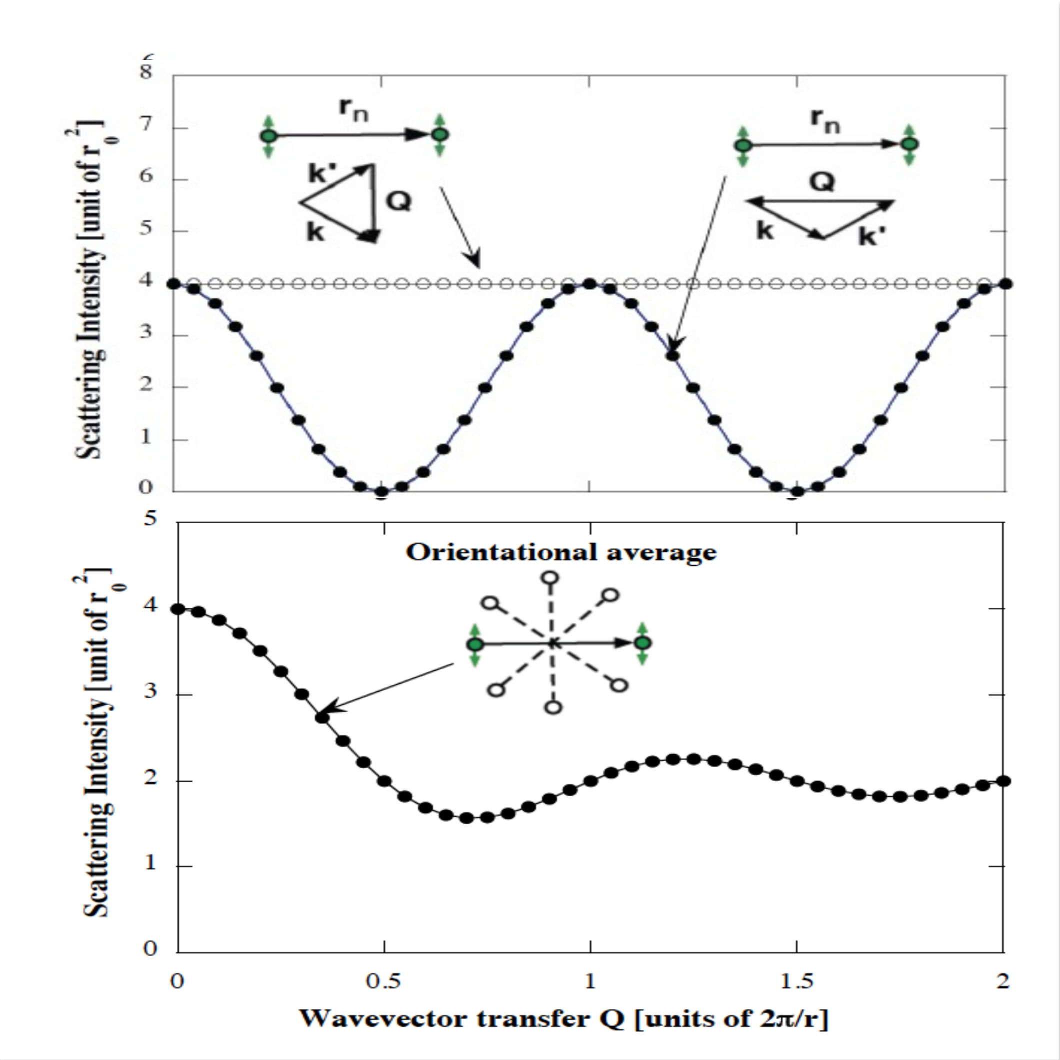
$$\frac{d\sigma}{d\Omega} = \frac{\psi_{sc}^2}{\psi_0^2} L^2 = 2r_0^2[1 + \cos(\mathbf{Q}\cdot\mathbf{r})]$$

Differential scattering cross section

Q = wavevector transfer or scattering vector

RANDOM DISTRIBUTION OF TWO FREE ELECTRONS

The scattering intensity depends from the relative orientation of scattering vector Q and the vector r_n. (with neglet the polarization)



Scattering cross section (two electrons):

$$\frac{d\sigma}{d\Omega} = 2r_0^2(1 + \cos(\mathbf{Q}\cdot\mathbf{r}))$$

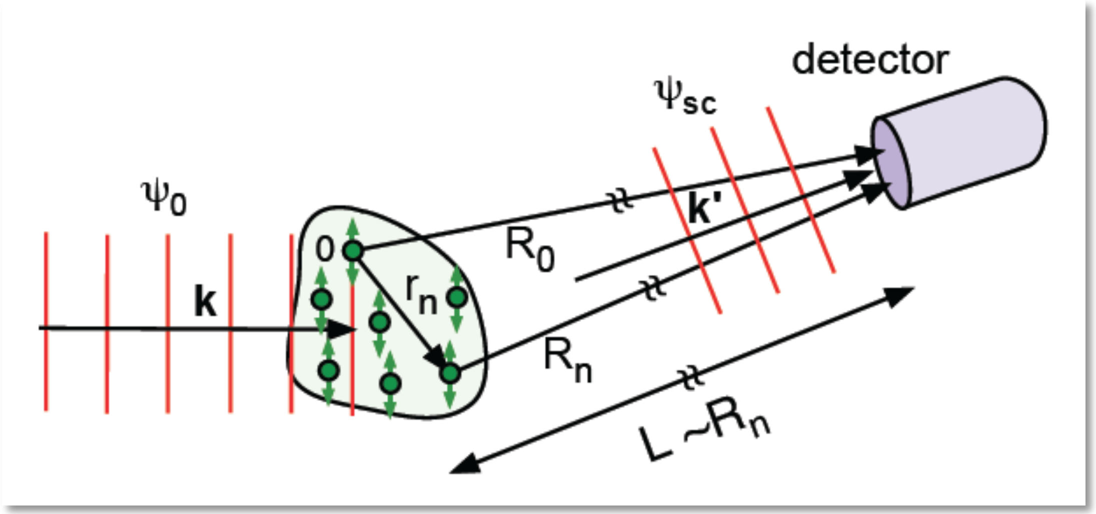
Scattering cross section (two electrons): orientational average

$$\langle\frac{d\sigma}{d\Omega}\rangle_{\mathbf{or.av.}} = 2r_0^2(1 + \langle e^{(i\mathbf{Q}\cdot\mathbf{r})}\rangle_{\mathbf{or.av.}})$$

$$\langle e^{(i\mathbf{Q}\cdot\mathbf{r})}\rangle_{\mathbf{or.av.}} = \frac{\sin(Qr)}{Qr}$$

THOMSON SCATTERING BY MANY FREE ELECTRONS

In general if we have a random distribution of electrons, the scattering function is obtained sum "coherently" all the individual terms



$$\frac{d\sigma}{d\Omega} = \frac{\psi_{sc}^2}{\psi_0^2} L^2$$

$$\begin{aligned}
\psi^{sc} &= \sum_n \psi_n^{sc} = -r_0 \sum_n \frac{e^{i\mathbf{Q}\cdot\mathbf{R}_n}}{R_n} \\
&\approx \frac{-r_0}{L} \sum_n e^{i\mathbf{Q}\cdot\mathbf{R}_n} = \frac{-r_0}{L} \sum_n e^{i\mathbf{Q}\cdot(\mathbf{R}_0+\mathbf{r}_n)} = \\
&\approx \frac{-r_0}{L} e^{i\mathbf{Q}\cdot\mathbf{R}_0} \sum_n e^{i\mathbf{Q}\cdot\mathbf{r}_n}
\end{aligned}$$

Thomson differential scattering cross section for a electron charge distribution

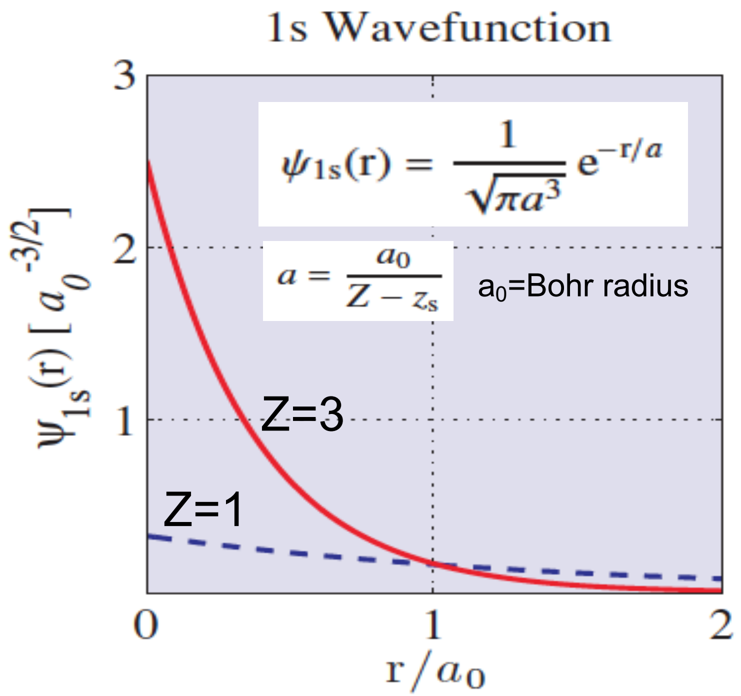
$$\frac{d\sigma}{d\Omega} = r_0^2 |\sum_n e^{i\mathbf{Q}\cdot\mathbf{r}_n}|^2$$

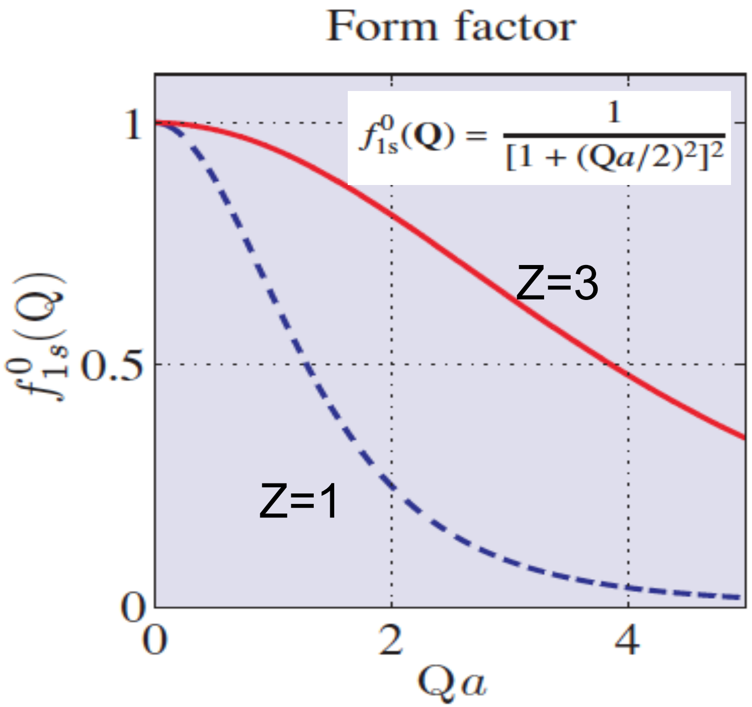
THOMSON SCATTERING BY ONE ATOM

The form factor is related to the Fourier transform of charge density distribution:

$$f^0(\mathbf{Q}) = -r_0 \int \rho(\mathbf{r}) e^{i\mathbf{Q}\cdot\mathbf{r}} d\mathbf{r} = \begin{cases} Z & \text{for } \mathbf{Q} \to 0 \\ 0 & \text{for } \mathbf{Q} \to \infty \end{cases}$$

The Q dependence is due to the fact that the Thomson scattering is produced by all atomic electrons, which have a spatial extent of the same order of magnitude as the X-ray wavelength.



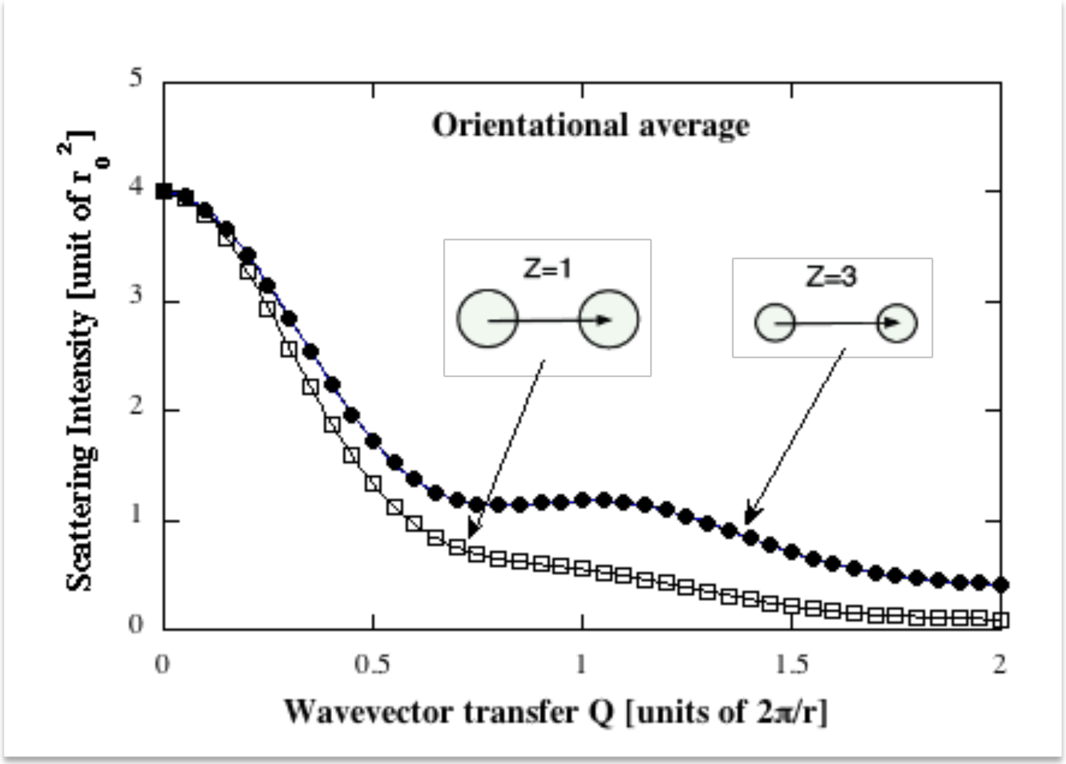


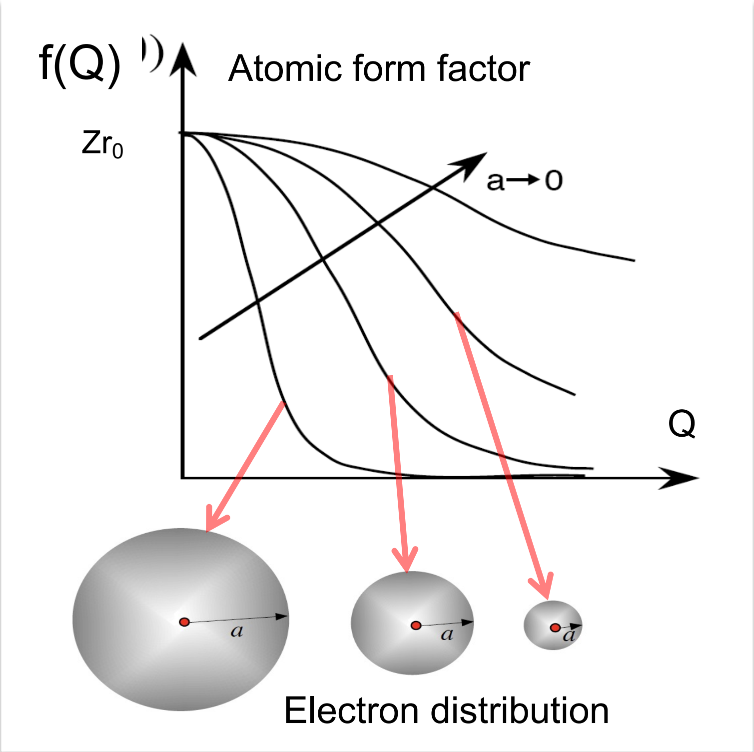
Z=1 H
Z=3 Li

SCATTERING BY TWO ATOMS

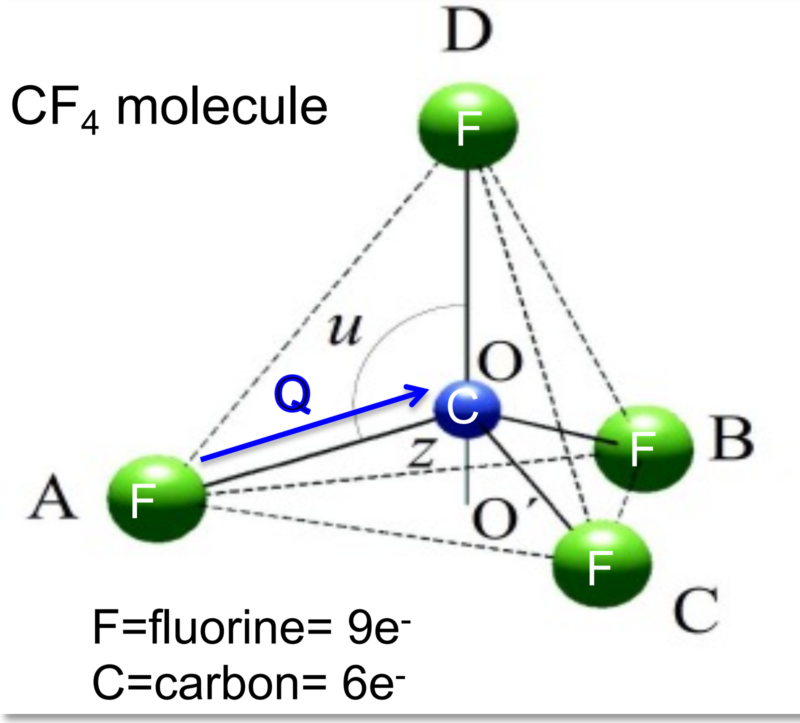
The scattering of two atoms which have a spatial extent of electron distribution of the same order of magnitude as the X-ray wavelength.

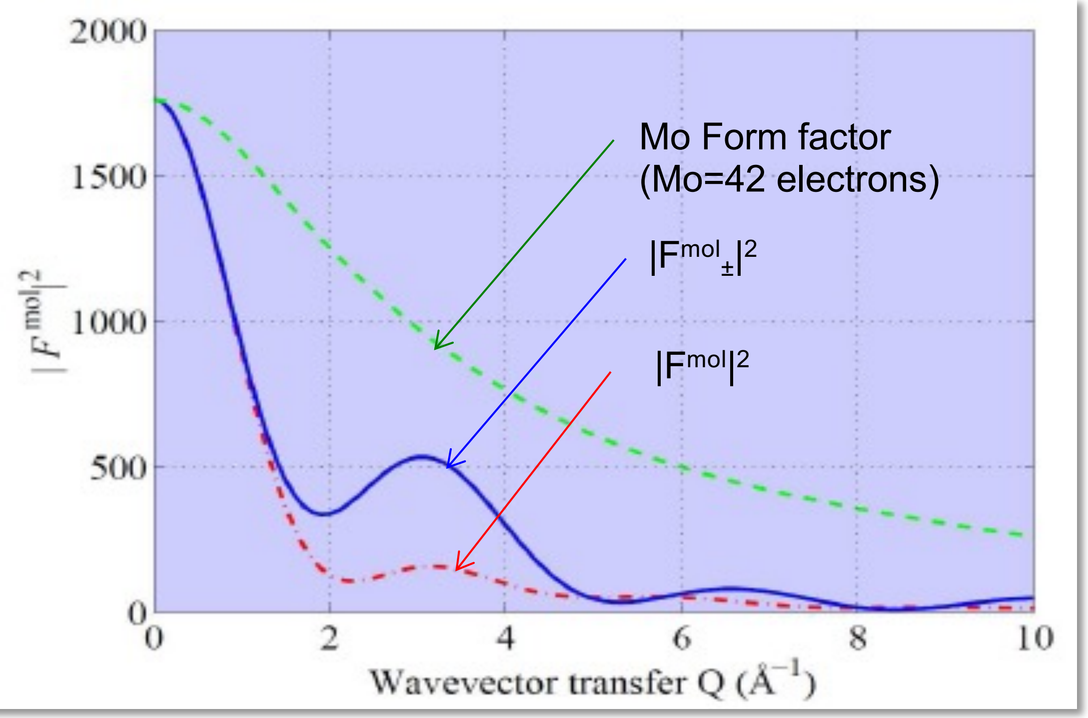
$$\langle I(\mathbf{Q})\rangle_{\text{orient. av.}} = f_1^2 + f_2^2 + 2 f_1 f_2 \langle e^{i\mathbf{Q}\cdot\mathbf{r}}\rangle_{\text{orient. av.}}$$





SCATTERING FROM A MOLECULE





Molecular structure factors
$$F^{\mathrm{mol}}(\mathbf{Q}) = \sum_j f_j(\mathbf{Q})\, e^{i\mathbf{Q}\cdot\mathbf{r}_j}$$

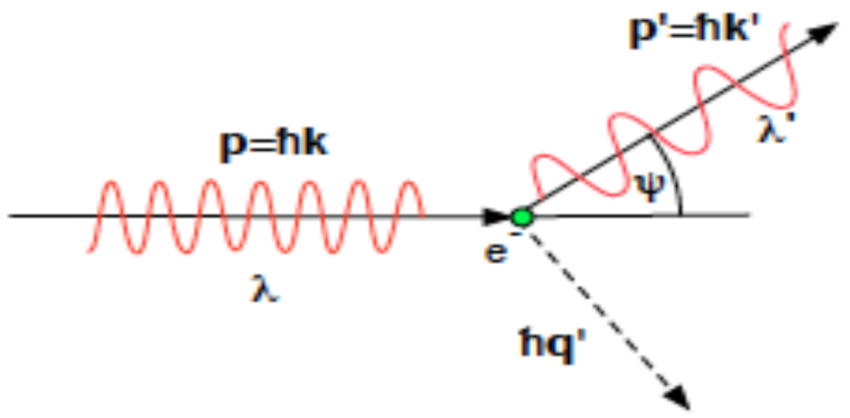
Q // C-F bond
$$F^{\mathrm{mol}}_{\pm}(\mathbf{Q}) = f^{\mathrm{C}}(\mathrm{Q}) + f^{\mathrm{F}}(\mathrm{Q})\left[3e^{\mp iQR/3} + e^{\pm iQR}\right]$$

Orientational average
$$|F^{\mathrm{mol}}|^2 = |f^{\mathrm{C}}|^2 + 4|f^{\mathrm{F}}|^2 + 8 f^{\mathrm{C}} f^{\mathrm{F}} \frac{\sin(QR)}{QR} + 12|f^{\mathrm{F}}|^2 \frac{\sin(Q\sqrt{8/3}R)}{Q\sqrt{8/3}R}$$

COMPTON SCATTERING (BY A FREE ELECTRON)

Inelastic collision between a photon and an electron at the rest in which part of the the photon energy is transferred to the electron (photon "red shift")

$$\lambda' = \lambda + \frac{h}{m_e c^2}(1-\cos\psi) = \lambda + \lambda_c(1-\cos\psi)$$



$$m_e c^2 + \hbar c k = \sqrt{(m_e c^2)^2 + (\hbar c q')^2} + \hbar c k'$$

Compton scattering wavelength

$$\lambda_c = \frac{h}{m_e c^2} = 0.0243 \quad \text{Å}$$

Fine structure constant

$$\alpha = \frac{r_0}{(\lambda_c/2\pi)} \sim \frac{1}{137}$$

Energy shift

$$\frac{\mathcal{E}}{\mathcal{E}'} = \frac{k}{k'} = \frac{\lambda'}{\lambda} = 1 + \frac{\lambda_c}{\lambda}(1-\cos\psi)$$

Maximum "red-shift" when ψ=180 deg.
No variation when $\psi=0^0$

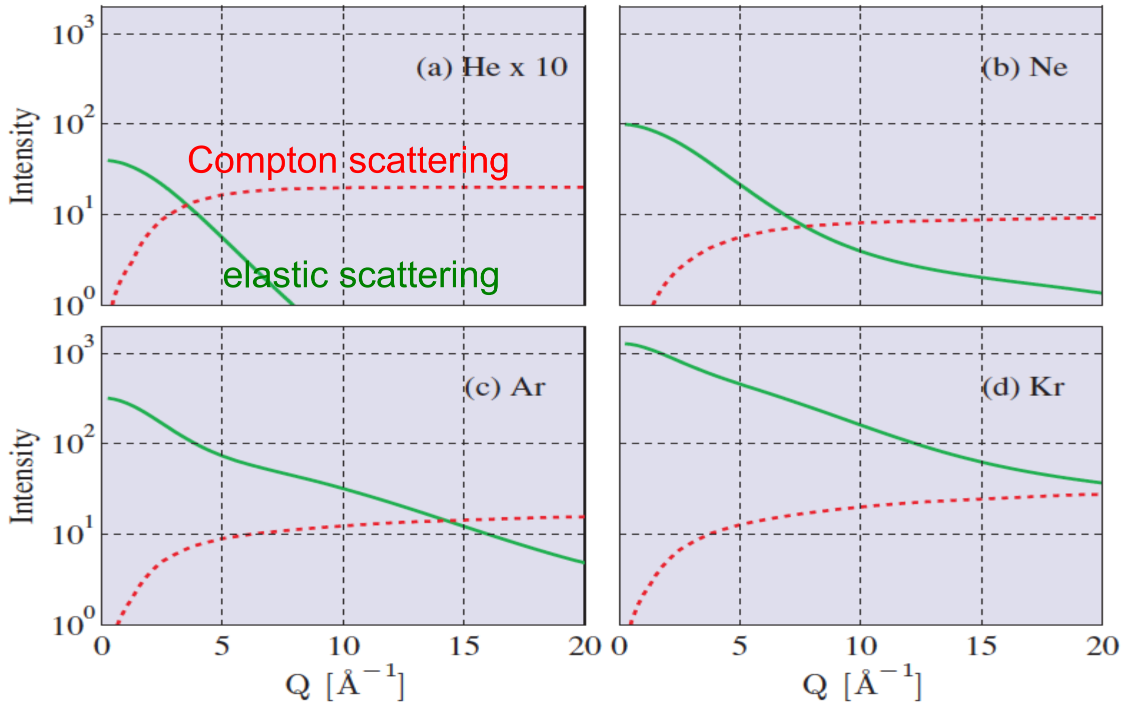
This scattering is **incoherent** and contribute only to the background.

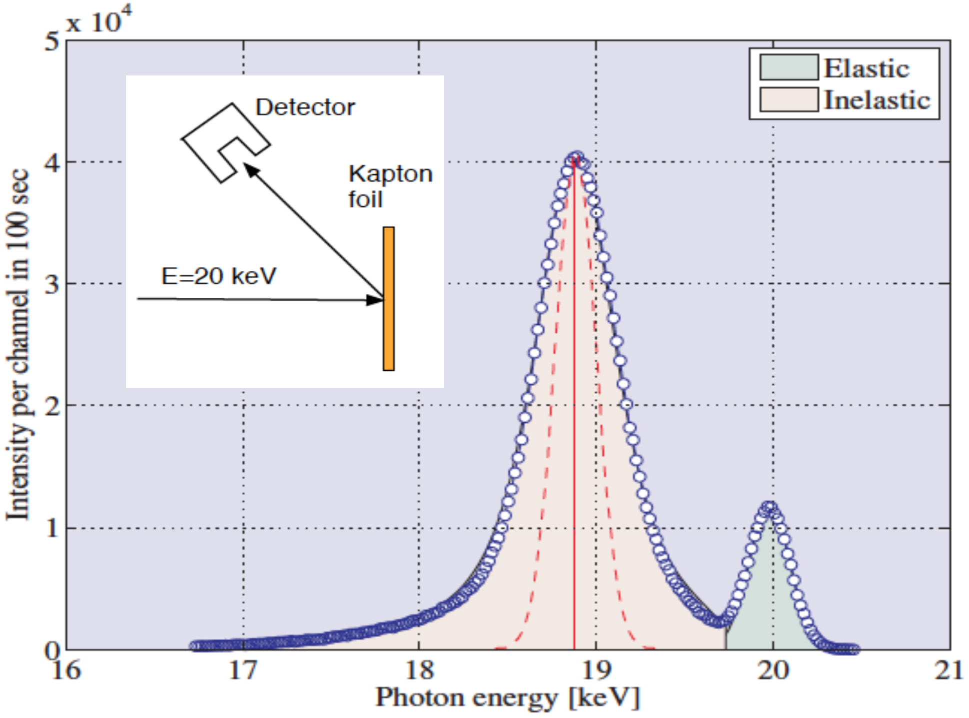
INCOHERENT INELASTIC COMPTON SCATTERING

The inelastic scattering dominates at high Q vectors and for low Z elements

Thomson scattering intensity approach Z^2 when $Q \rightarrow 0$
Compton scattering approaches Z when $Q \rightarrow \infty$

Elastic and inelastic scattering in noble gas

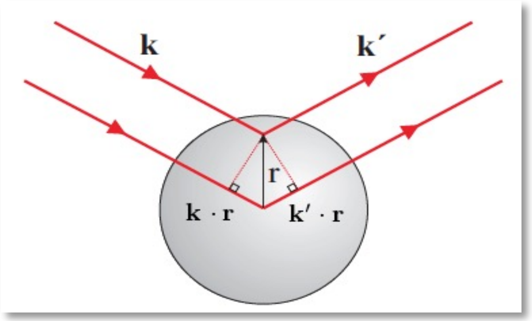




COHERENT ELASTIC SCATTERING(THOMSON)

Scattering processes conserve the number of photons
If the photon energy is conserved, the scattering is elastic. If not. It is inelastic

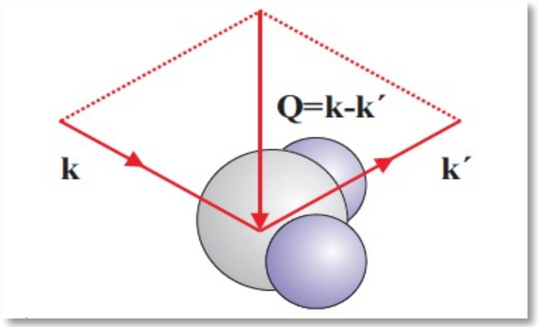
one atom



Atomic form factor

$$f^0(\mathbf{Q}) = -r_0 \int \rho(\mathbf{r}) e^{i\mathbf{Q}\cdot\mathbf{r}} d\mathbf{r}$$

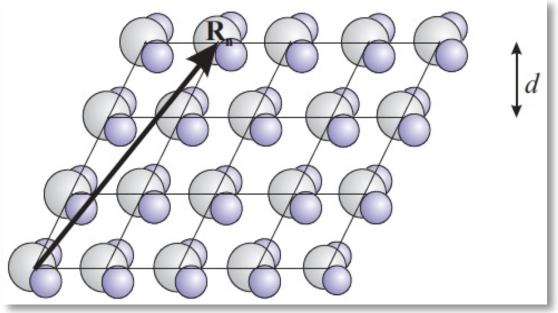
a molecule



Molecule structure factors

$$F^{\mathrm{mol}}(\mathbf{Q}) = \sum_j f_j(\mathbf{Q})\, \mathrm{e}^{i\mathbf{Q}\cdot\mathbf{r}_j}$$

a crystal



Crystal structure factors

$$F^{\mathrm{crystal}}(\mathbf{Q}) = \overbrace{\sum_j f_j(\mathbf{Q})\mathrm{e}^{i\mathbf{Q}\cdot\mathbf{r}_j}}^{\text{Unit cell structure factor}} \overbrace{\sum_{\mathrm{n}} \mathrm{e}^{i\mathbf{Q}\cdot\mathbf{R}_\mathrm{n}}}^{\text{Lattice sum}}$$

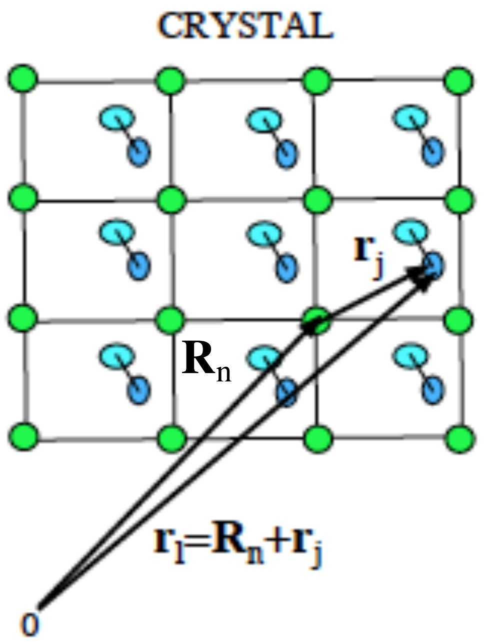
CRYSTAL STRUCTURE FACTOR

The Fourier transform of the crystal (the crystal structure factor) is equal to the product of the FT of lattice and the basis

$$F^{crystal}(\mathbf{Q}) = -r_0 \sum_{\mathbf{R}_n+\mathbf{r}_j}^{all\ atoms} f_j(\mathbf{Q}) e^{i\mathbf{Q}\cdot(\mathbf{R}_n+\mathbf{r}_j)}$$

$$= -r_0 \sum_{n}^{lattice} e^{i\mathbf{Q}\cdot\mathbf{R}_n} \sum_{j}^{unit\ cell} f_j(\mathbf{Q}) e^{i\mathbf{Q}\cdot\mathbf{r}_j}$$

FT Lattice FT Basis



$$S_N(\mathbf{Q}) = \sum_{n}^{lattice} e^{i\mathbf{Q}\cdot\mathbf{R}_n}$$

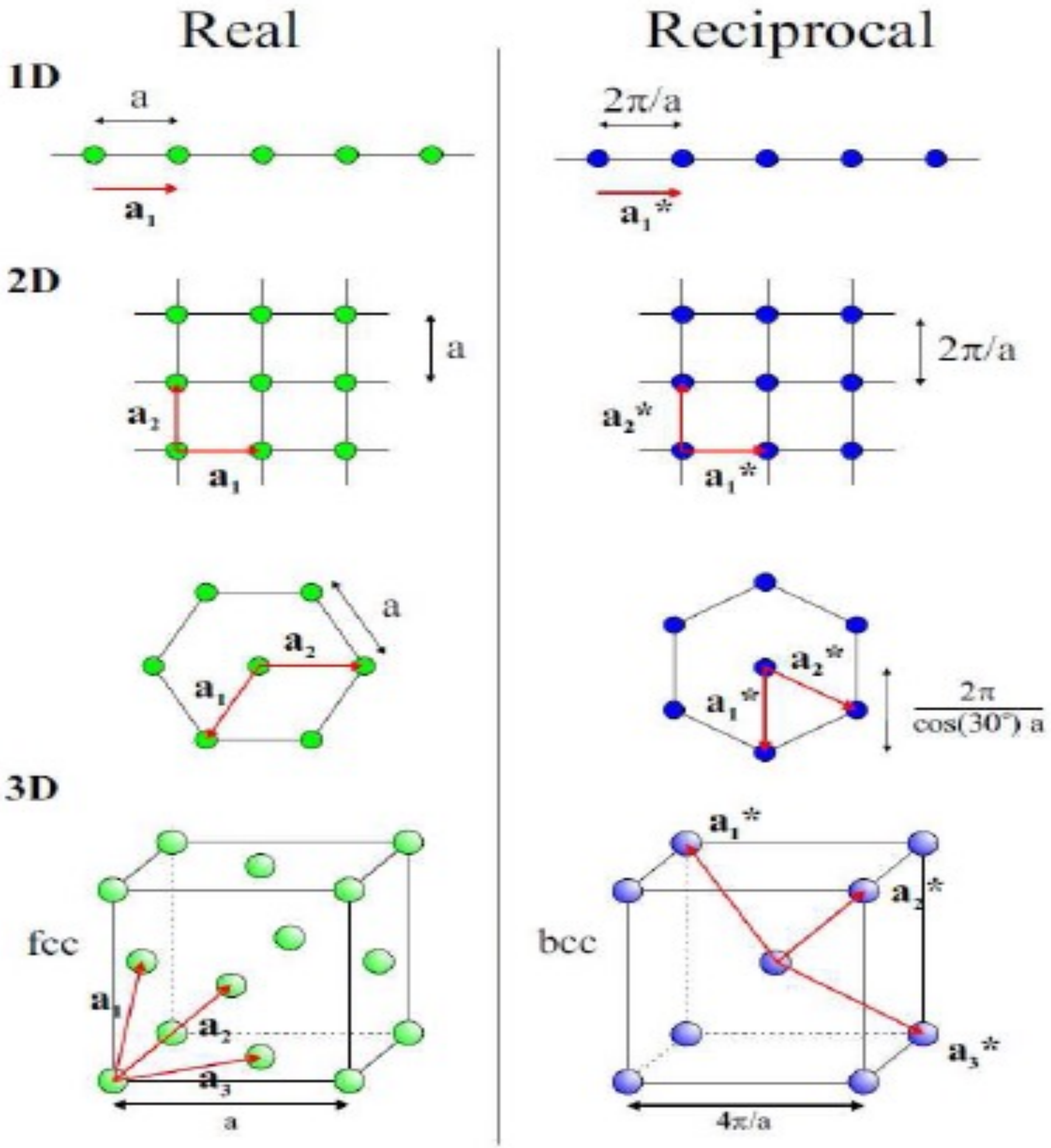
The lattice sum is non vanishing only when:

$$\mathbf{Q}\cdot\mathbf{R}_n = 2\pi \times \text{integer}$$

$$\mathbf{G}_{hkl}\cdot\mathbf{R}_n = 2\pi \times integer = 2\pi(hn_1 + kn_2 + ln_3)$$

Laue conditions

EXAMPLE OF RECIPROCAL SPACES



Example: fcc lattice

$$\mathbf{a}_1 = \frac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}})$$

$$\mathbf{a}_2 = \frac{a}{2}(\hat{\mathbf{z}} + \hat{\mathbf{x}})$$

$$\mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}})$$

$$\mathbf{a}_1^* = \frac{4\pi}{a}\left(\frac{\hat{\mathbf{y}}}{2} + \frac{\hat{\mathbf{z}}}{2} - \frac{\hat{\mathbf{x}}}{2}\right)$$

$$\mathbf{a}_2^* = \frac{4\pi}{a}\left(\frac{\hat{\mathbf{z}}}{2} + \frac{\hat{\mathbf{x}}}{2} - \frac{\hat{\mathbf{y}}}{2}\right)$$

$$\mathbf{a}_3^* = \frac{4\pi}{a}\left(\frac{\hat{\mathbf{x}}}{2} + \frac{\hat{\mathbf{y}}}{2} - \frac{\hat{\mathbf{z}}}{2}\right)$$

EQUIVALENCE BRAGG-LAUE

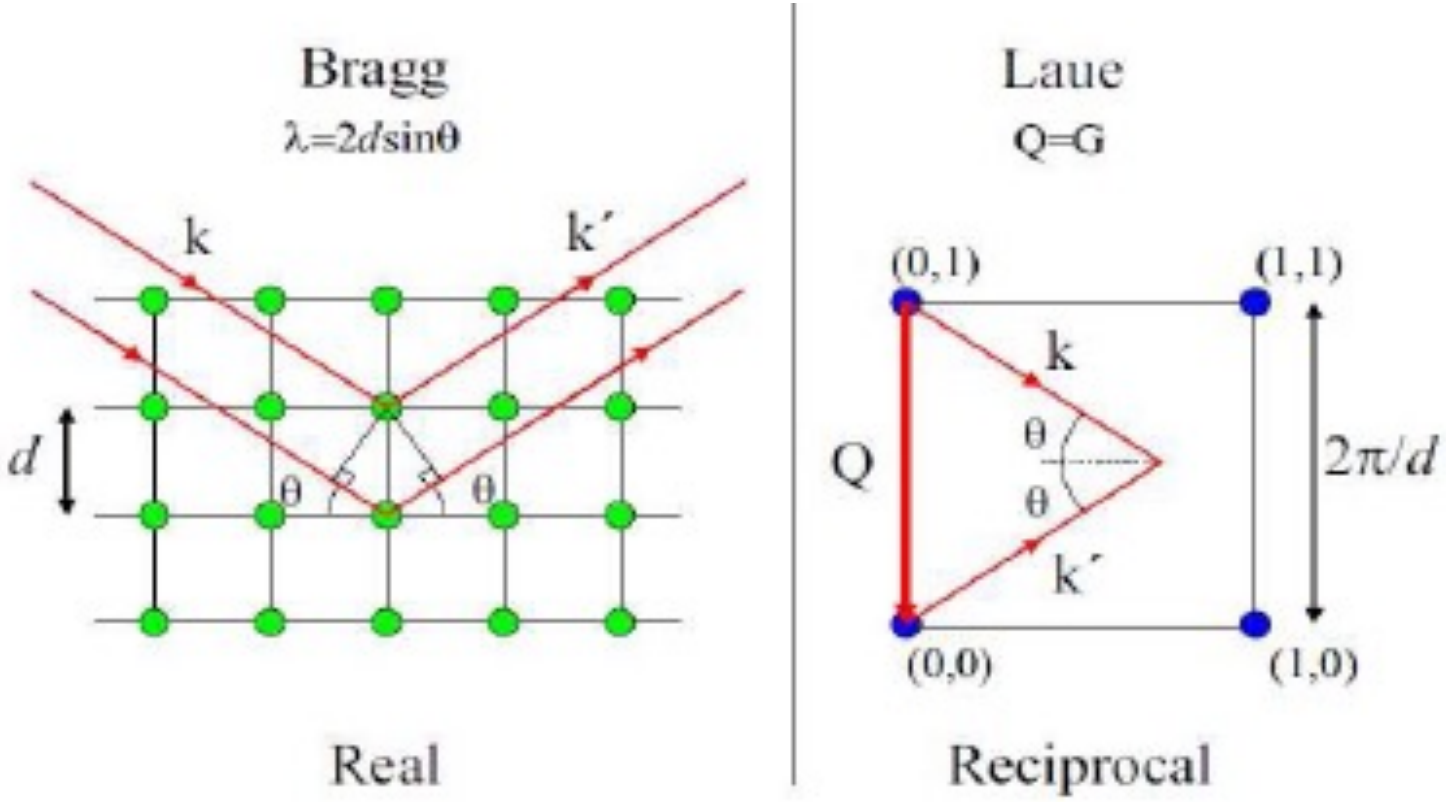
Bragg's law:

$$n\ \lambda = 2\ d_{hkl}\ sin\theta_B$$

Laue's condition

$$\mathbf{k}' - \mathbf{k} = \mathbf{Q} = 2\pi\ \mathbf{G}_{hkl}$$

$$|\mathbf{G}_{hkl}| = 2\pi / d_{hkl}$$

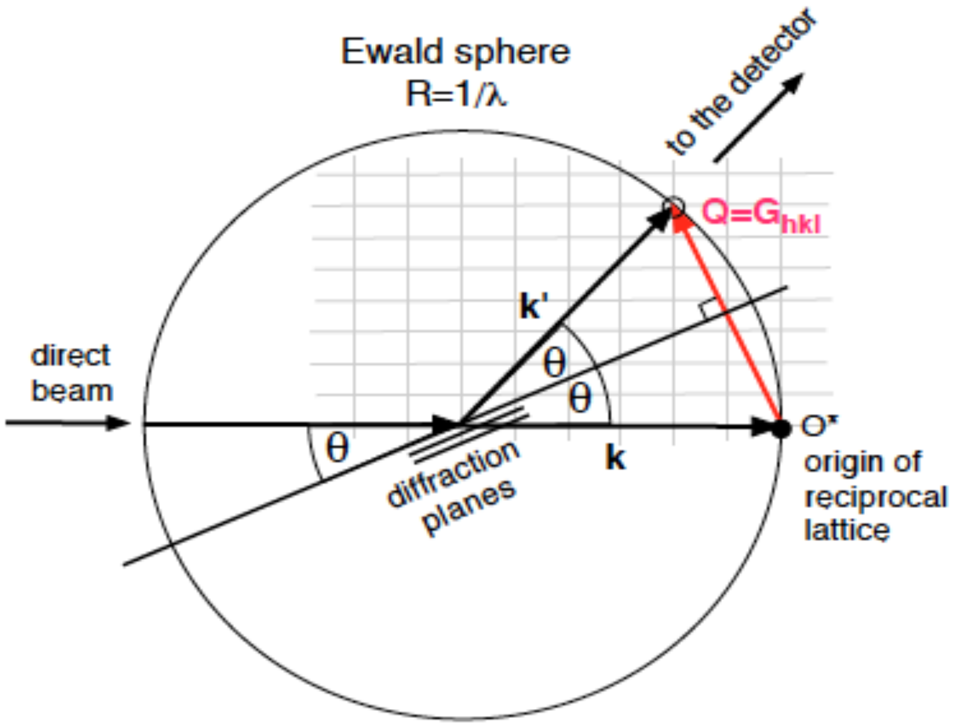


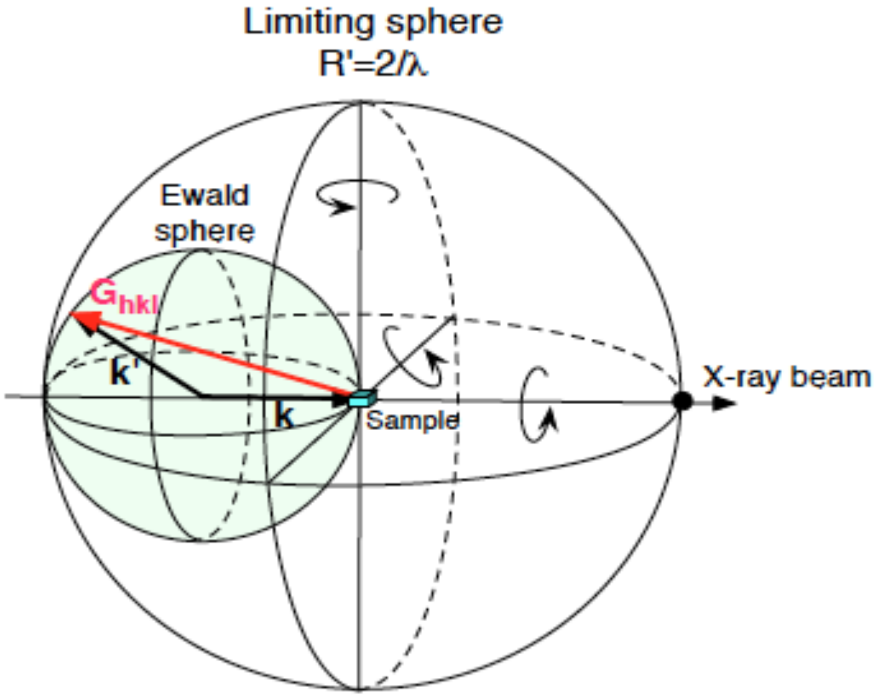
$$\left(\frac{d\sigma}{d\Omega}\right)_{Bragg} = N\frac{(2\pi)^3}{v_0} r_0^2 \sum_{hkl} \delta(\mathbf{Q} - \mathbf{G}_{hkl})\ |F(hkl)|^2$$

Differential cross section for the Bragg diffraction in crystals

EWALD SPHERE

Geometric construction that allows one to visualize the Bragg' law during the elastic diffraction experiment





Only all the reciprocal lattice points G_{hkl} intercepting the Ewald sphere fulfill the Bragg conditions

All the G_{hkl} contained in limiting sphere could be reached by rotating the sample about the goniometer axis

POWDER DIFFRACTION

Size and symmetry of the unit cell

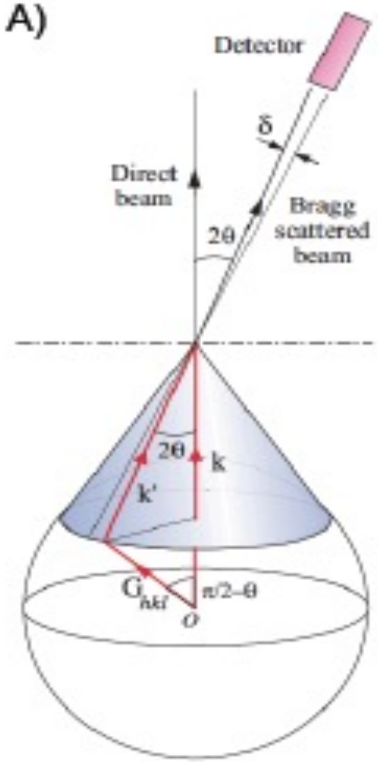
Debye-Scherrer cone

$$2\pi|\mathbf{G}|_{hkl}\sin(\frac{\pi}{2}-\theta)=2\pi|\mathbf{G}|_{hkl}\cos\theta$$

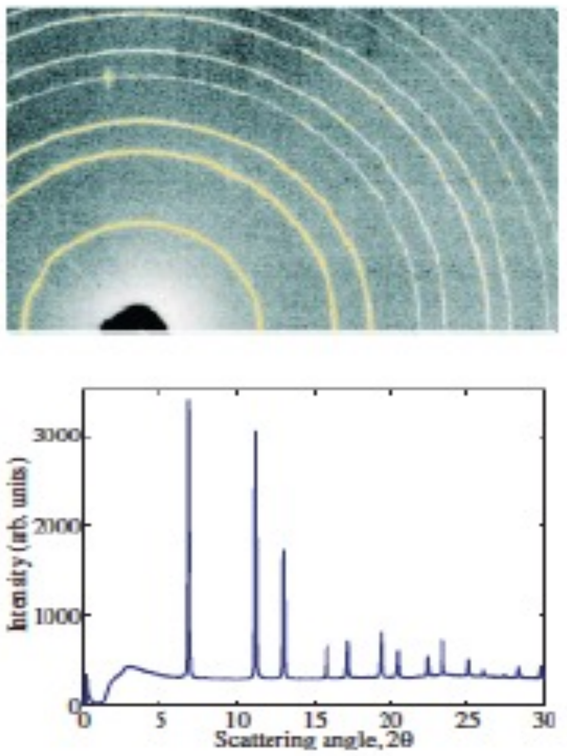
Detector aperture δ

$$\delta k/(2k\sin 2\theta)$$

A)



B)



$$I(hkl)_{Powder} = |F_{hkl}|^2 m_{hkl}\cos\theta\frac{1}{\sin 2\theta}\frac{1}{\sin 2\theta}P(\cos 2\theta_{hkl})$$

Multiplicity m_{hkl}

$$m_{hkl}\cos\theta.$$

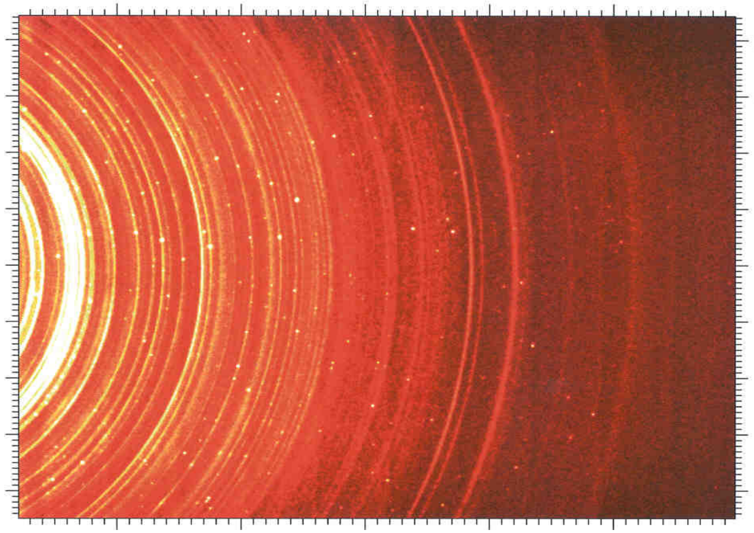
Lorentz factor

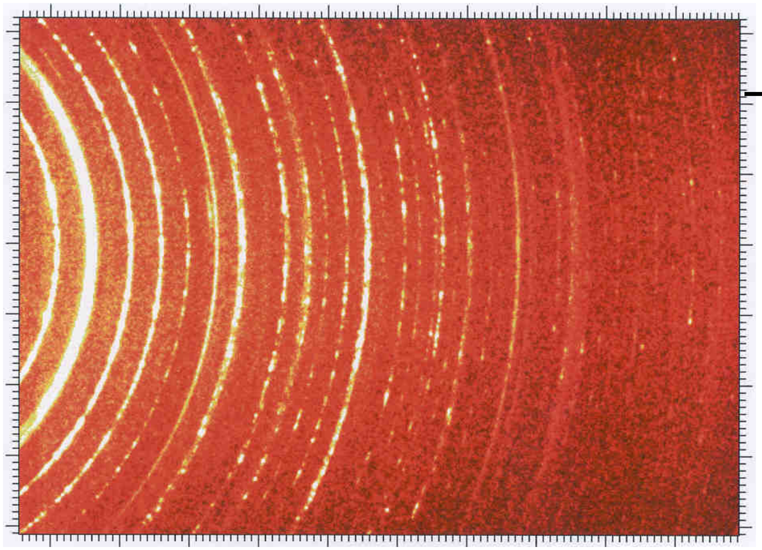
$$\frac{1}{\sin 2\theta}$$

Polarization factor

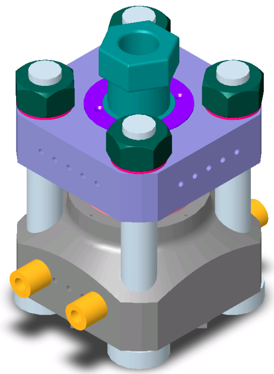
EXAMPLE : HIGH PRESSURE SYNTESIS OF SULFUR

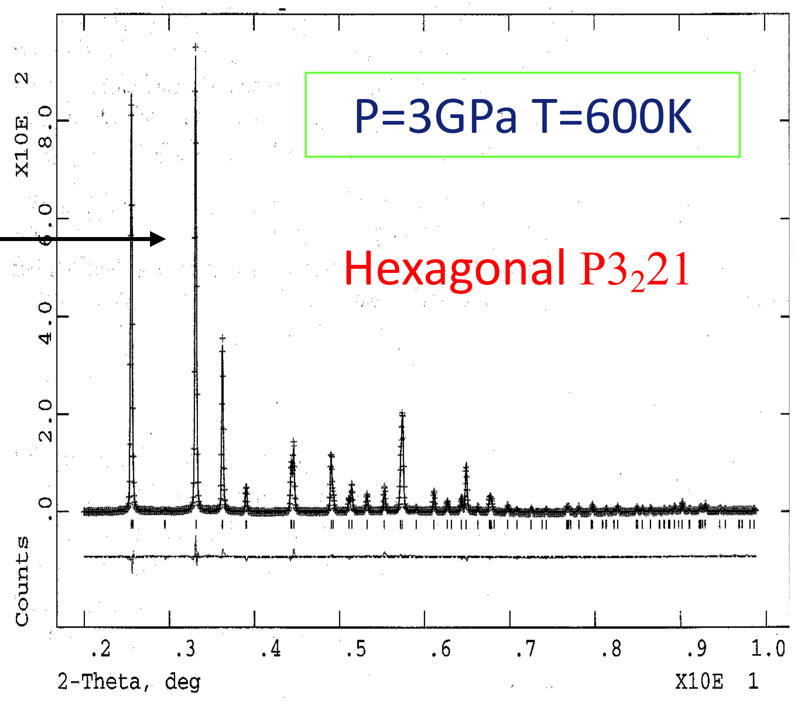
- Pressure up to 17 GPa on 2 mm^3 sample volume
- Resistive heating up to 2000 K

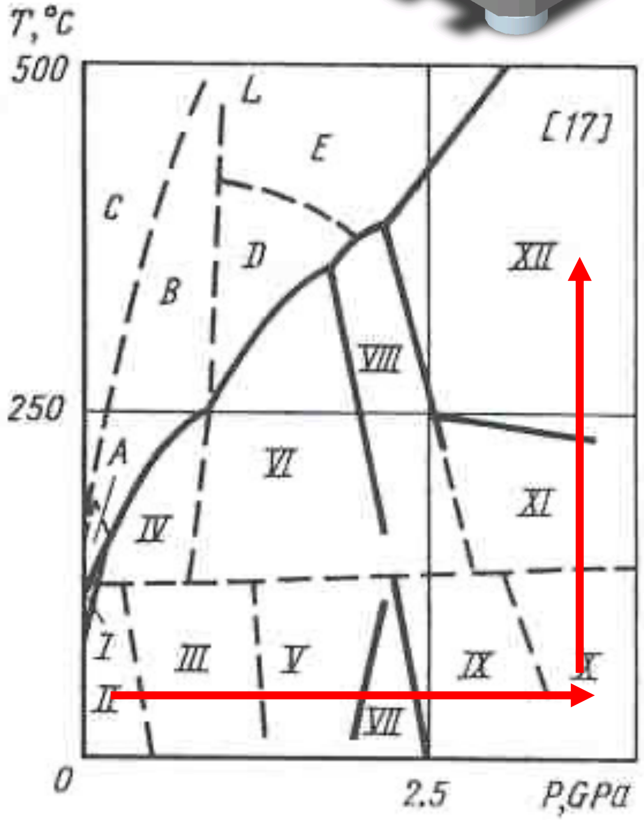




At RT-RP, Orthorhombic Fddd based on S_8 rings (molecular units)

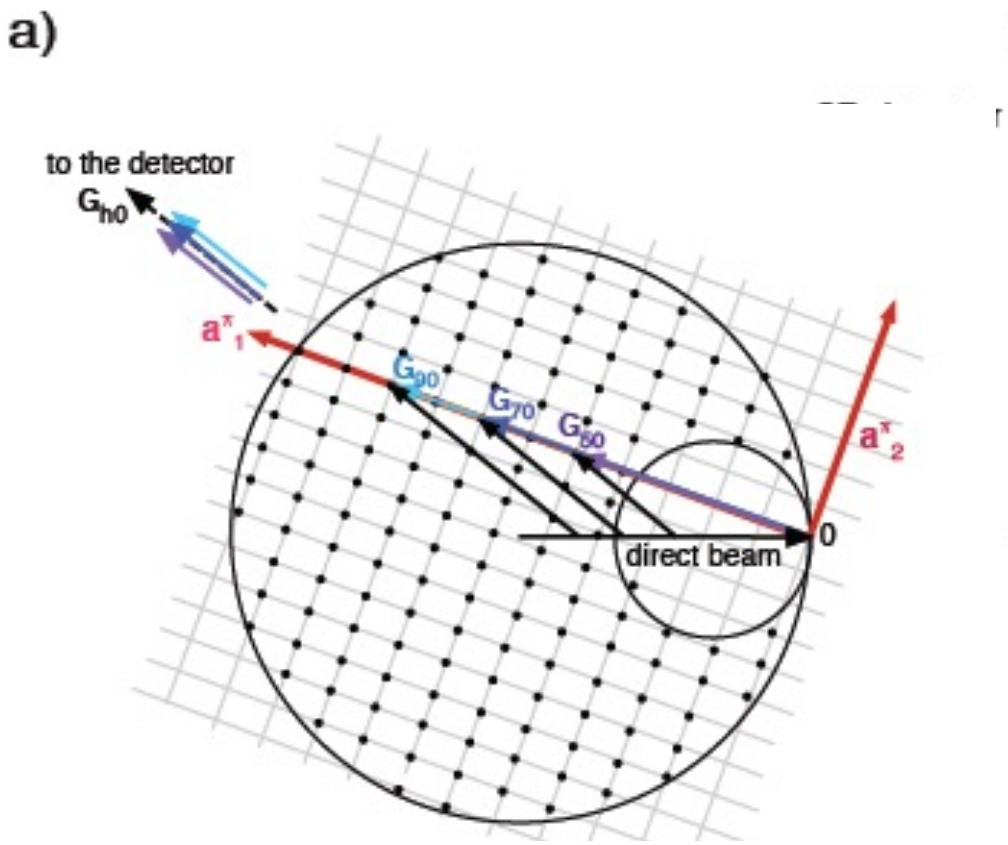




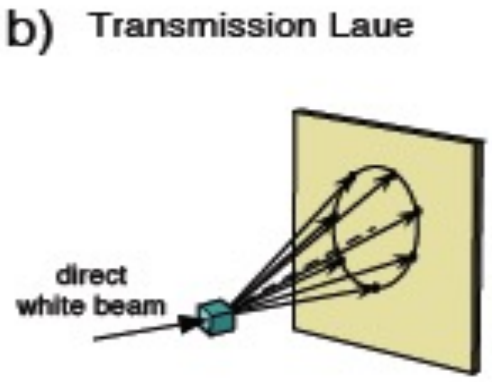


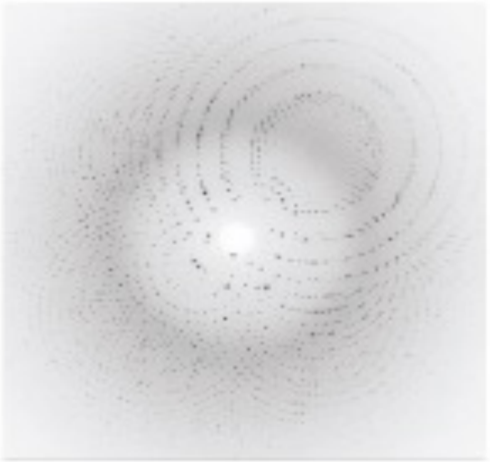
WHITE BEAM LAUE PATTERN

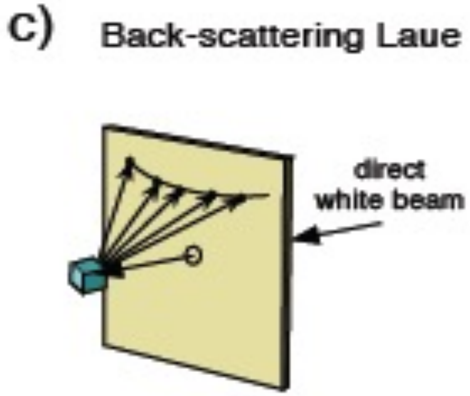
Polychromatic beam technique used in protein crystallography or in more complex structures.
Data collection of a large number of reflections

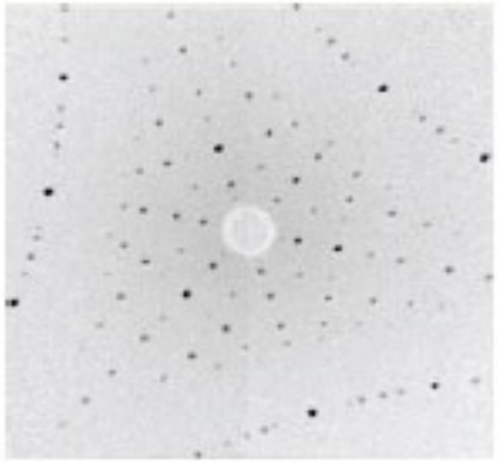


All the lattice points contained in the grey area contribute to the Bragg diffraction

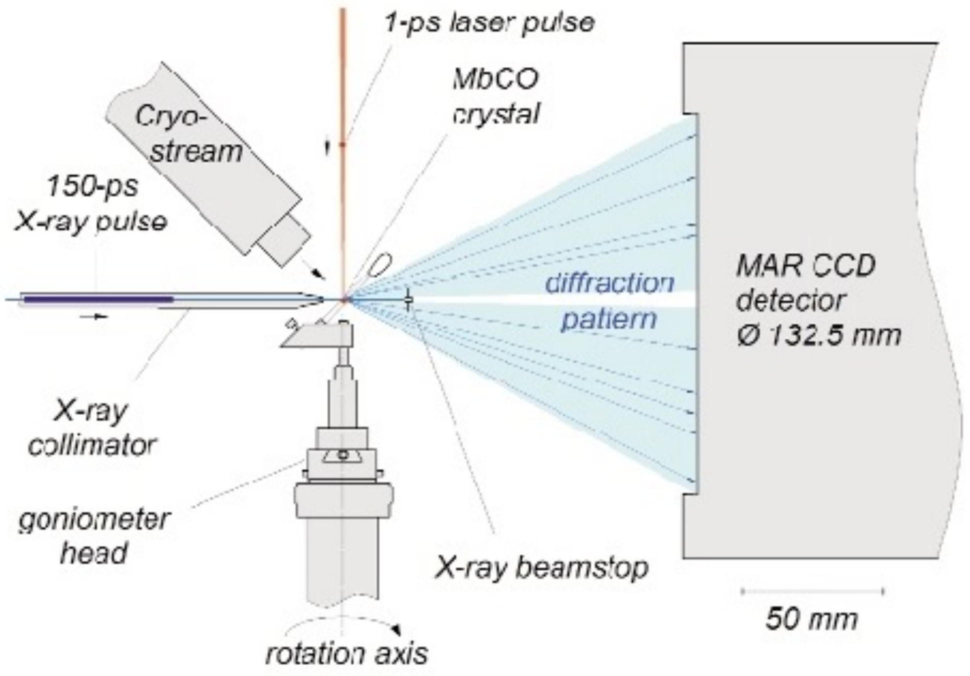


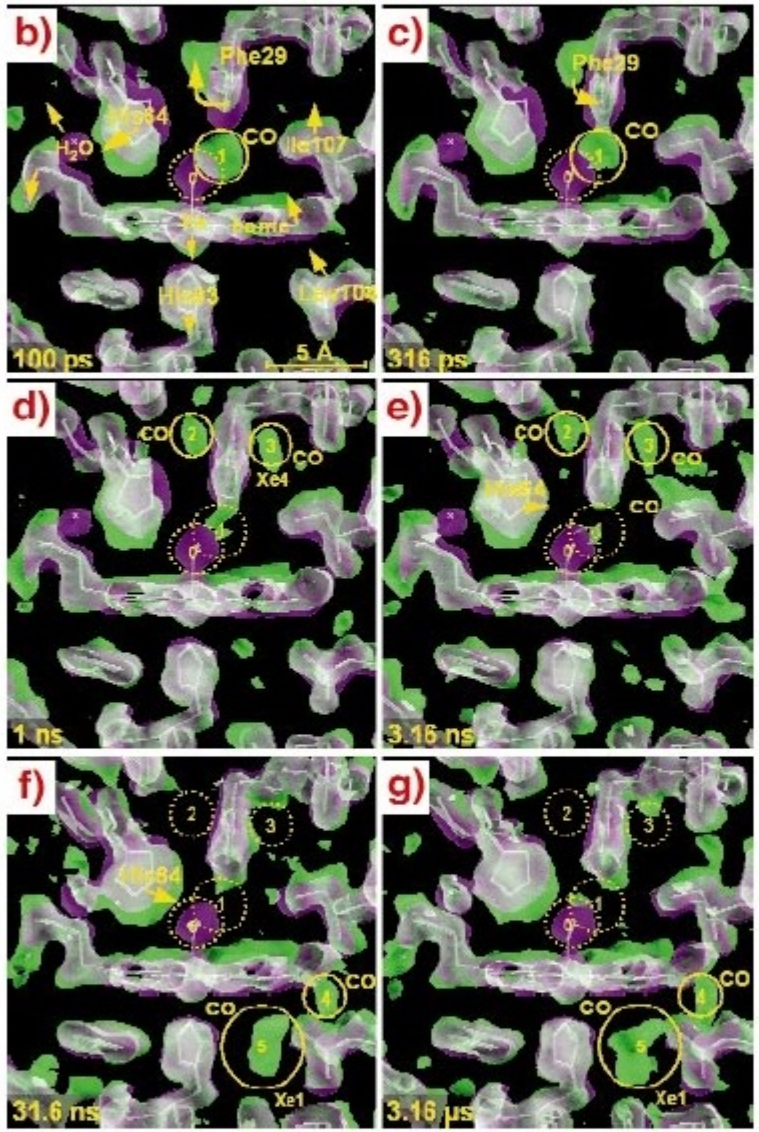






Time-resolved MX using the Laue technique (White/Pink beam)

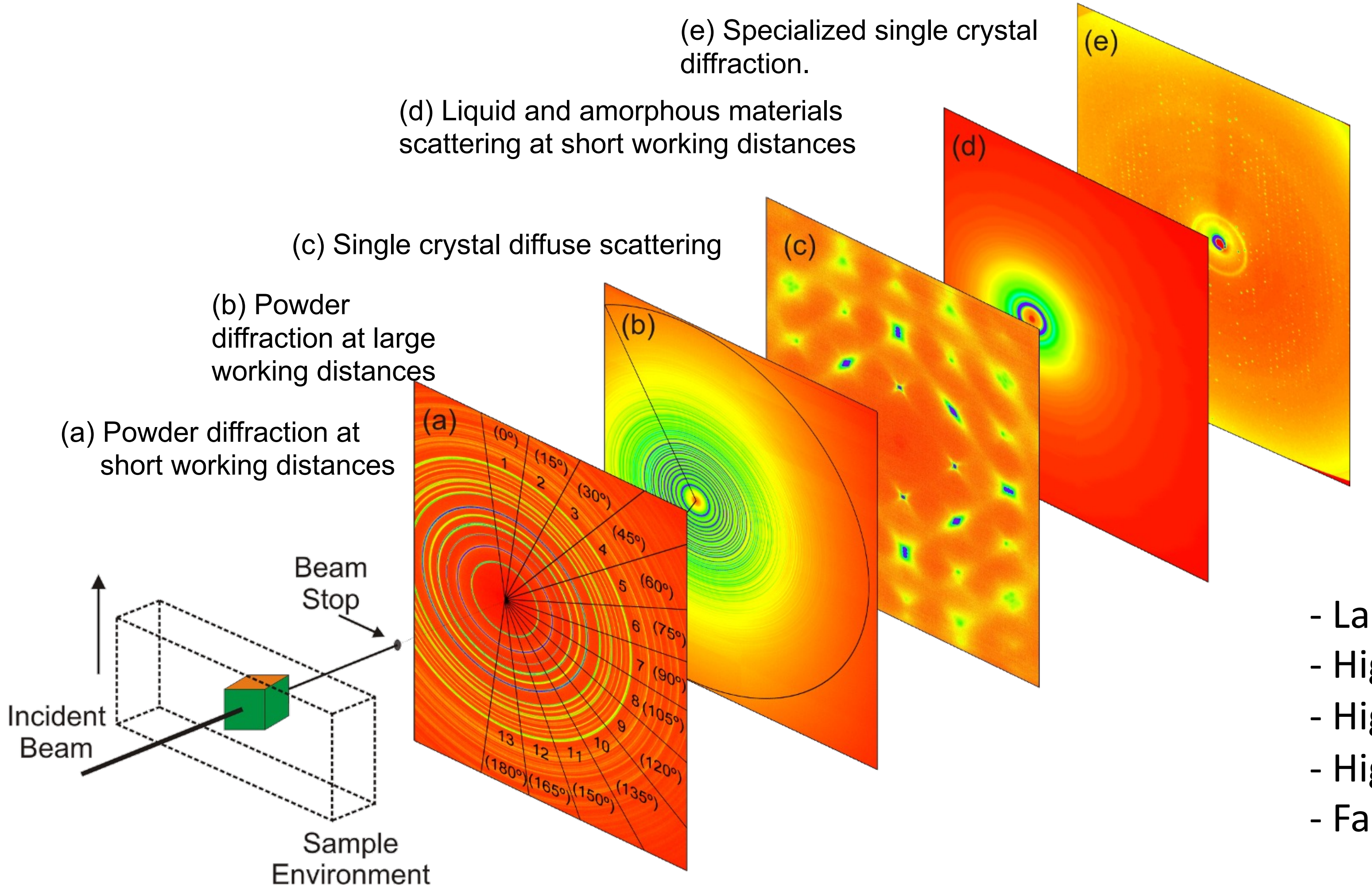




Structure of MbCO at different time delays after photolysis. The bound CO dissociates, eventually becoming trapped in sites 4 and 5, where it remains out to the microsecond time scale.

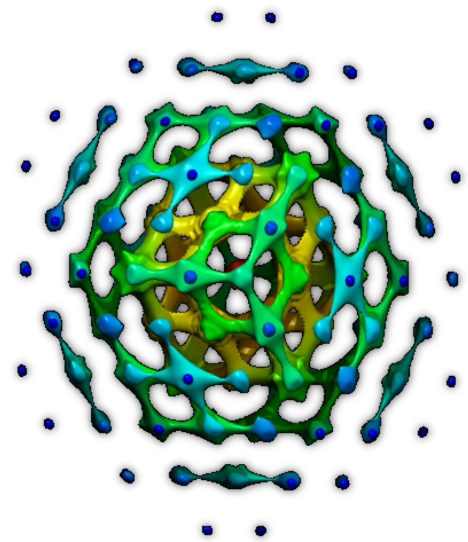
F. Schotte *et al.*, (2003), *Science*, 300, 1944-1947.

- **Multi-length scale problems**



- Large input surface (>150 mm diameter)
- High spatial resolution (50 to 100 mm)
- High dynamic range (14 bits or more)
- High sensitivity (quantum efficiency)
- Fast read-out (a few seconds or less)

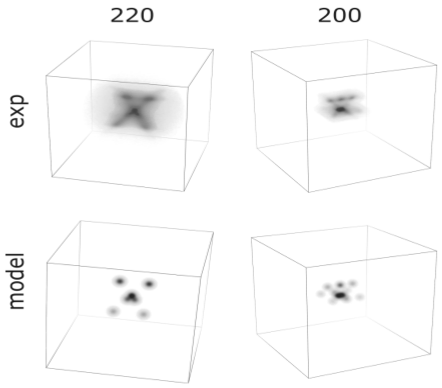
State-of-the-art methods for diffuse scattering/diffraction studies of crystalline materials



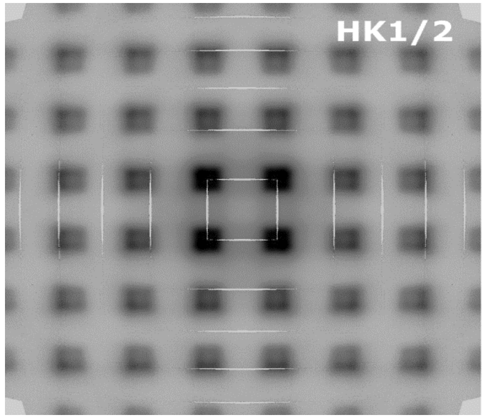
- Direct space real structure of systems with correlated disorder
- Time-resolved diffuse scattering studies of phase transitions
- Electron-phonon coupling in strongly correlated electron system
- Shape determination of Fermi surface in metallic systems
- Vibrational properties of nano-modulated and low-dimensional systems

➢ Absorption

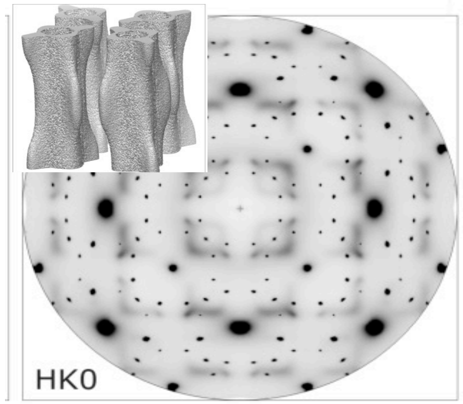
Multiple phase crystal



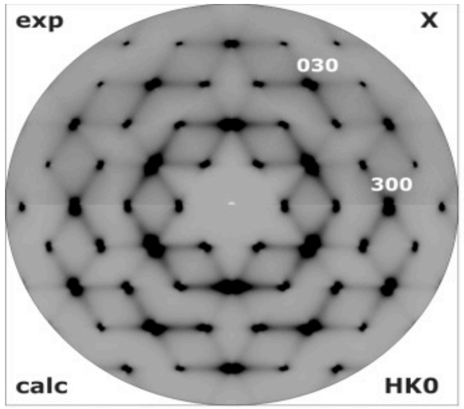
Static disorder



Structured diffuse scattering



Thermal diffuse



Inelastic X-ray scattering

LATTICE VIBRATIONS

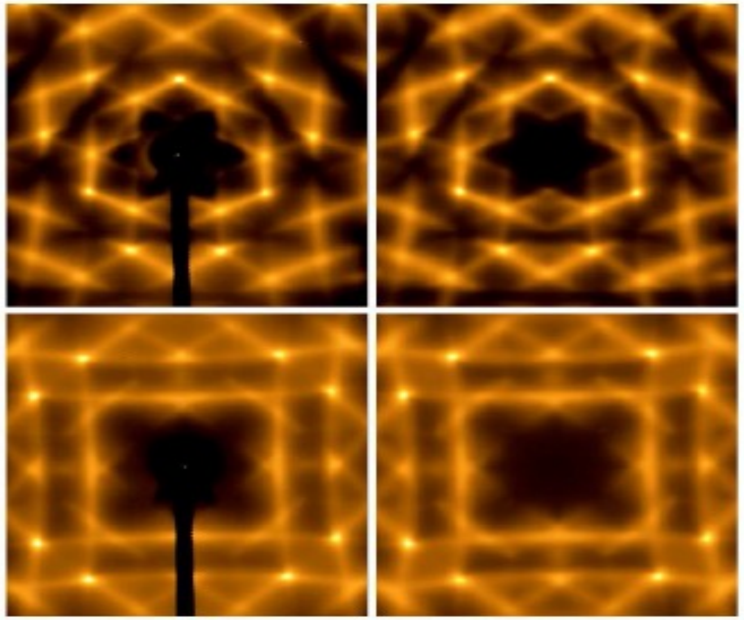
Vibrations around equilibrium position

$\mathbf{u}_n(t)$ Istantaneous displacement
Around the equilibrium position

$\langle \mathbf{u}_n \rangle = 0$ Temporal (thermal) average

Origin:
- Thermal vibration
- Zero point fluctuations

Thermal diffuse scattering:



Istantaneous structure factor:

$$F^{crystal}(\mathbf{Q},t) = -r_0 \sum_n^{all\ atoms} f_n(\mathbf{Q}) e^{i\mathbf{Q}\cdot(\mathbf{R}_n+\mathbf{u}_n(t))}$$

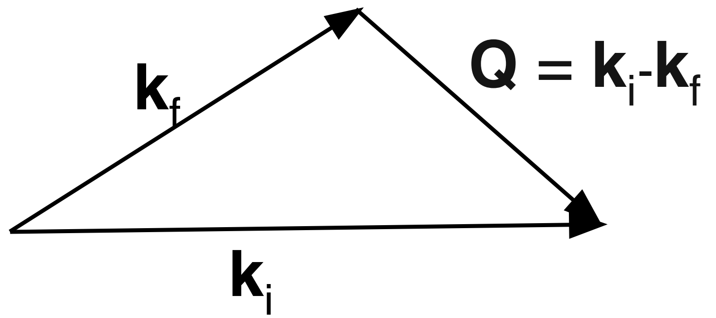
Scattering intensity proportional to the thermal average

$$\begin{aligned} I(\mathbf{Q}) &= \langle F(\mathbf{Q},t)F^*(\mathbf{Q},t)\rangle \\ &= r_0^2 \sum_n \sum_m f_n(\mathbf{Q}) f_m^*(\mathbf{Q}) e^{i\mathbf{Q}\cdot(\mathbf{R}_n-\mathbf{R}_m)} \langle e^{i\mathbf{Q}\cdot(\mathbf{u}_n-\mathbf{u}_m)}\rangle \end{aligned}$$

INELASTIC X-RAY SCATTERING

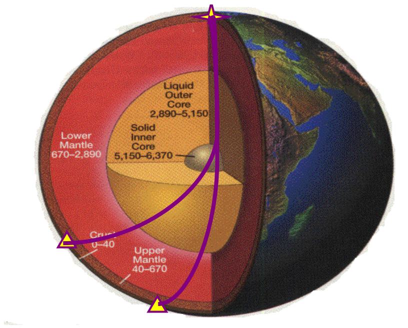
- High energy resolution studies of collective motion in solids and liquid phases
- Simultaneous information on energy E and momentum Q transferred between the photons and the electonic systems of interest

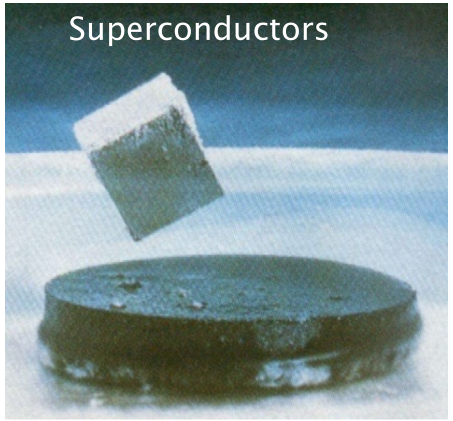
• Energy transfer: $E_i - E_f = \Delta E$ = **1 meV – 200 meV**
• Momentum transfer: Δk= **1 – 180 nm^{-1}**



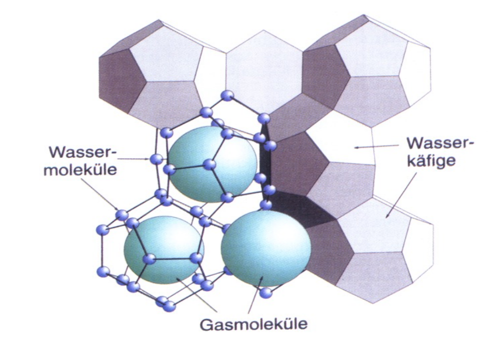
- Phonon dispersion in single crystals with small sample volume
- Collective dynamics in disordered systems
- Phonon dispersion in geophysical relevant materials
- Lattice dynamics in thin films and interfaces

Sound velocities and elasticity

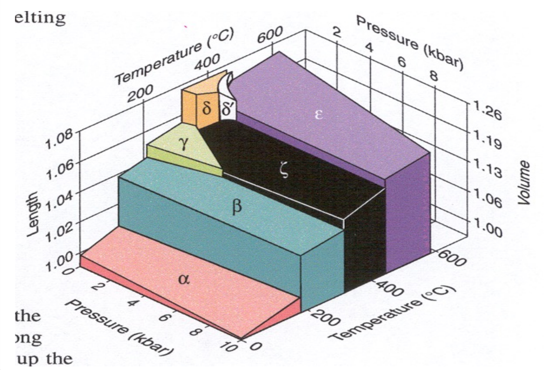




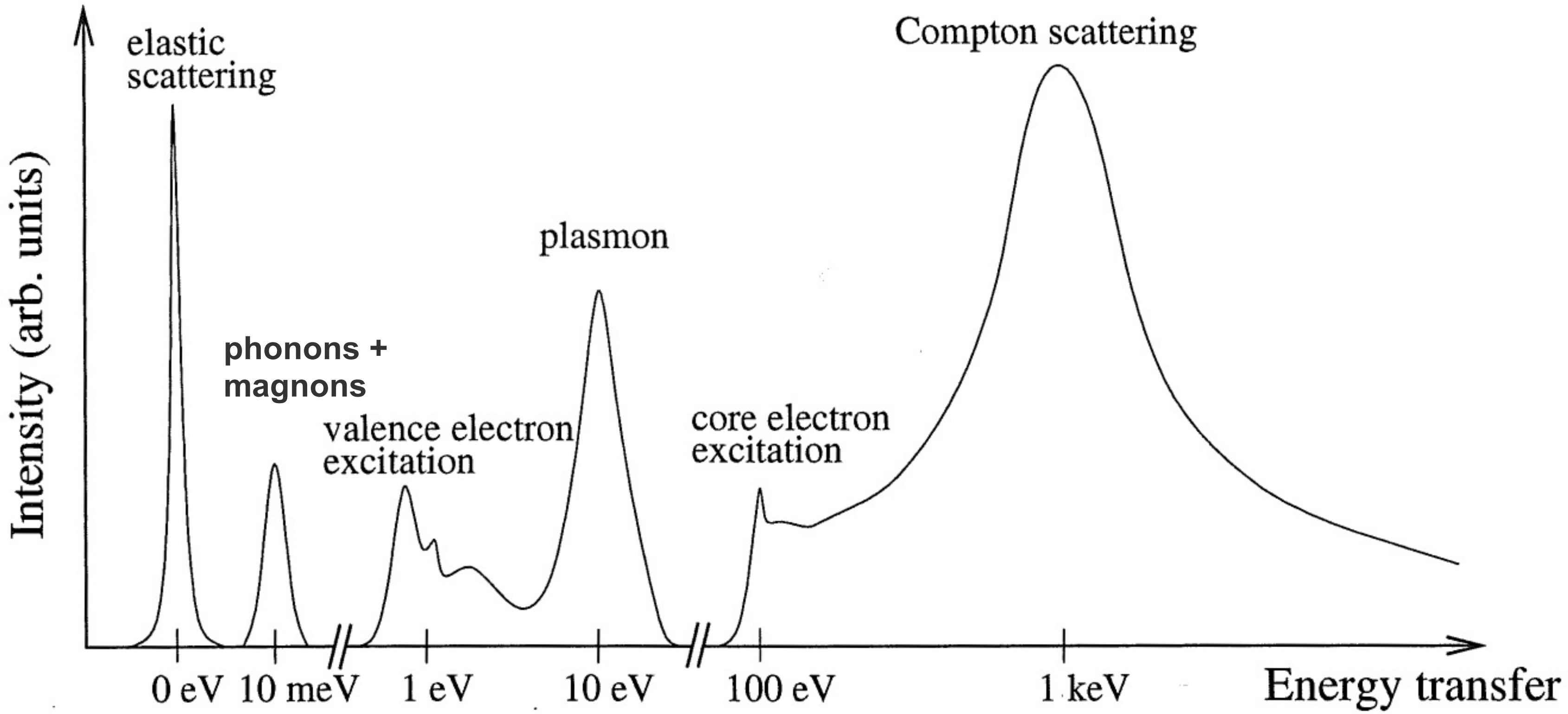
Thermal Conductivity



Phase stability

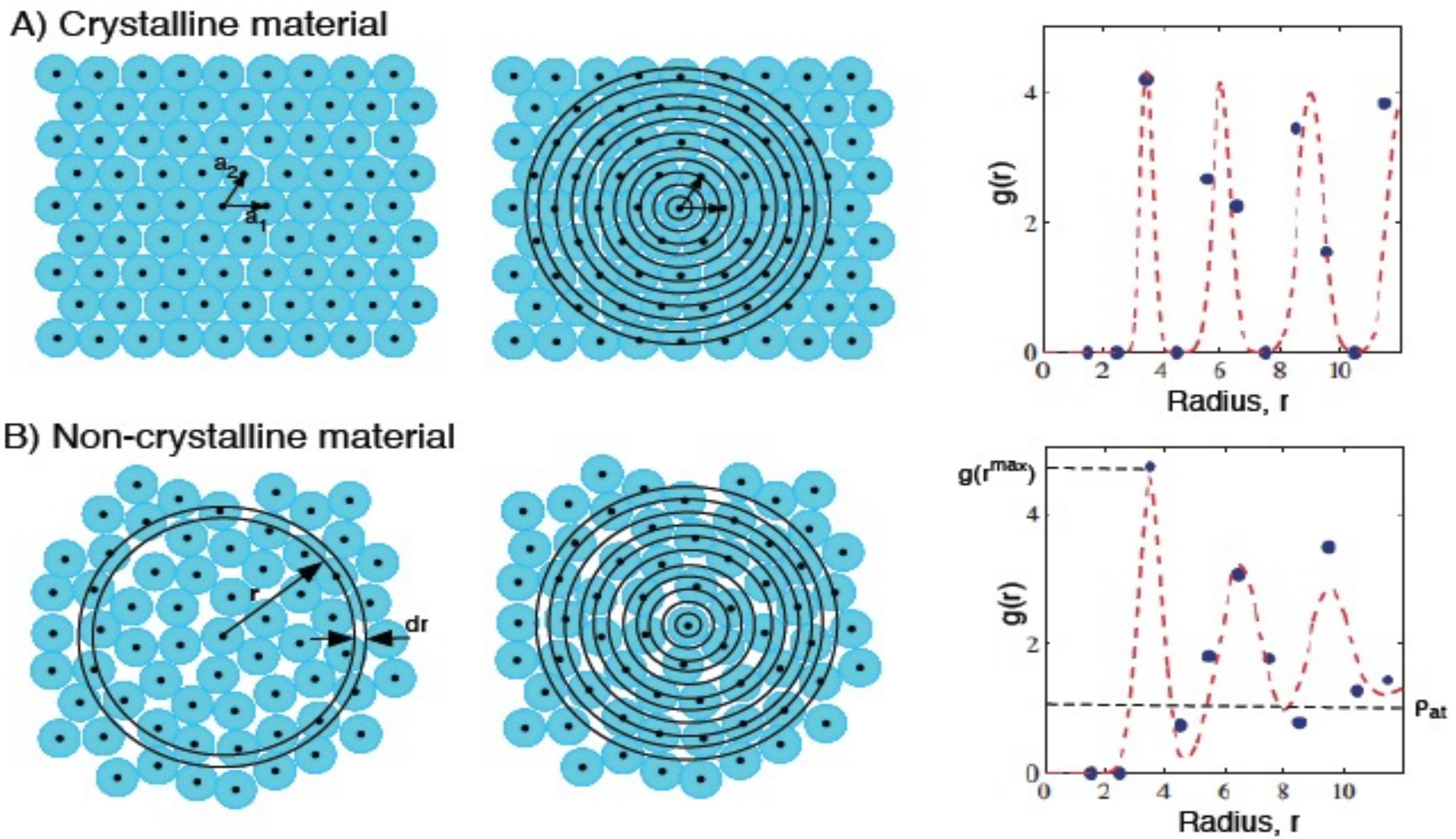


Schematic inelastic X-ray spectrum



Scattering in non-crystalline materials

NON CRYSTALLINE MATERIALS



Radial distribution function:

$$g(r) = \frac{\rho(r)}{\rho_{at}}$$

Radial electronic density:

$$\rho(r)^{2D} = \frac{N(r)}{2\pi r dr}$$

$$\rho(r)^{3D} = \frac{N(r)}{4\pi r^2 dr}$$

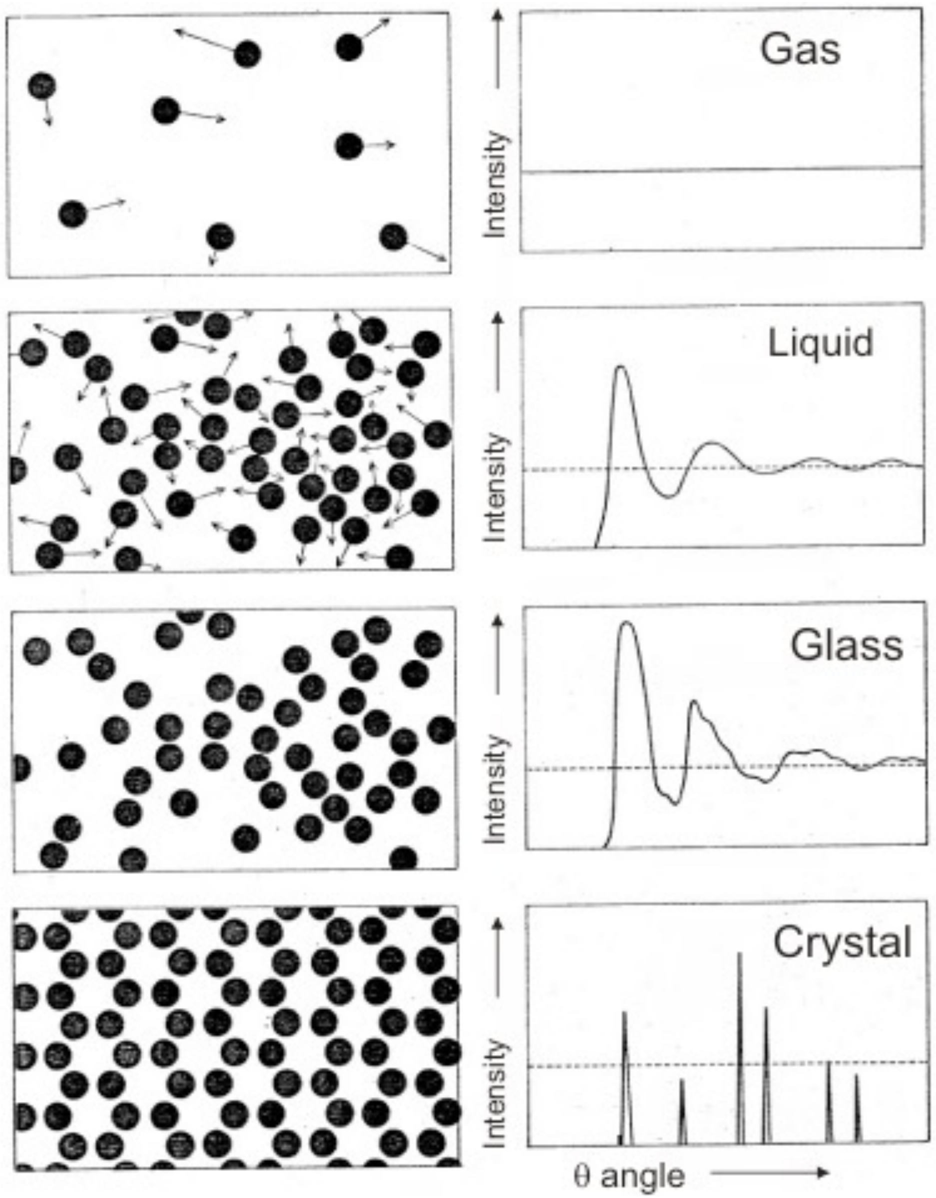
Averaged areal el. density

ρ_{at}

$g(r) \rightarrow 1 \qquad \rho(r) \rightarrow \rho_{at}$

The radial distribution function g(r) is the FT of the scattered intensity I(Q).

SCATTERING INTENSITIES : FROM GAS TO SOLIDS



SCATTERING OF GLASSES AND LIQUIDS

Short range order I^{SRO}

$$I(Q) = Nf^2(Q) + f^2(Q)\sum_n \int_V [\rho(\mathbf{r}_{nm}) - \rho_{at}]\, e^{i\mathbf{Q}\cdot\mathbf{r}_{nm}} dV_m$$

Small angle scattering I^{SAXS}

$$+ \quad f^2(Q)\sum_n \int_V [\rho_{at}]\, e^{i\mathbf{Q}\cdot\mathbf{r}_{nm}} dV_m$$

Scattering intensity

Deviation of the electron density between two different scattering centers with respect to the **averaged electron density**

$$(\rho_n(\mathbf{r}_{nm}) - \rho_{at})$$

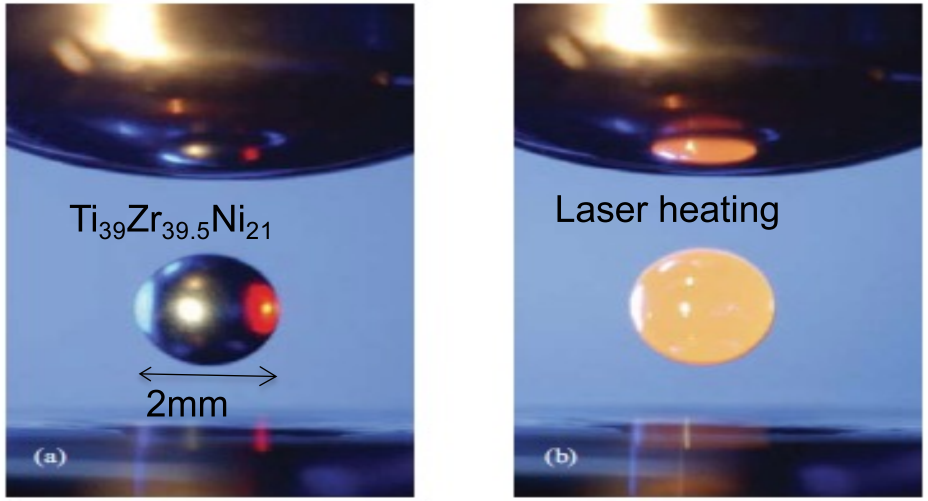
electron density at $r_{nm}=(r_n-r_m)$ with respect at r_n

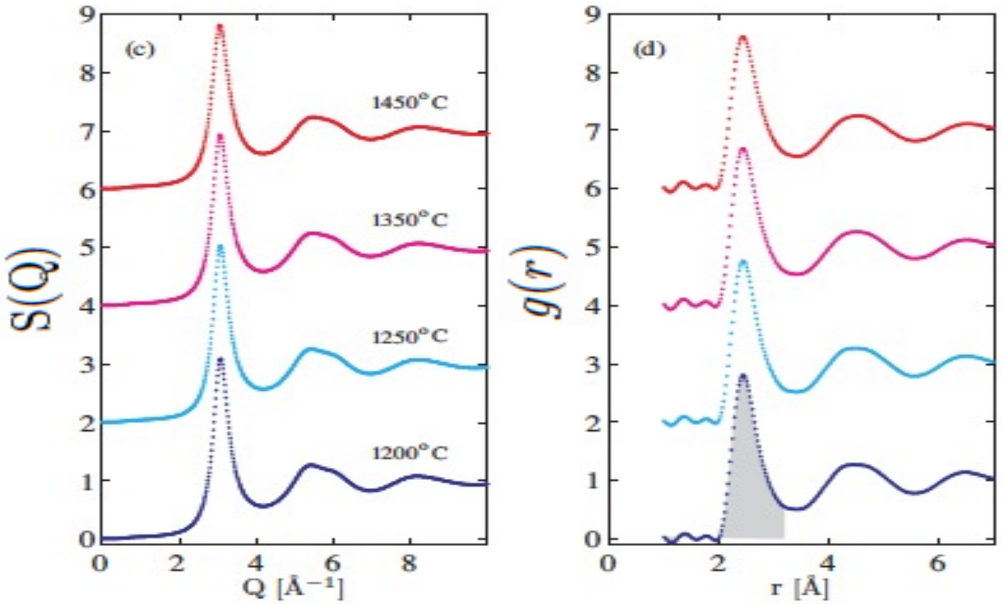
we add and subtract this term at the scattering intensity

I^{SRO} : Structural information on interatomic distances

I^{SAXS} : Information on shape. Morphology and size of molecular aggregate

Electrostatic levitation





Liquid/glass "structure factor"

$$S(Q) = \frac{I^{SRO}(Q)}{N f(Q)^2} = 1 + \frac{4\pi}{Q} \int_0^{\infty} r\,[\rho(r) - \rho_{at}]\,\sin(Qr)\,dr$$

Radial distribution function of Liquid/glass

$$g(r) = 1 + \frac{1}{2\pi^2 r \rho_{at}} \int_0^{\infty} Q\,[S(Q) - 1]\,\sin(Qr)\,dQ$$

The **peak position** indicate the first neighbour distance r=2.5 Å

The **integral** of the first peak gives the number of the atoms in the first coordination shell

$$N_{nn} = \int_{r_1}^{r_2} \rho_{at}\, g(r) 4\pi r^2\, dr$$

N~12 nearest neighbours
Icosahedral coordination

SMALL ANGLE X-RAYS SCATTERING (SAXS)

Scattering at small Q vectors is sensitive to the uniform electron distribution in molecules of shaped large object (polymers, biological macro-molecules ...)

$$I^{saxs}(Q) = f^2(Q) \sum_n \int_V \rho_{at} e^{i\mathbf{Q}\cdot(\mathbf{r}_n - \mathbf{r}_m)} dV_m = \left| \int_V \rho_{sl} e^{i\mathbf{Q}\cdot\mathbf{r}_n} \right|^2$$

Scattering length density: $\rho_{sl} = f(Q)\rho_{at}$ Fourier transform of charge density

For diluted molecules in solutions:

$$I^{saxs}(Q) = (\rho_{sl_p} - \rho_{sl_0}) \int_{V_p} e^{i\mathbf{Q}\cdot\mathbf{r}_n} dV_p$$

Particle scattering length density

Solvent scattering length density

Particle "form factor"

$$F(Q) = \frac{1}{V_p} \int_{V_p} e^{i\mathbf{Q}\cdot\mathbf{r}_n} dV_p$$

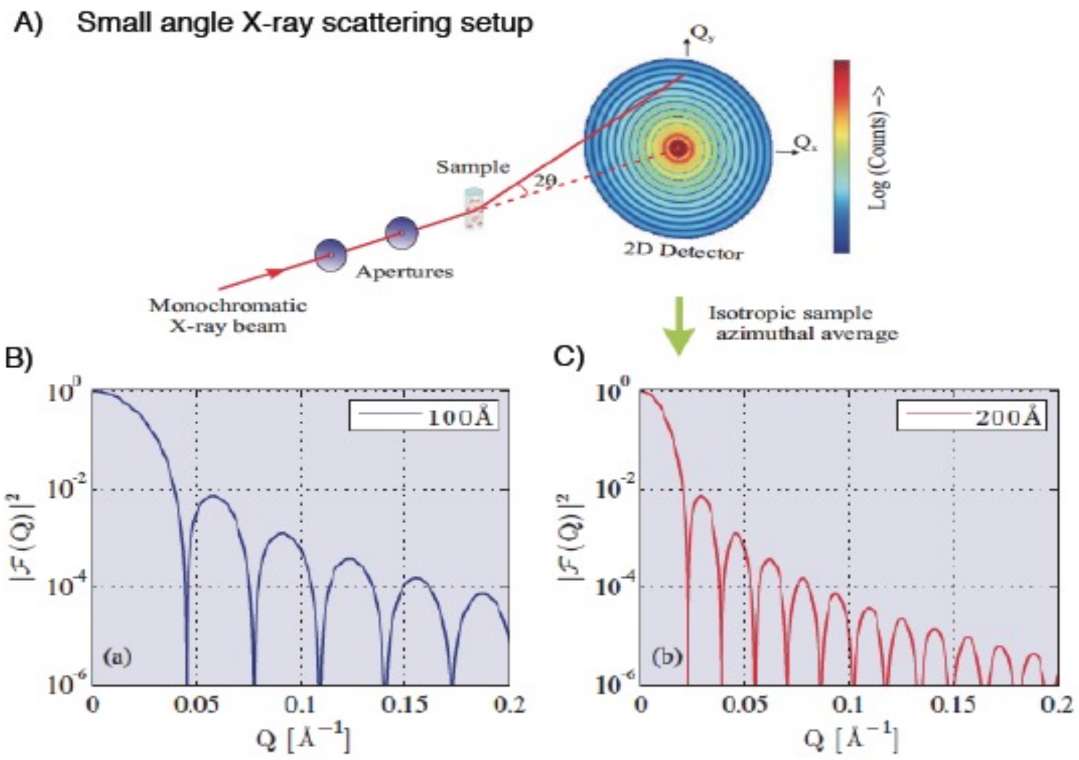
V_p particle volume

EX.: SAXS ON RIGID SPHERES

Small angle scattering experiment on a rigid sphere of radius R

$$I^{saxs}(Q) = \Delta\rho^2 V_p^2 |F(Q)|^2$$

$\Delta\rho$= excess of number of electrons with respect to the solvent
F(Q) form factor of the sphere
V_p=volume of the sphere



Form of the a sphere of radius R

$$\begin{aligned} F^{sphere}(Q) &= \frac{1}{V_p}\int_0^R\int_0^{2\pi}\int_0^{\pi} e^{iQr\cos\theta} r^2 \sin\theta d\theta d\phi dr \\ &= \frac{4\pi}{V_p}\int_0^R \frac{\sin(Qr)}{Qr} r^2 dr \\ &= 3\left[\frac{\sin(QR) - QR\cos(QR)}{Q^3R^3}\right] \\ &= = \frac{3J_1(QR)}{QR} \end{aligned}$$

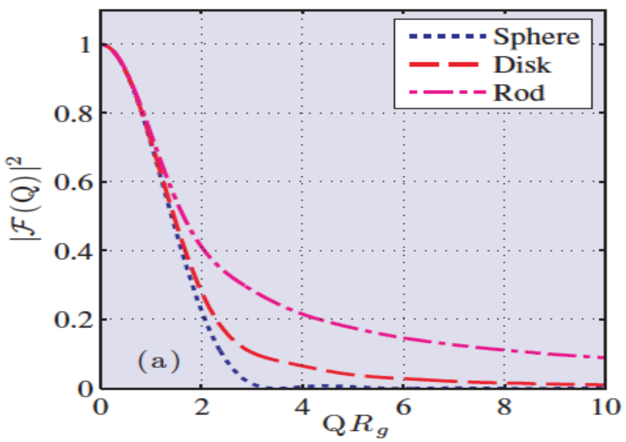
Long wavelength limit

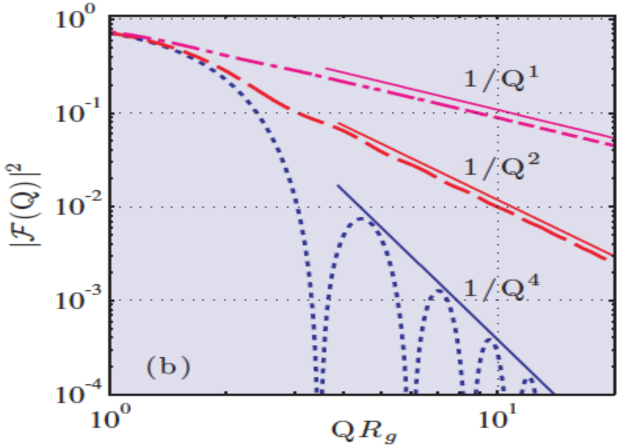
$$QR << 1$$

$$I^{saxs}(Q) = \Delta\rho^2 V_p^2$$

PARTICLE DIMENSIONALITY

	$\|\mathcal{F}(Q)\|^2$	Radius of gyration R_g
Sphere ($d = 3$)	$\left(\frac{3J_1(QR)}{QR}\right)^2$	$\sqrt{\frac{3}{5}}\, R$
Disc ($d = 2$)	$\frac{2}{Q^2R^2}\left(1 - \frac{J_1(2QR)}{QR}\right)$	$\sqrt{\frac{1}{2}}\, R$
Rod ($d = 1$)	$\frac{2Si(QL)}{QL} - \frac{4\sin^2(QL/2)}{Q^2L^2}$	$\sqrt{\frac{1}{12}}\, L$





Radius of giration

$$R_g^2 = \frac{1}{V_p}\int_{V_p} r^2 dV_p$$

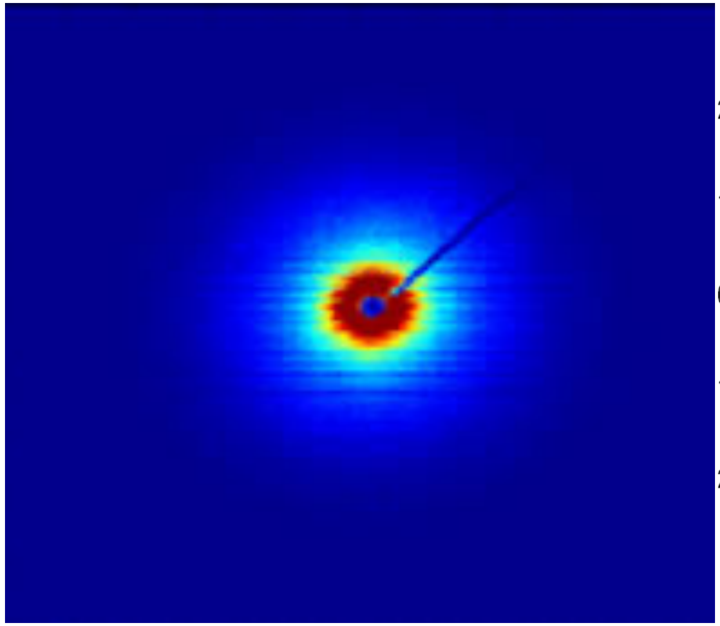
$$R_g^2 = \frac{\int_{V_p} \rho_{sl,p}(\mathbf{r})\, r^2\, dV_p}{\int_{V_p} \rho_{sl,p}(\mathbf{r})\, dV_p}$$

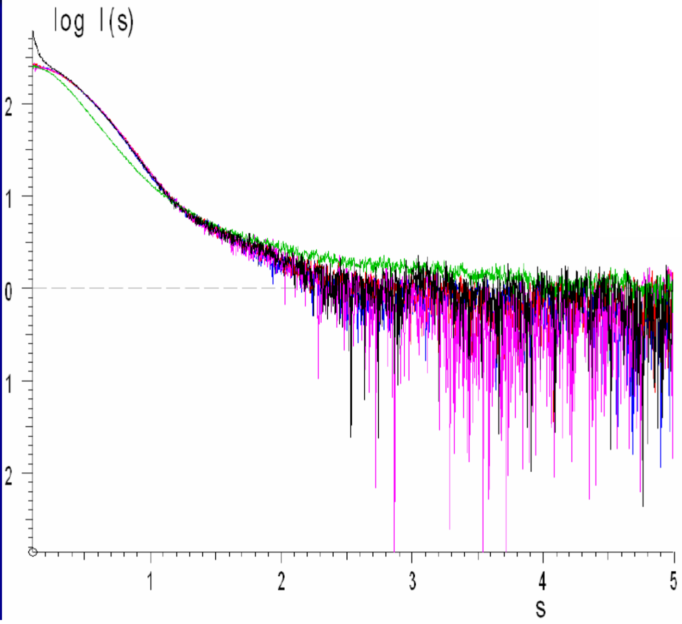
Uniform sphere

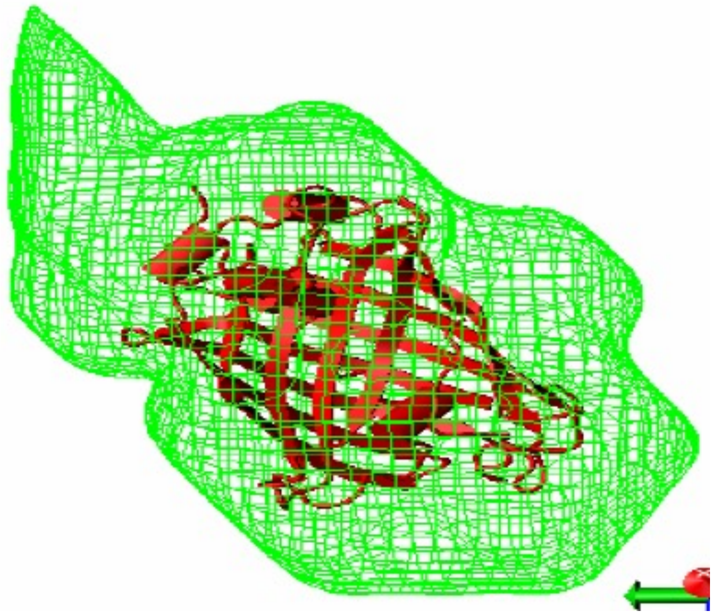
$$I_1^{SAXS}(Q) \approx \Delta\rho^2 V_p^2 e^{-Q^2R_g^2/3}$$

Small Angle X-ray Scattering (SAXS) is a technique for studying structure at <u>low resolution</u> in <u>solution</u> & under <u>normal biophysical/biochemical conditions</u>

Information from SAXS:
- model independent parameters (Rg, I(0))
- *ab initio* shape determination
- rigid body modelling





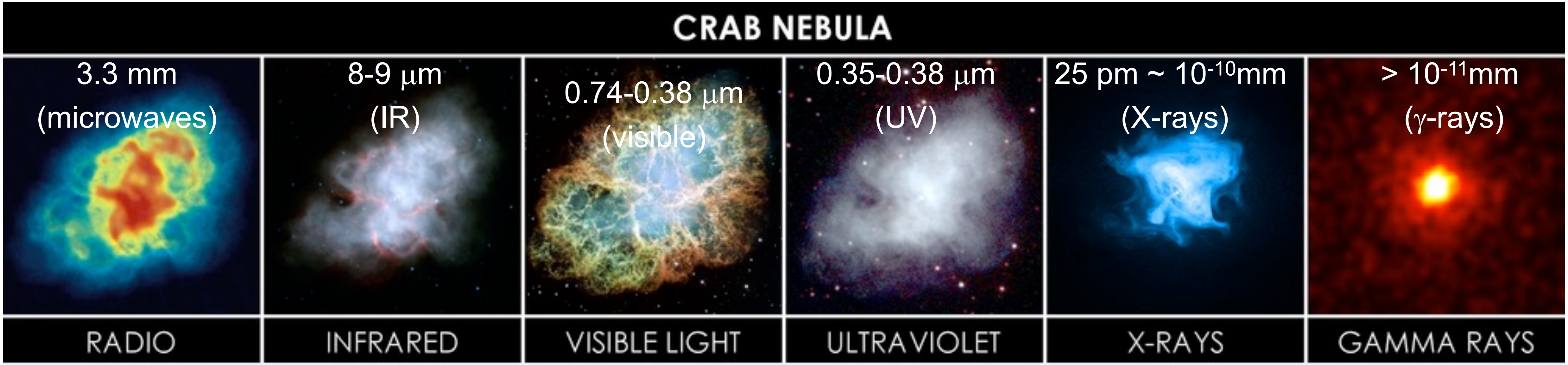


molecular shape, molecular interactions, kinetics, etc…

X-rays absorption

PHOTON ABSORPTION/EMISSION

The absorption of electromagnetic radiation change with the wavelength and depends from the characteristic properties of photon/matter interaction.



The crab nebula in radio, infrared, visible, ultraviolet, x-ray and gamma-ray wavelengths.

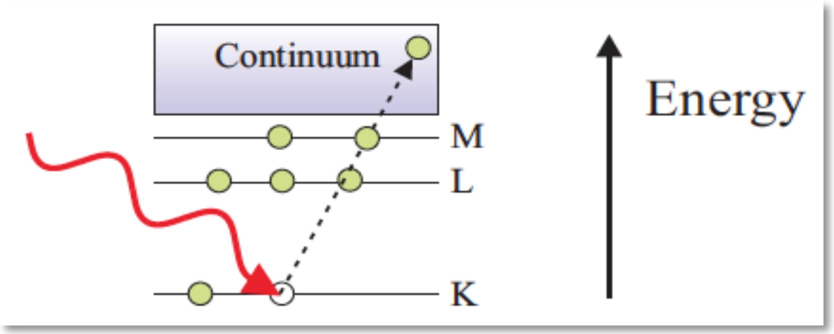
Sources: Radio: NRAO/AUI and M. Bietenholz, J.M. Uson, T.J. Cornwell; Infrared: NASA/JPL-Caltech/R. Gehrz (University of Minnesota); Visible: NASA, ESA, J. Hester and A.Loll (Arizona State University); Ultraviolet: NASA/Swift/E. Hoversten, PSU, X-ray: NASA/CXC/SAO/F. Seward et al.; Gamma: NASA/DOE/Fermi LAT/R. Buehler

ABSORPTION AND EMISSION PROCESSES

Absorption and emission processes are tools for basic analysis of the electronic structure of atom, molecules and solids over different energy scales.

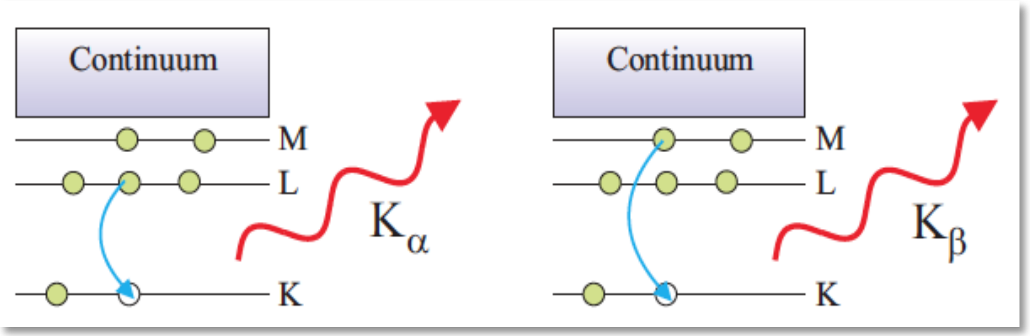
Photo-electric absorption

Photon absorbed and electron emitted in the continuum



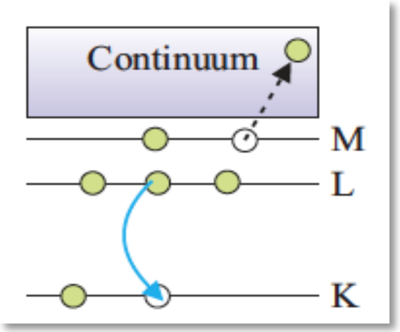
Fluorescent emission

An electron from the outer shell fill the hole and emit a photon



Auger electron emission

The atom relax into the ground state by emitting an electron

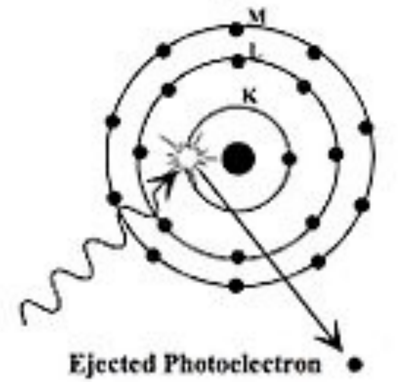


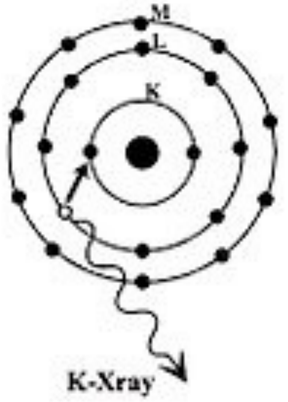
The interaction Hamiltonian is the weak relativistic limit of Dirac's equation (terms v/c < 1)

$$
\begin{aligned}
H &= \frac{1}{2m}\left(\vec{p}+\frac{e}{c}\vec{A}\right)^2 + V(r) \\
H_{int} &= -\frac{e}{2mc}(\vec{p}\cdot\vec{A}+\vec{A}\cdot\vec{p}) + \frac{e^2}{2mc^2}\vec{A}\cdot\vec{A} \\
&= -\frac{e}{mc}\vec{A}\cdot\vec{p} + \frac{e^2}{2mc^2}\vec{A}\cdot\vec{A}
\end{aligned}
$$

Absorption and emission processes

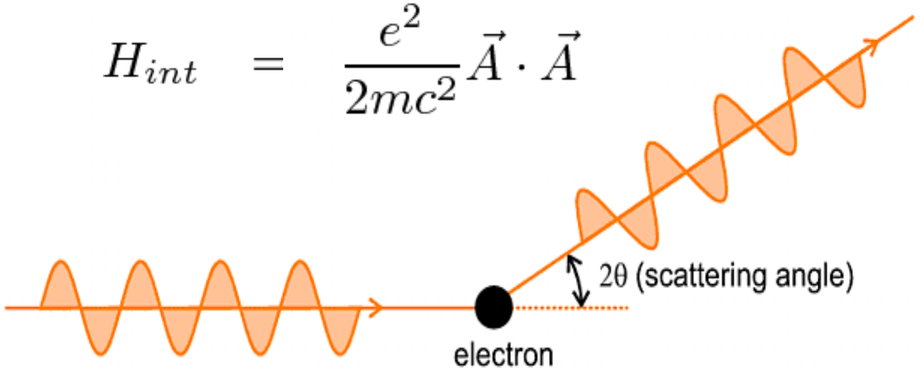
$$H_{int} = -\frac{e}{mc}\vec{A}\cdot\vec{p}$$





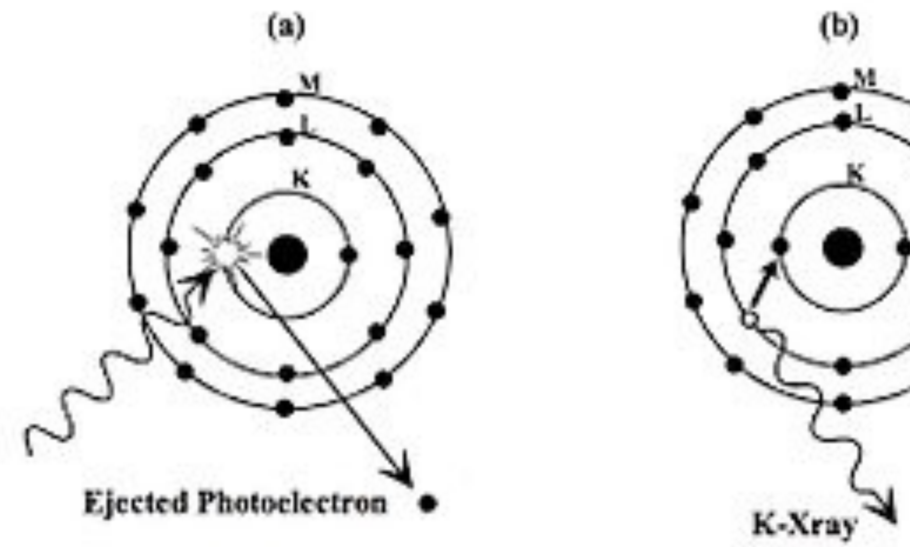
Scattering processes

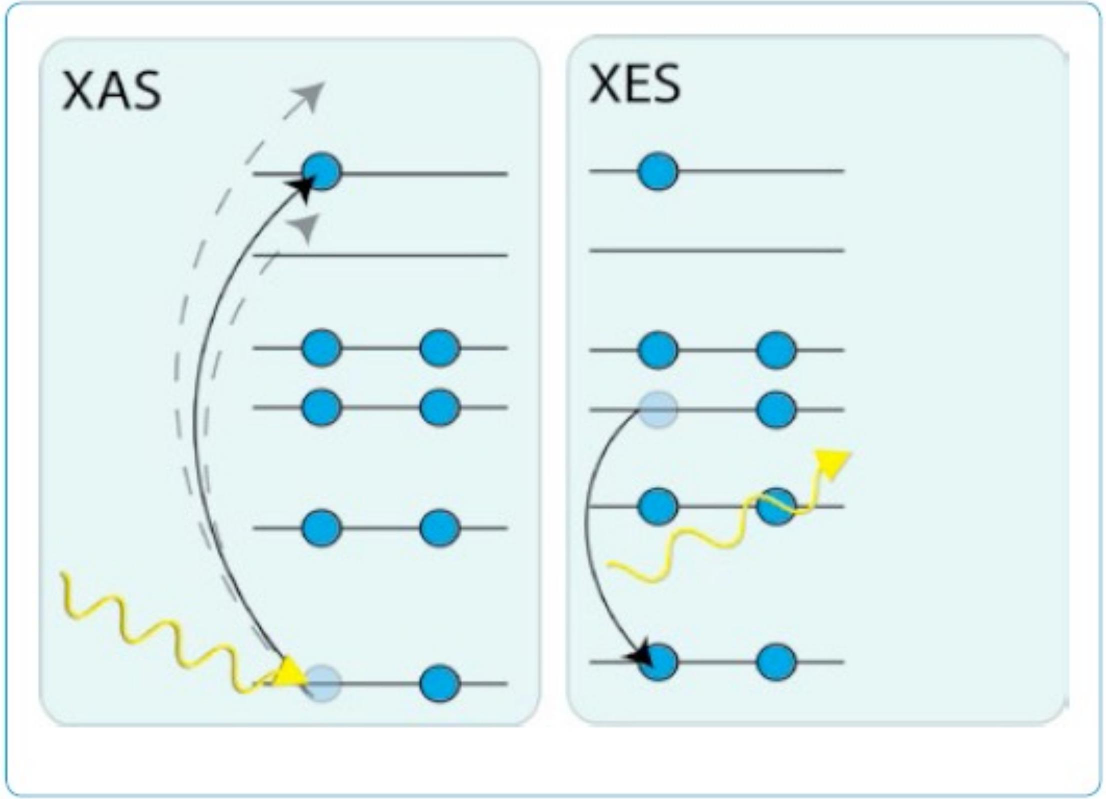
$$H_{int} = \frac{e^2}{2mc^2}\vec{A}\cdot\vec{A}$$



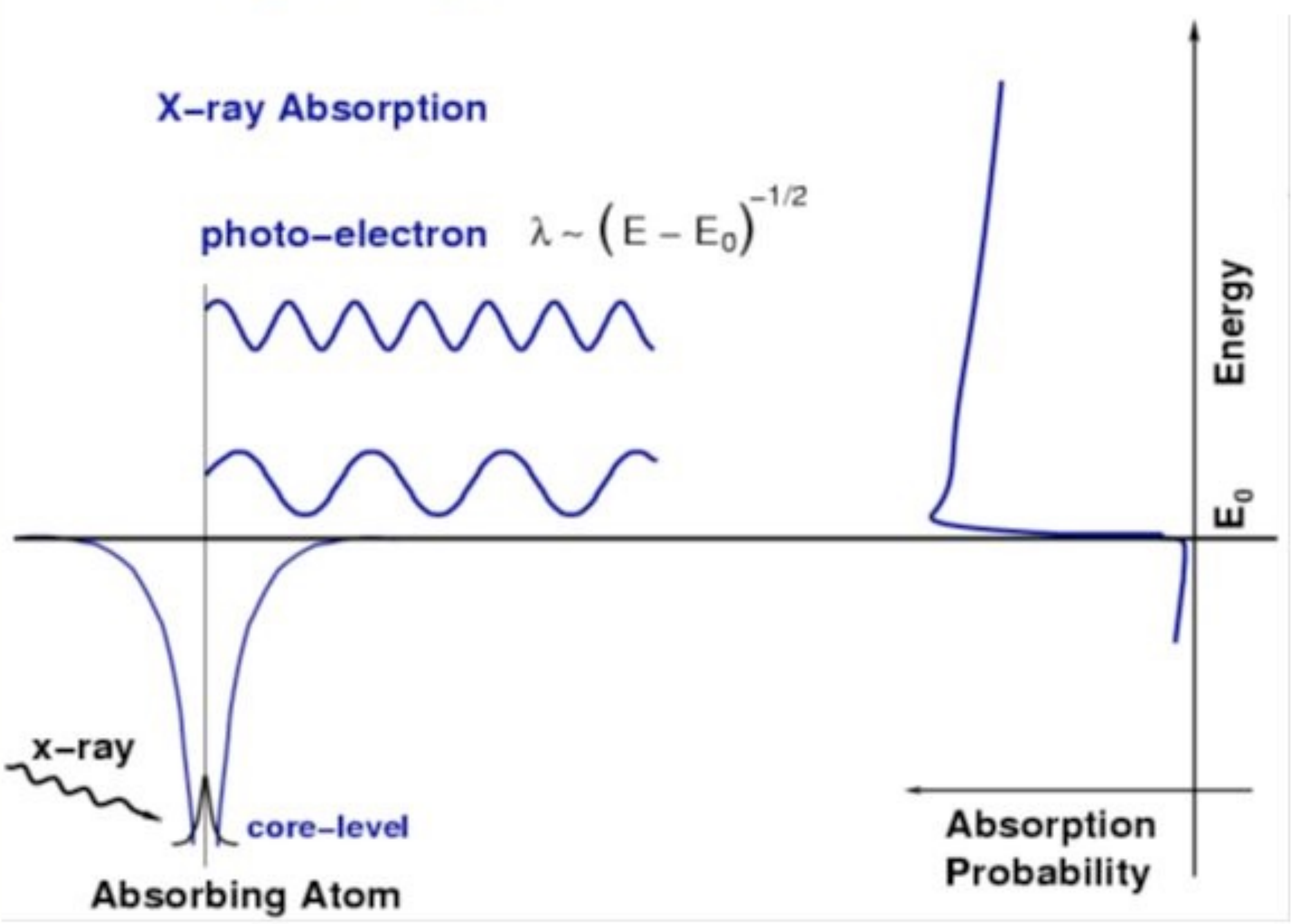
Absorption and emission processes of photo-electrons probe the atomic level and valence orbital symmetries of the material under investigation.

$$H_{int} = -\frac{e}{mc}\vec{A}\cdot\vec{p}$$





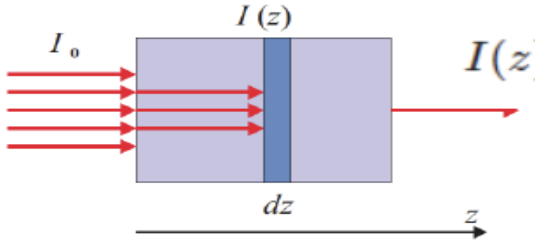
ABSORPTION OF AN ISOLATED ATOM



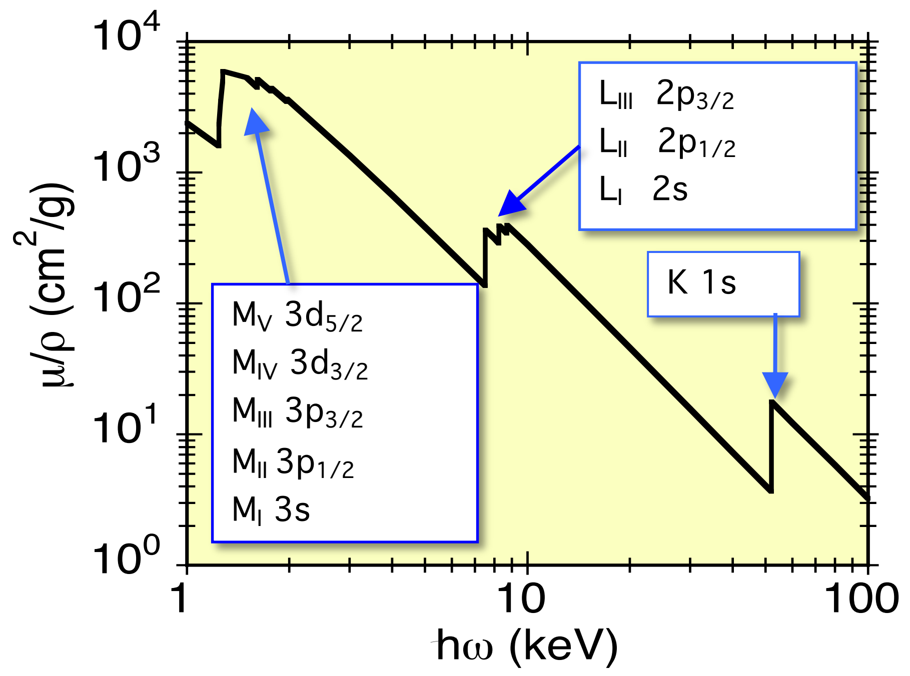
X-RAY ABSORPTION EDGES

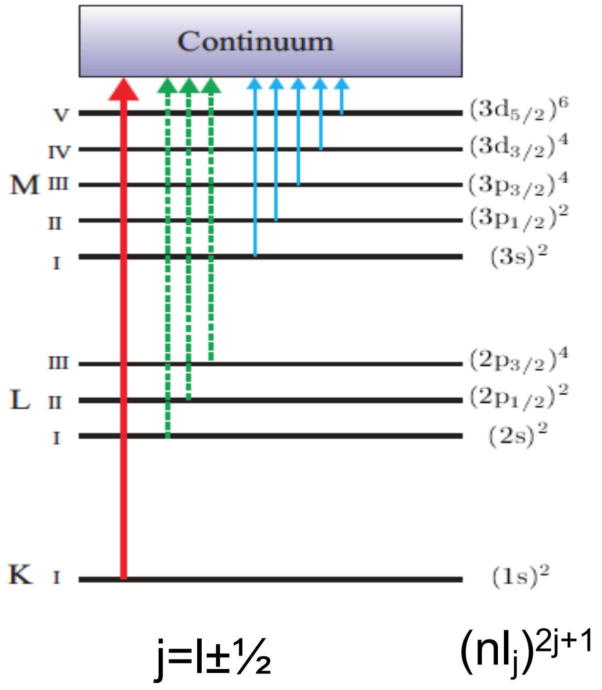
X-rays energies are able to extract atomic electrons from the atomic core.
The **element-specific** energies of the discontinuous jumps in the x-rays absorption spectra are called absorption edges.

$$\mu = \rho_a \sigma_a = \left(\frac{\rho_m N_A}{A}\right) \sigma_a$$

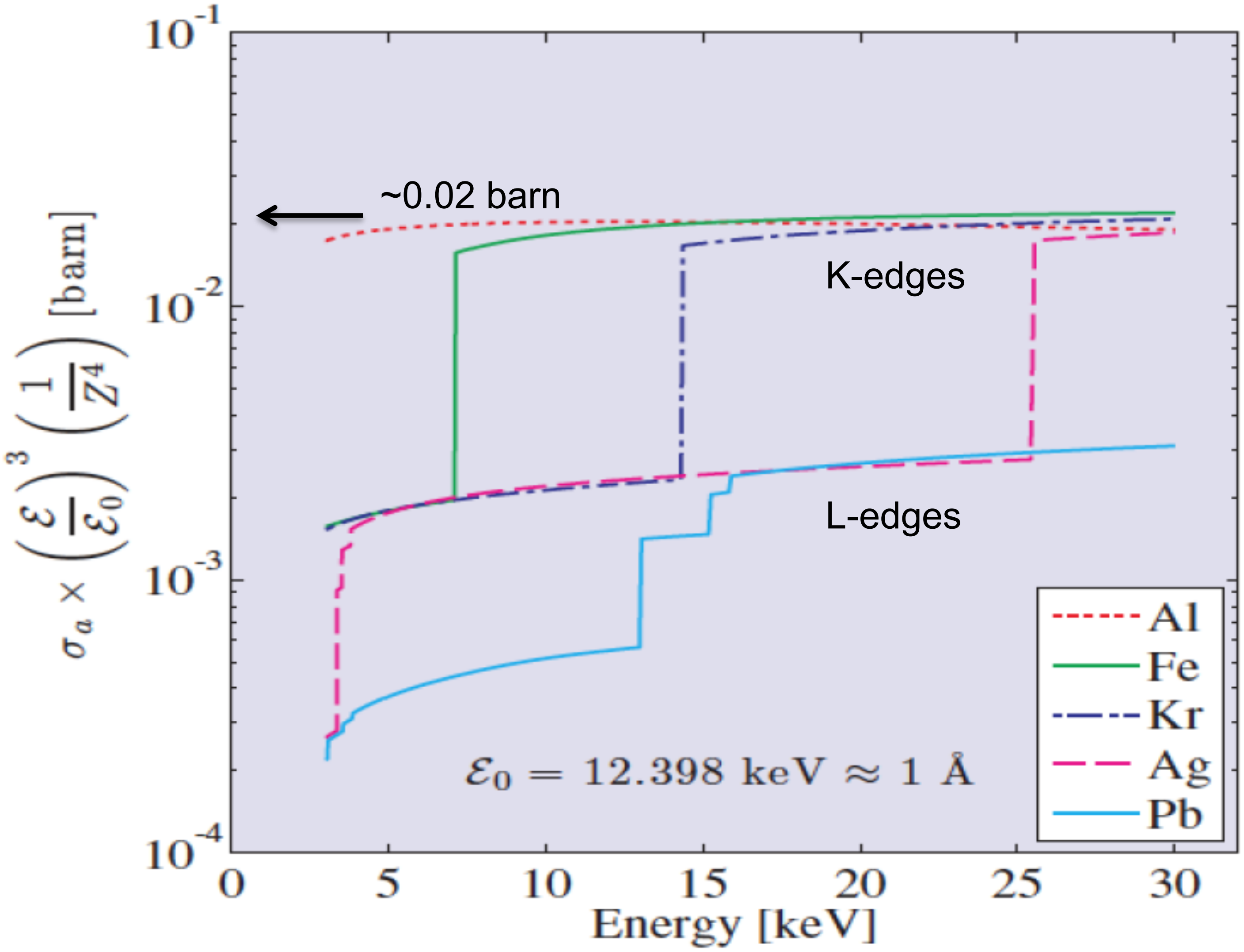


$$I(z) = I_0 \, e^{-\mu z}$$



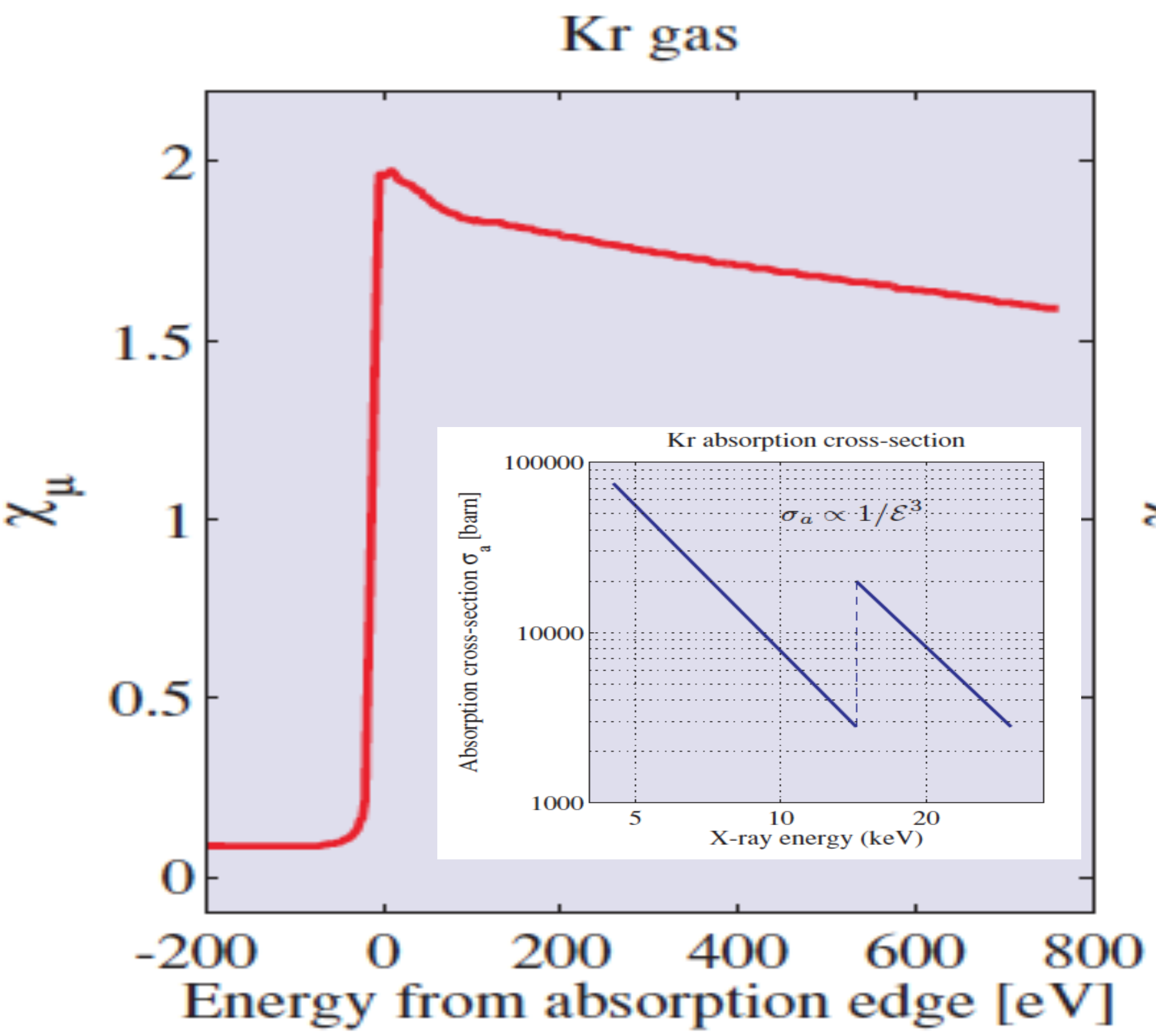


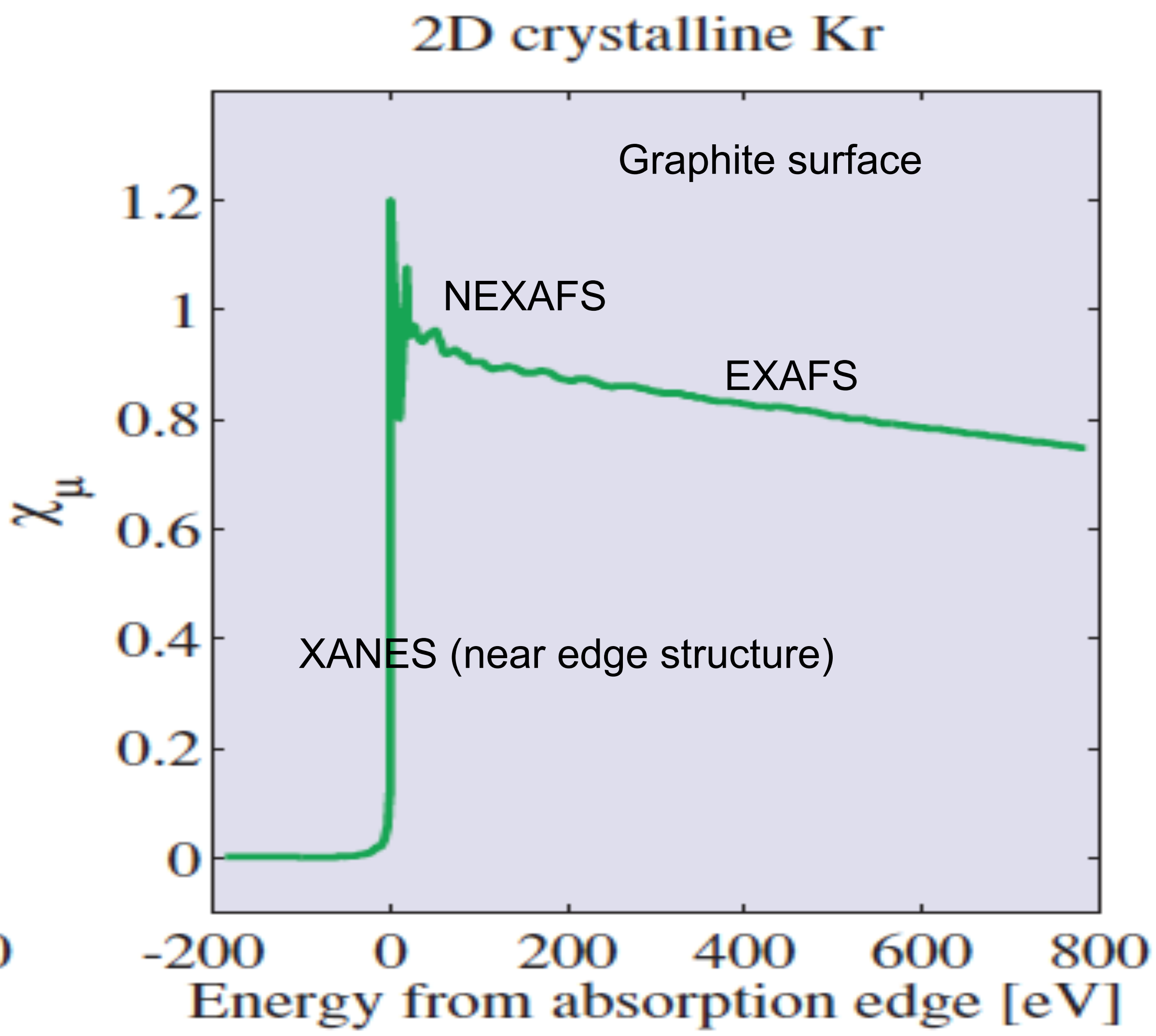
ABSORPTION EDGES SCALE FACTORS : EXPERIMENT

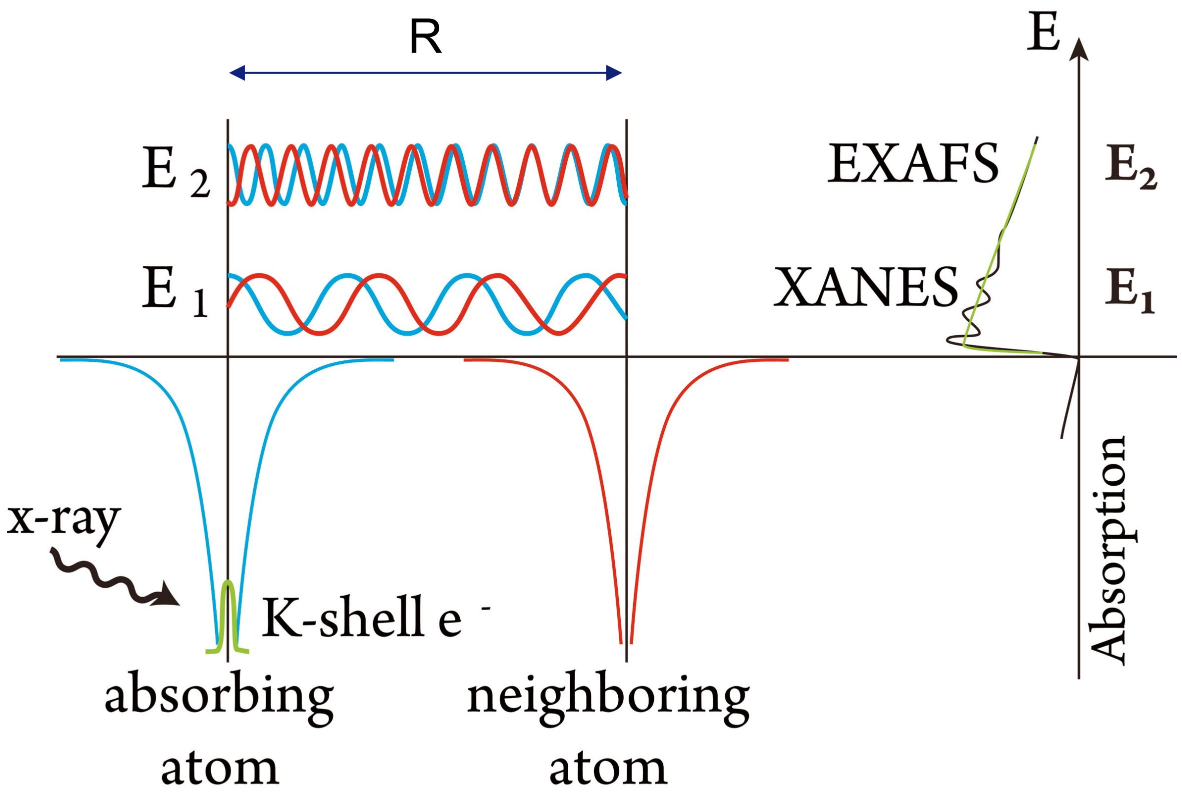


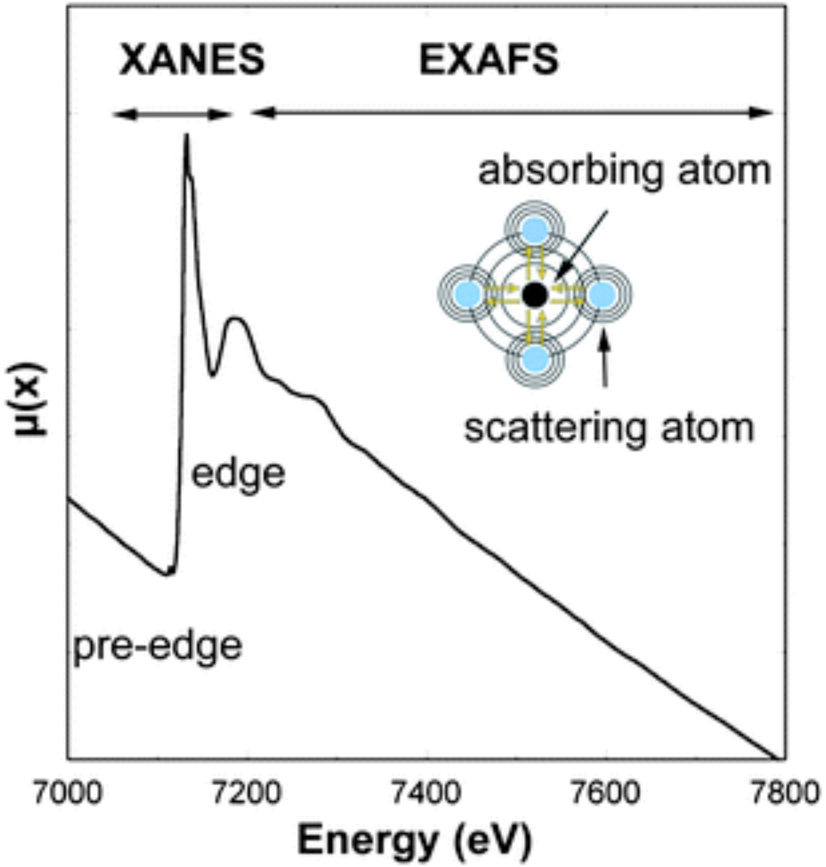
$$\sigma_{abs} \propto (\hbar\omega)^{-3} Z^4$$

ABSORPTION IN GAS AND CRYSTALLINE MATERIALS





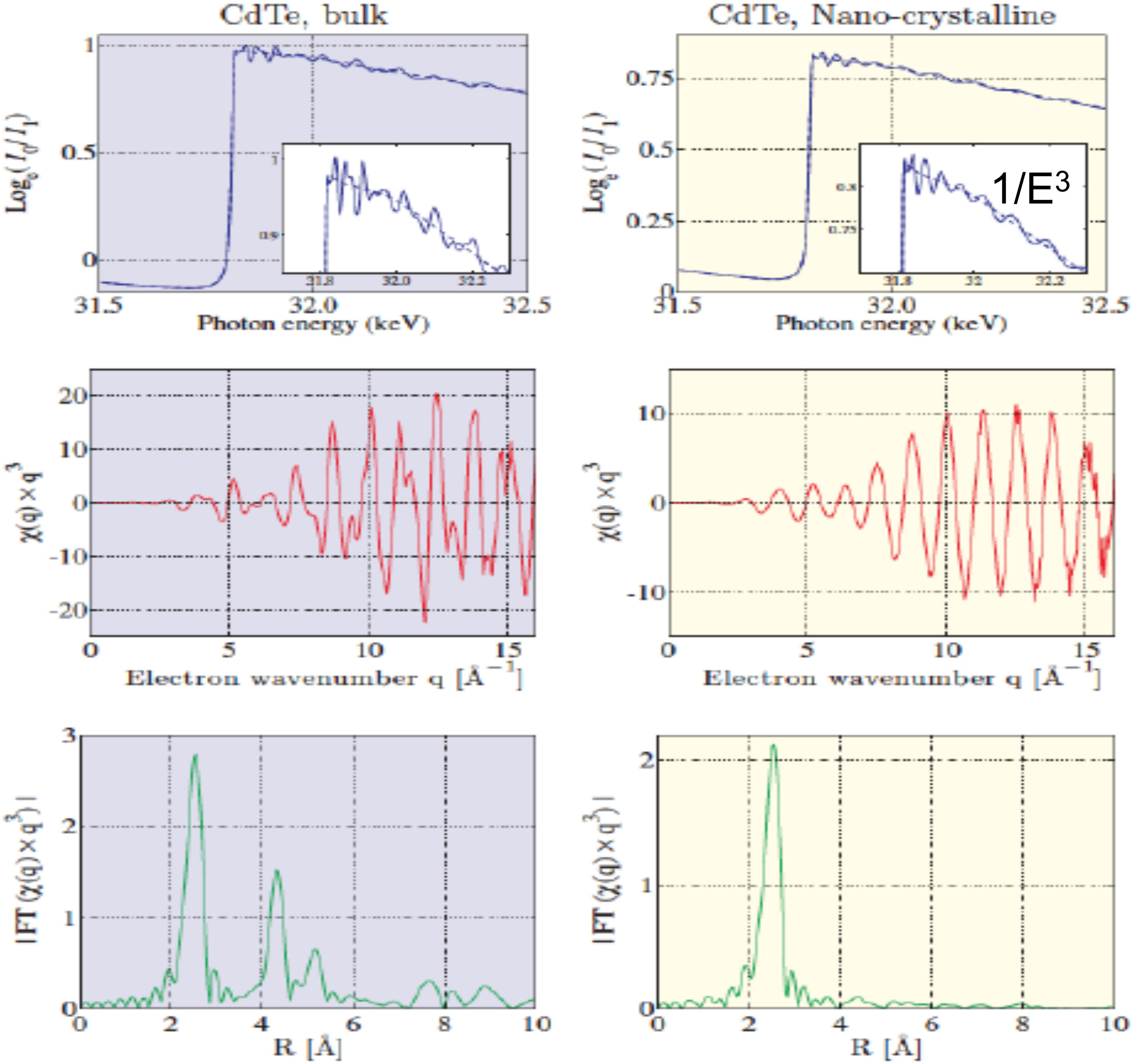




$$\psi_{backscatt.}(0) = t(q)\frac{e^{i(2qR+\delta)} + c.c.}{qR^2}$$

2R= double distance (neighbour)-(absorbing atom)
t(q) = scattering amplitude of neighbour atom
δ = phase shift

EXAMPLE: CdTe NANO-CRYSTALS - I

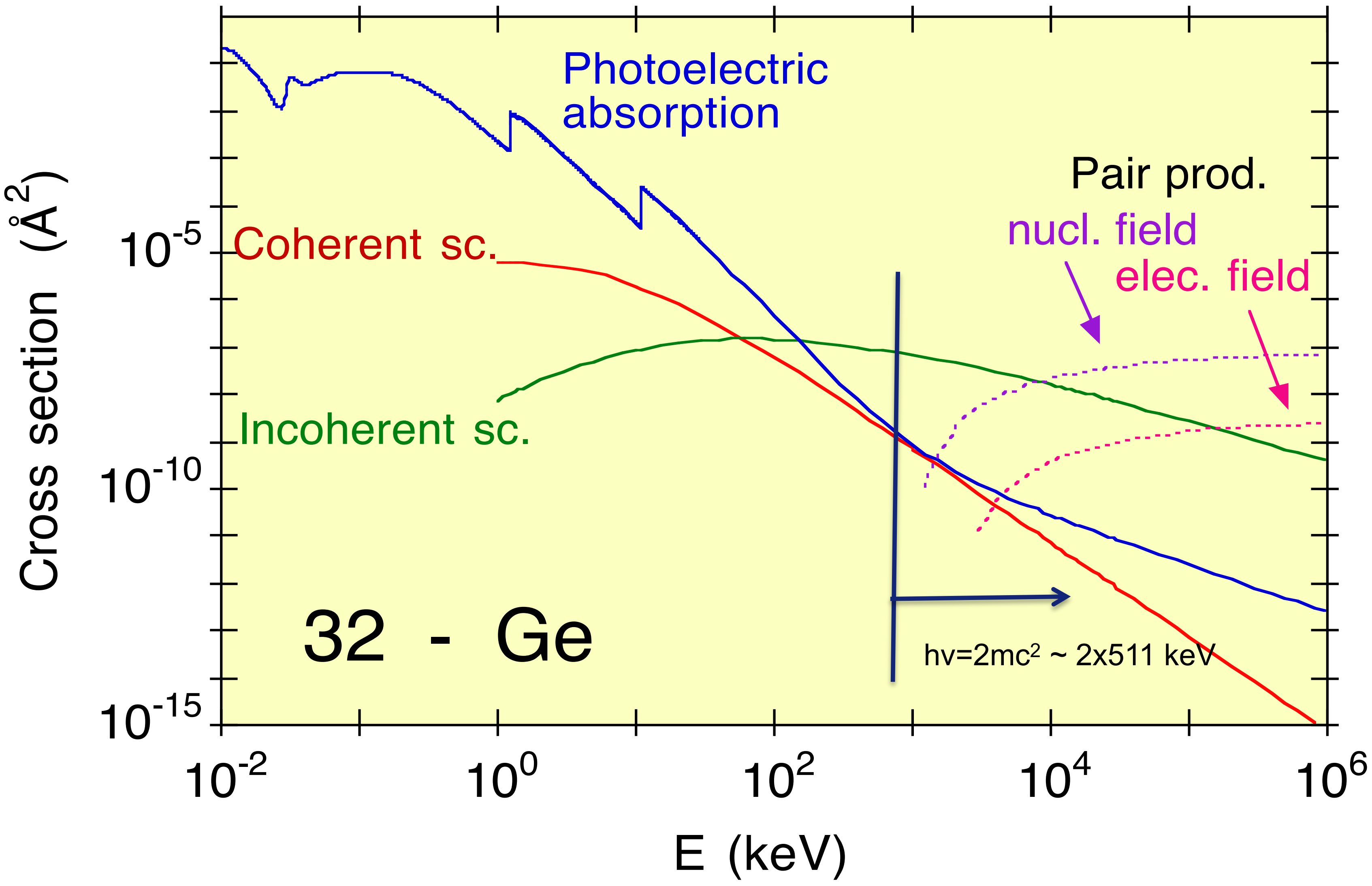


Te K-edge

Nano-crystals:
N=3.55
Only first neighbours
(reduced clusters)

Bulk
N=4
Complex EXAFS structure

SCATTERING AND ABSORPTION CROSS SECTIONS



POLARIZATION DEPENDENT ABSORPTION

Linear dichroism
Produced by the preferential absorption of one of the two orthogonal photon polarization

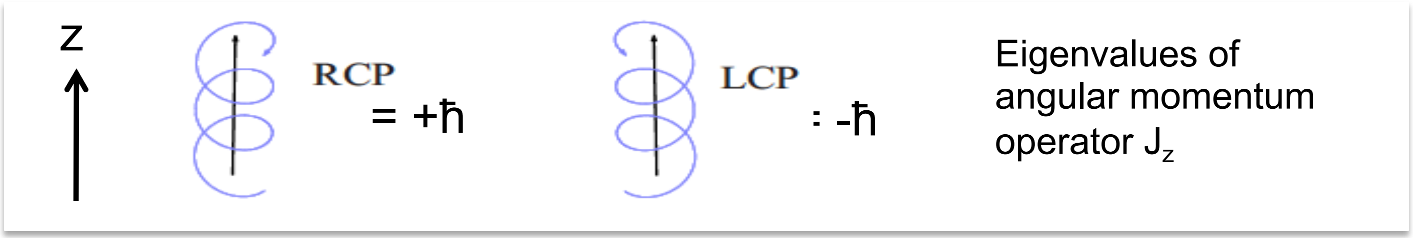
Linearly oriented polimers
When the electric field is parallel to the preferential molecular axis, it is absorbed

Circular dichroism
Produced by the preferential absorption of one of the two circular photon polarization

Combination of $\lambda/4$ and linear polarized filters have the different effect on circular polarization.
Circular dichroism is found also in chiral molecules which select only one circular polarization (ex. sugar)

Quantum description of a a circular polarised photon beam:

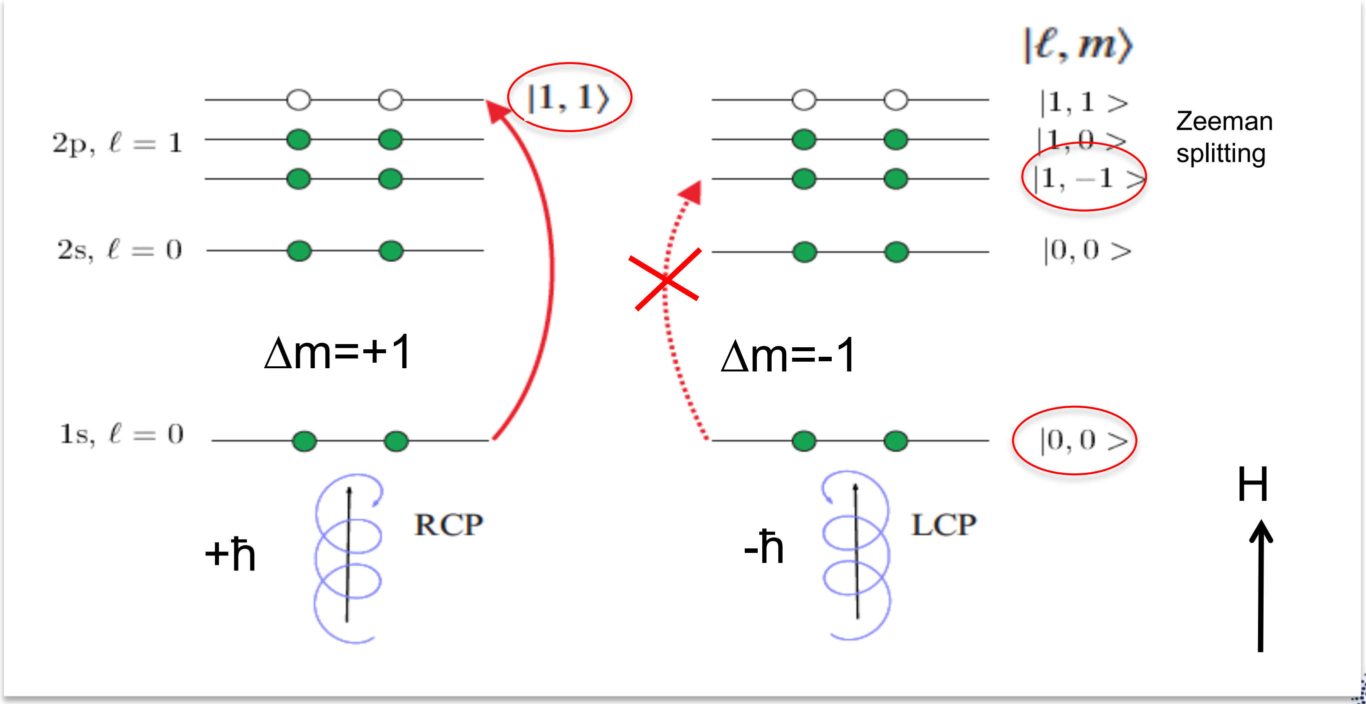
RCP and LCP eigenstates of J_z



The sum rule for the conservation of angular momentum in electronic transition produces a difference in the absorption of RCP and LCP photons.

Ex.: Dipole electric transitions in Oxigen (E1)
selection rule: Δl±1
(odd function for coordinate exch.)

Transition allowed:
Δm=+1 for RCP
Δm=-1 for LCP

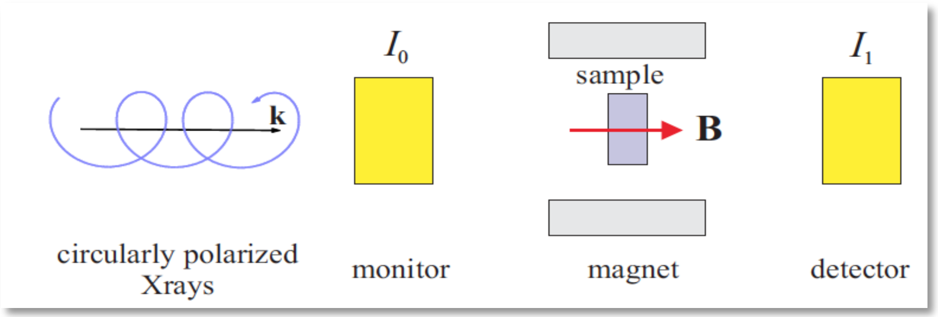


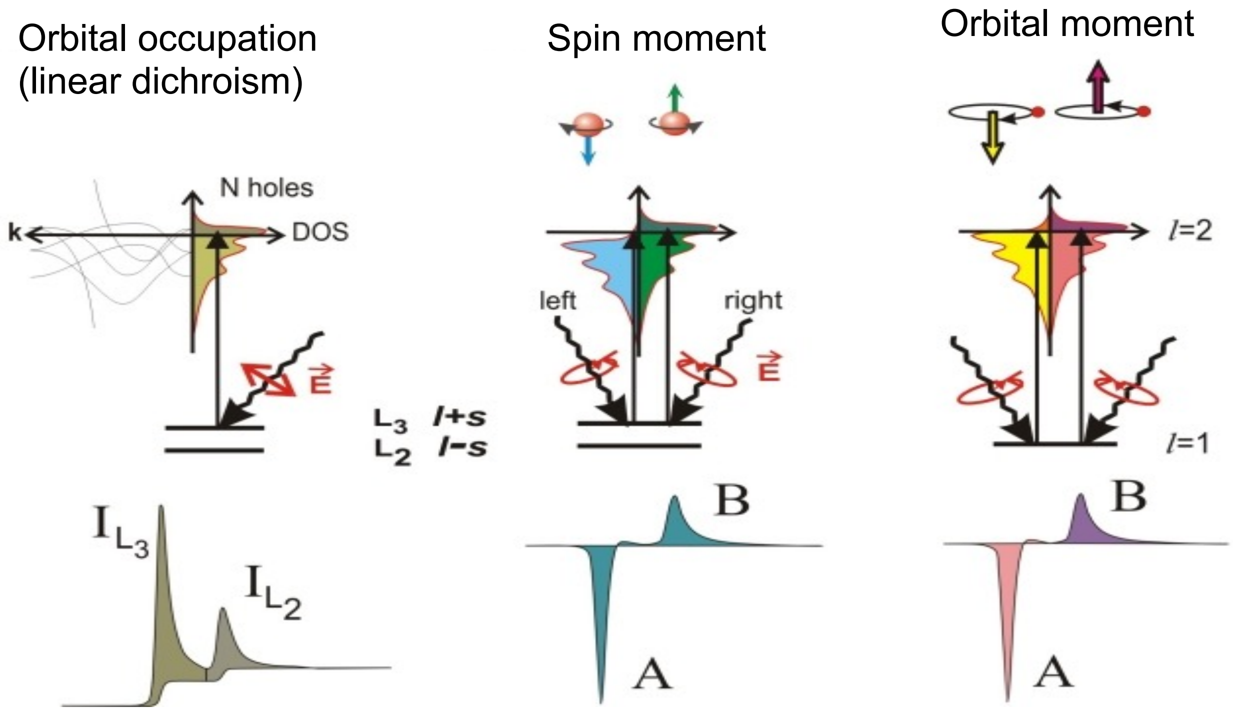
X-RAY MAGNETIC CIRCULAR DICROISM

X-ray magnetic dichroism is the difference in the absorption coefficients $\mu^{\pm}$ of left (-) and right (+) circularly polarized x-rays.

$$\mu^{+}(E) = \left(\frac{1}{d}\right) \ln\left(\frac{I_0^{+}(E)}{I_1^{+}(E)}\right)$$

$$\mu^{-}(E) = \left(\frac{1}{d}\right) \ln\left(\frac{I_0^{-}(E)}{I_1^{-}(E)}\right)$$

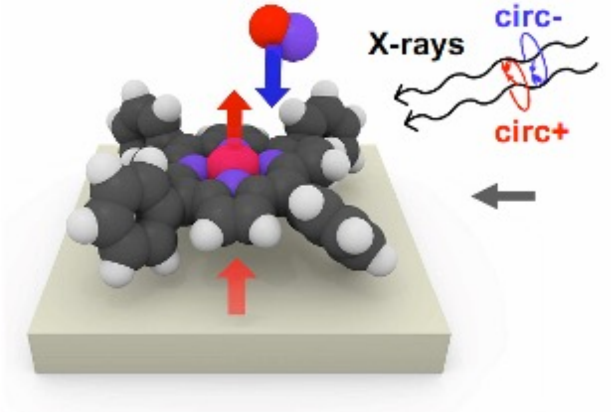




SINGLE MOLECULE MAGNETS ON FERROMAGNETIC METALS

A. Lodi Rizzini et al., *Phys. Rev. Lett. 107, 177205 (2011)*

Single molecule magnets are ideal candidates for magnetic data storage and quantum computing applications.

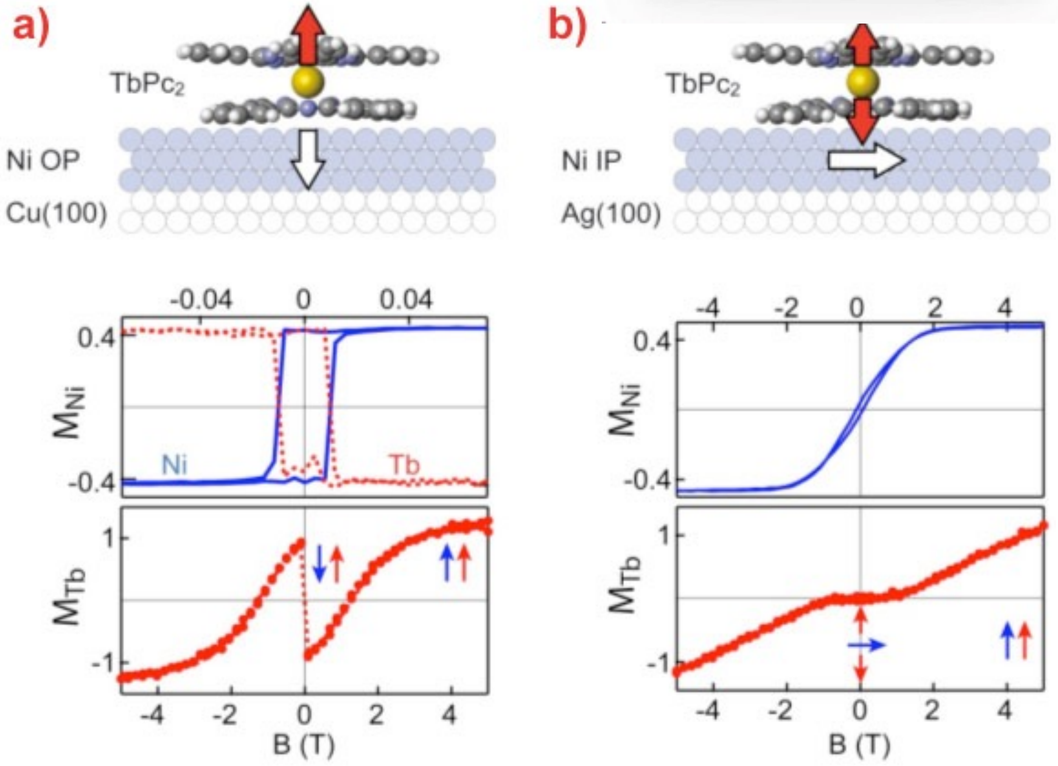


Element-resolved magnetization measurements using X-ray magnetic circular dichroism (soft x-rays)

Tb-complex on Ni metal film

a) Cu(110) substrate -> out-of-plane magnetization
b) Ag(100) substrate -> in-plane magnetization

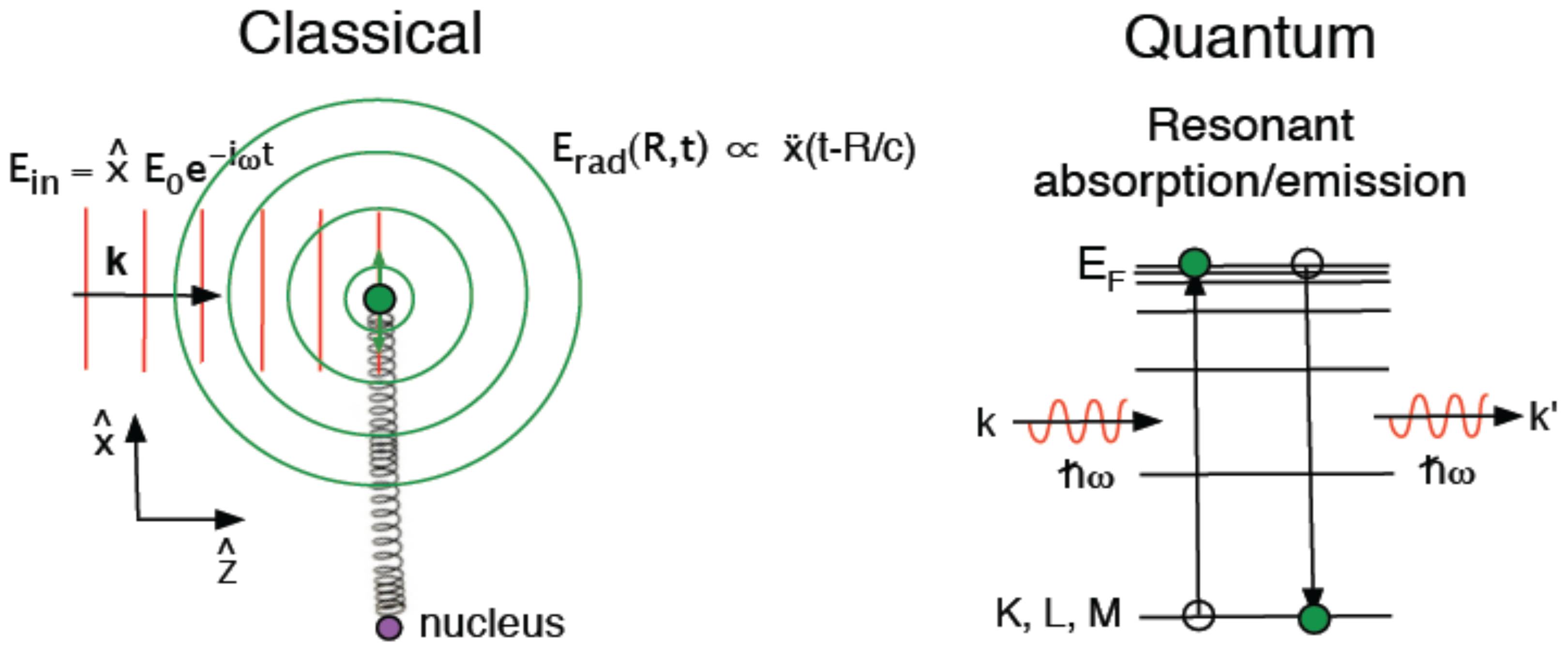
a) Ni AF to Tb at H=0
H-dependent F or AF coupling
finite remanent magn. up to 100K
square hysteresis loop
b) Frustrated Tb magnetization
zero remanence at H=0



X-rays optical properties

SCATTERING FROM BOUND ELECTRONS

We suppose the electron be subject to the electric field E_{in} of an incident X-ray beam and to a damping term Γ proportional to the electron velocity $\dot{x}$ which represents dissipation of energy.



Γ= damping factor
ω_s= resonant frequency

$1/\Gamma$= core-hole lifetime
$\hbar\omega_s$= resonant energy

THE CLASSICAL FORCED OSCILLATOR

The amplitude of the forced oscillations:

$$x_0 = -\left(\frac{e\,\mathrm{E}_0}{m}\right)\frac{1}{(\omega_s^2 - \omega^2 - i\,\omega\Gamma)}$$

Γ= damping factor
ω_s= resonant frequency

The radiated field E_{rad} is proportional to the acceleration of the electron $\ddot{x}$(t-R/c) at the detector position R and at retarded time t'=t-R/c:

$$\ddot{x}(t - R/c) = -\omega^2 x_0 \mathrm{e}^{-i\,\omega t}\mathrm{e}^{i\,(\omega/c)R}$$

$$\frac{\mathrm{E}_{\mathrm{rad}}(R,t)}{\mathrm{E}_{\mathrm{in}}} = -r_0\frac{\omega^2}{(\omega^2 - \omega_s^2 + i\,\omega\Gamma)}\left(\frac{\mathrm{e}^{ikR}}{R}\right)$$

$$f_s \approx -r_0\left(1 + \frac{\omega_s^2}{\omega^2 - \omega_s^2 + i\omega\Gamma}\right) = f_0 + f'(\omega) + i\,f''(\omega)$$ Total scattering length

Thomson term (Q dependence)

Frequency-dependent refraction index n(ω)

Absorption correction (dissipation term)

X-RAY ABSORPTION AND DISPERSION CORRECTIONS

Because the electrons are bound in atoms with discrete energies, a more elaborate model than that of a cloud of free electrons must be invoked.

The scattering amplitude includes two energy dependent term f'(ω) and f"(ω) which are called "dispersion corrections".

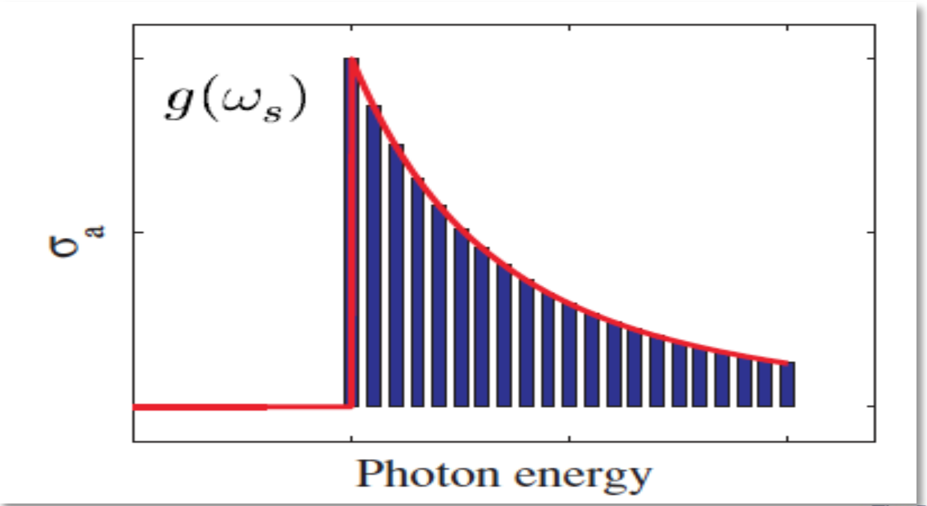
$$f(\mathbf{Q},\omega) = f^0(\mathbf{Q}) + f'(\omega) + i\,f''(\omega)$$

Thomson term
(Q dependence)

Frequency-dependent refraction index n(ω)

Absorption correction
(dissipation term)

The absorption cross section σ_a is a superposition of oscillators with relative weights, so-called oscillator strengths, $g(\omega_s)$, proportional to $\sigma_a(\omega = \omega_s)$.



SCATTERING AND REFRACTIVE INDEX

The existence of resonant scattering terms arising from the dispersion corrections can therefore be expected to lead to a frequency dependence of the refractive index n.

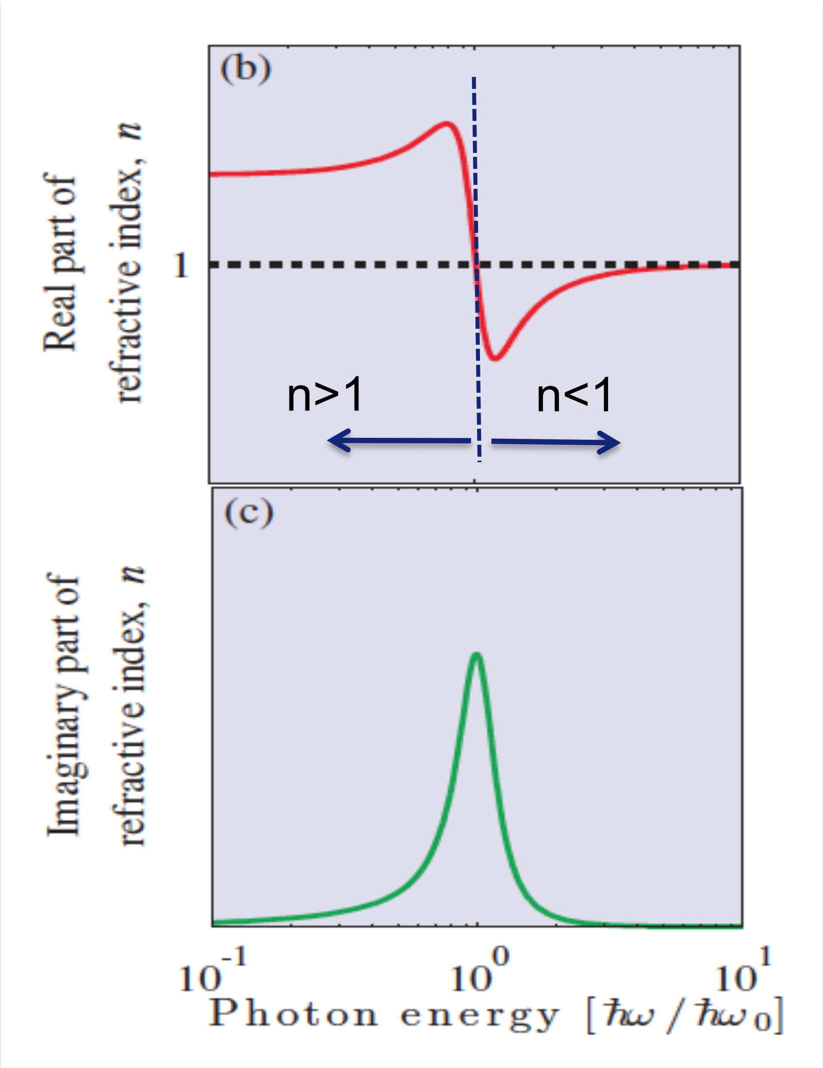
$$n^2 = 1 + \left(\frac{e^2\rho}{\epsilon_0 m}\right)\frac{1}{(\omega_s^2 - \omega^2 - i\,\omega\Gamma)}$$

For $\omega \ll \omega_s$ => n>1 visible light
For $\omega \gg \omega_s$ => n<1 x-rays

Notice that if $\omega \gg \omega_s \gg \Gamma$

$$n \approx 1 - \frac{1}{2}\frac{e^2\rho}{\epsilon_0 m\omega^2} = 1 - \frac{2\pi\rho r_0}{k^2}$$

Real part of refractive index



SCATTERING AND REFRACTION INDEX

Scattering and refraction are alternative ways to view the same physical phenomenon.

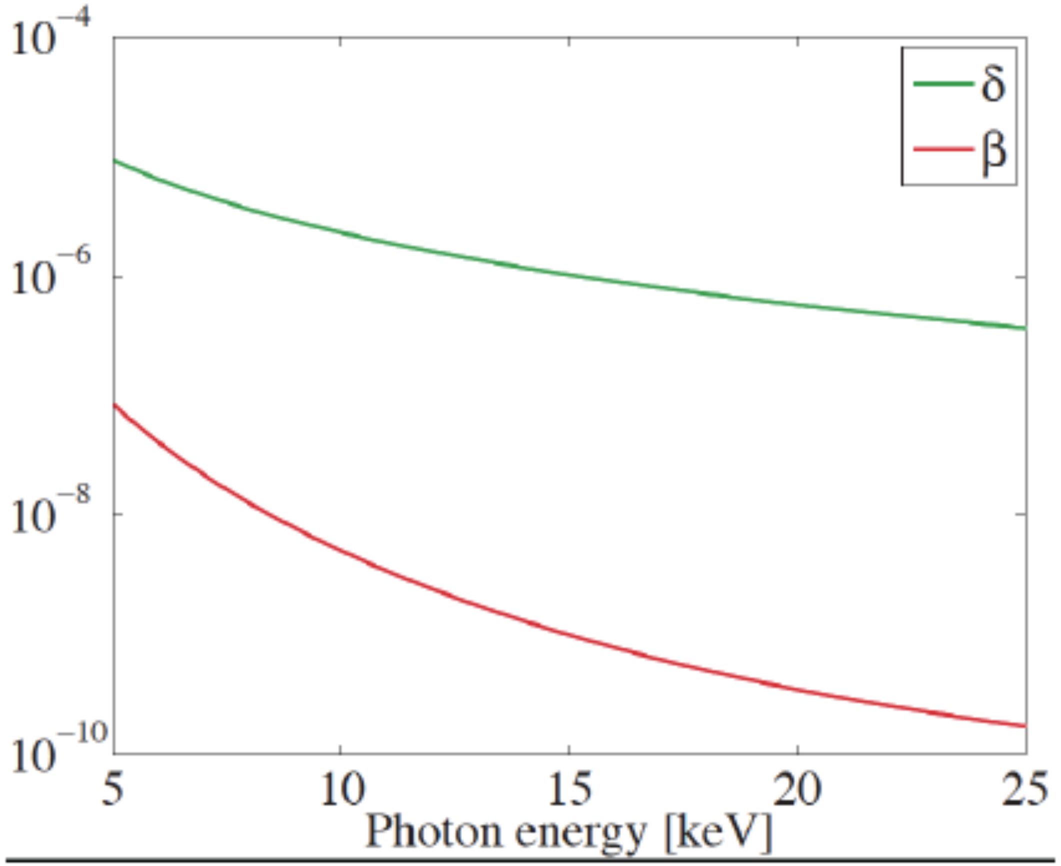
$n = 1 - \delta + i\beta$

$$\delta = (f^0(Q) + f')\frac{2\pi\rho_{at}r_0}{k^2}$$

$$\beta = -f''\,\frac{2\pi\rho_{at}r_0}{k^2}$$

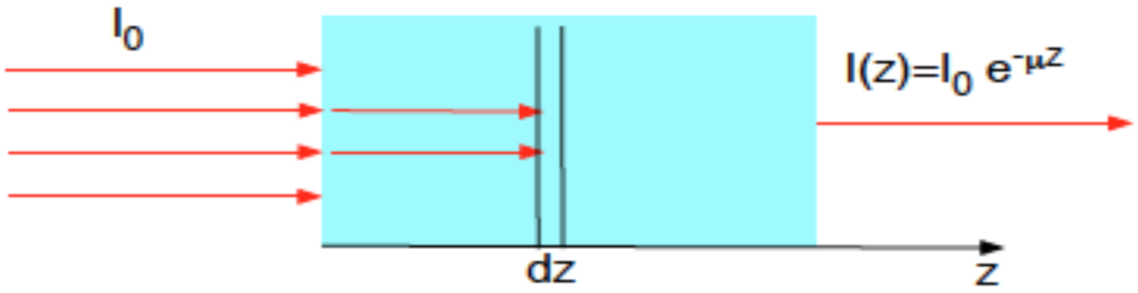
$$\rho_{at} = \sum_i \frac{Z_i}{V_m}$$

atomic number density



REFRACTIVE INDEX AND ABSORPTION COEFFICIENT μ

X-rays propagating from vacuum to a absorbing medium of thickness Z

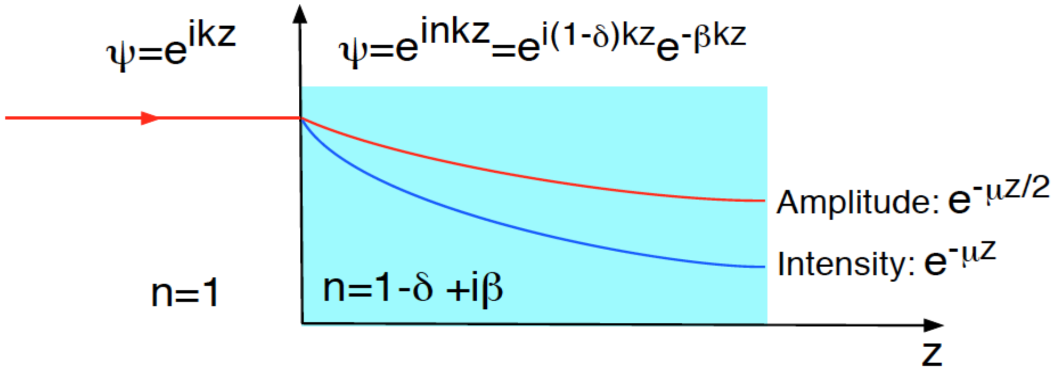


$I(z)$ attenuated transmitted wave

μ= absorption coefficient (m^{-1})

The attenuation length μ^{-1} is the distance where the intensity of the transmitted beam has dropped to 1/e

The waves amplitude in attenuated (β) and phase shifted (δ)



Relation between the absorption and the refraction index

$$\beta = \frac{\mu}{2k}$$

OPTICAL THEOREM

Taking into account the Thomson dispersion corrections

$$f(\mathbf{Q},\omega) = f^0(\mathbf{Q}) + f'(\omega) + i\, f''(\omega)$$

$$\begin{aligned} \delta &= (f^0(0) + f')\frac{2\pi\rho_{at}r_0}{k^2} \\ \beta &= -f''\,\frac{2\pi\rho_{at}r_0}{k^2} \end{aligned}$$

Forward direction Q=0

Relation between the imaginary part of anomalous dispersion and the absorption coefficient

$$f'' = -\left(\frac{k^2}{2\pi\rho_{at}r_0}\right)\frac{\mu}{2k}$$

And because $\mu = \rho_{at}\sigma_a$

$$f'' = -\left(\frac{k}{4\pi r_0}\right)\sigma_a \qquad \text{Optical Theorem}$$

REFRACTION: X-RAYS AND VISIBLE LIGHT

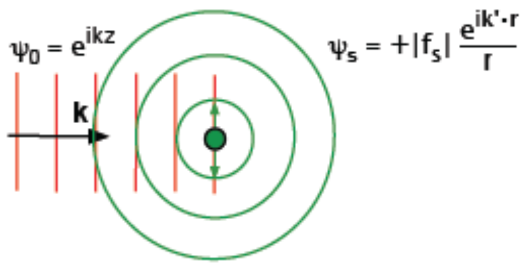
Snell law: $n_1 \cos\alpha = n_2 \cos\alpha'$

Refraction index for X-rays:

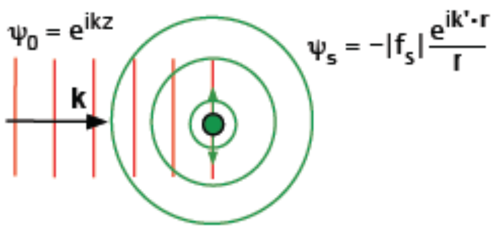
$$n = 1 - \delta + i\beta$$

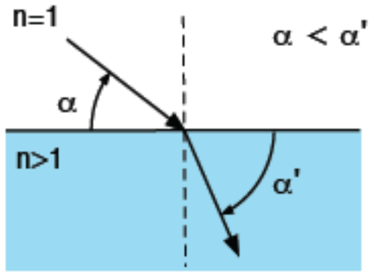
$\delta(\text{air}) \sim 10^{-8}$
$\delta(\text{solids}) \sim 10^{-5}$
$\beta \sim 10^{-8} << \delta$

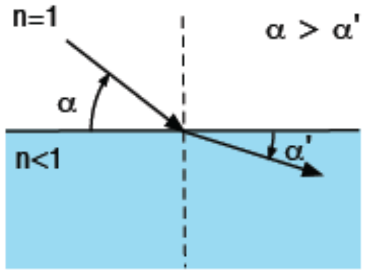
Visible light



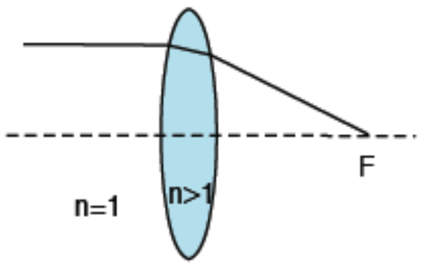
X-rays



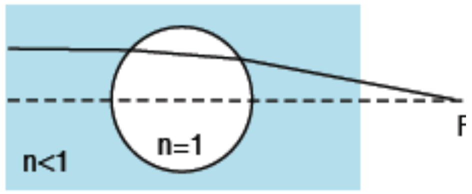




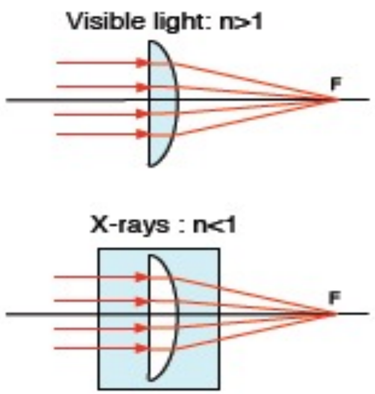
Optic lenses



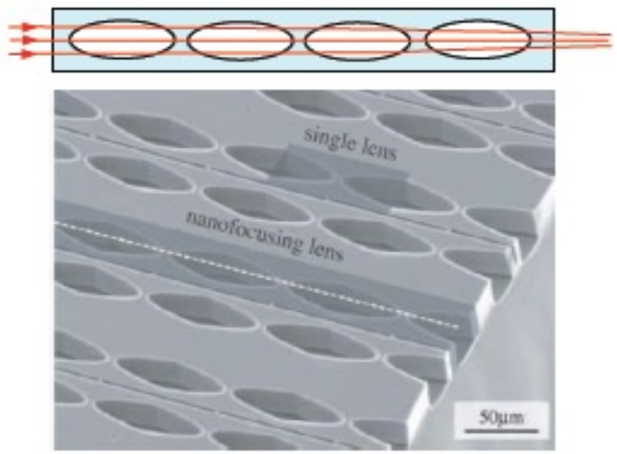
X-rays lenses



Low focusing power compared with the visible light

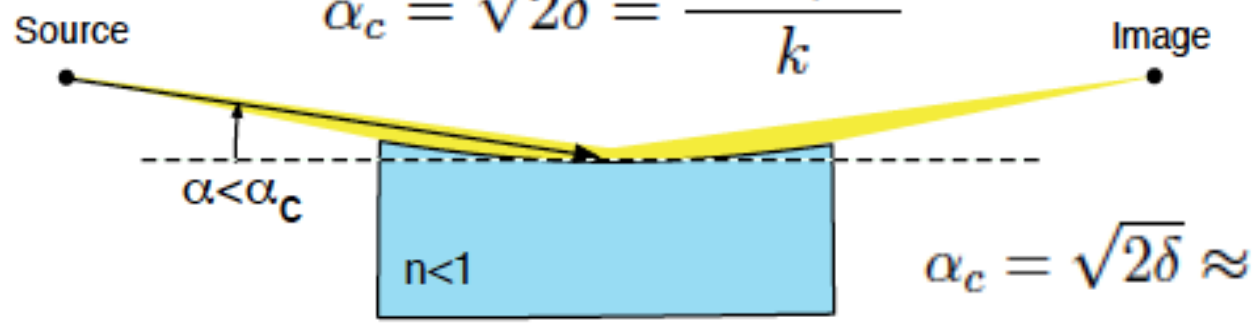


Compound refractive lenses for X-rays



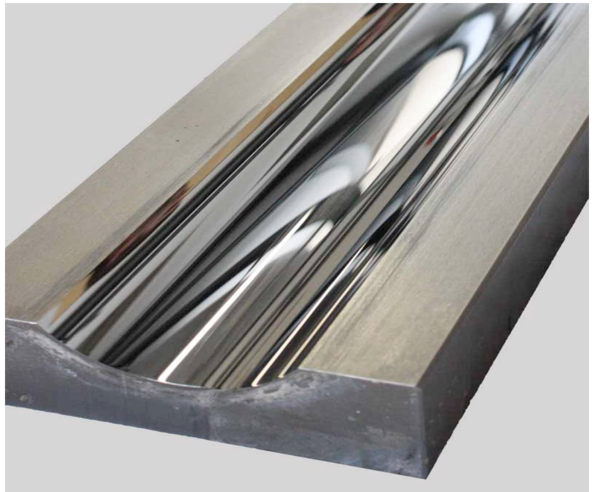
X-RAY FOCUSING MIRRORS

The critical angle for the total reflection



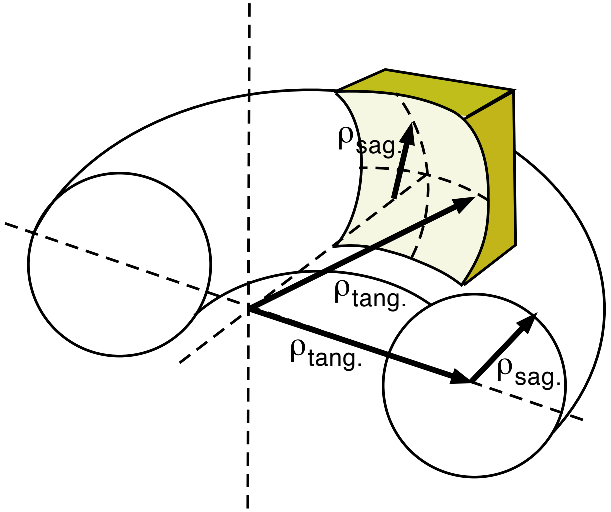
$$\alpha_c = \sqrt{2\delta} = \frac{\sqrt{4\pi\rho r_0}}{k}$$

$$\alpha_c = \sqrt{2\delta} \approx 5\text{mrad}$$



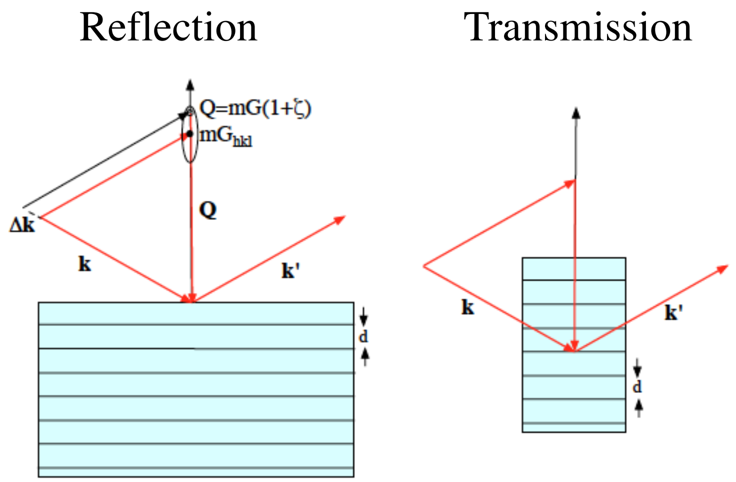
High quality mirrors are required for x-rays focusing and a large radius tangential focusing

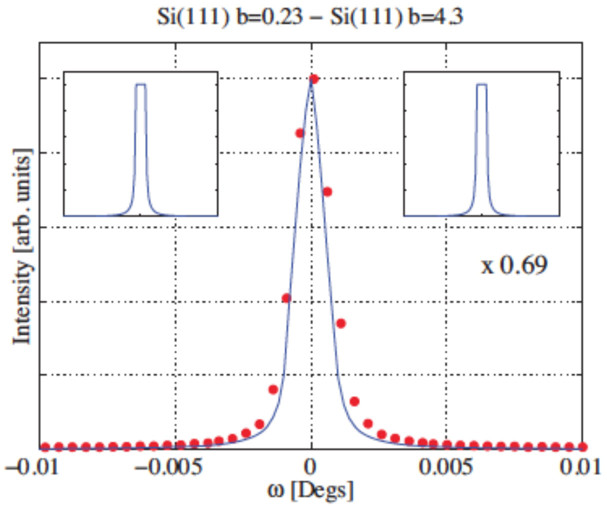
Ex: silicon mirror with toroidal shape
Distance from source p=76m,
Distance mirror object q=26m
θ=2.7 mrad
$\rho_{sagital}$=27 cm ρ_{tang}=27 km

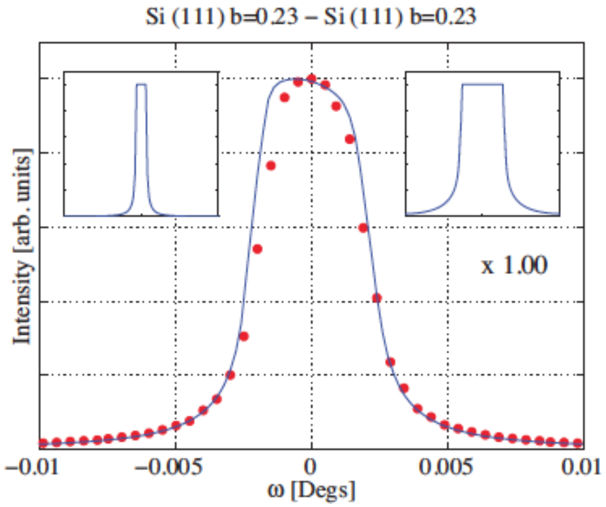


X-RAYS MONOCHROMATORS

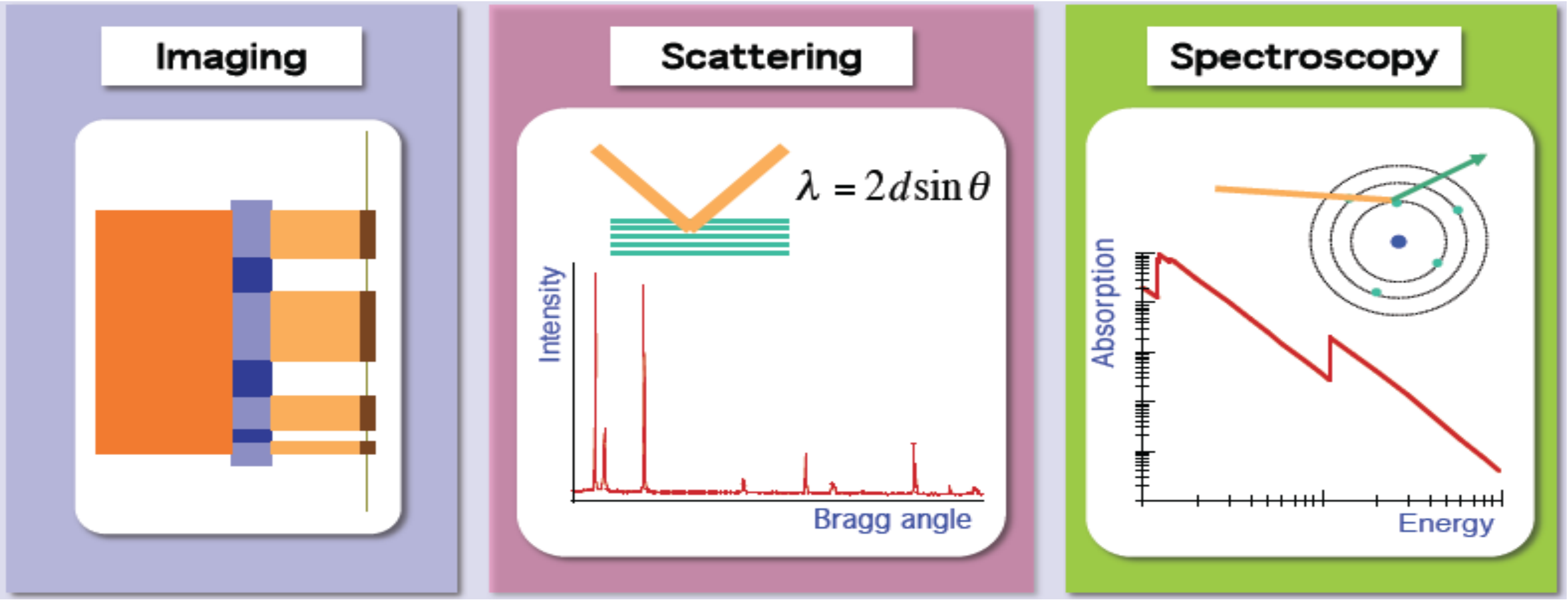
The Bragg diffraction from perfect crystals select a wavelength λ from the synchrotron radiation spectrum emitted by bending magnets or undulators





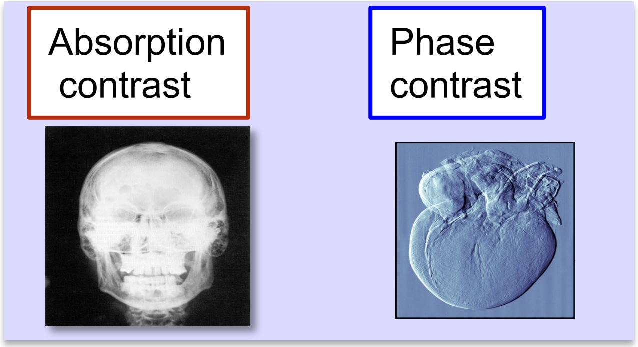


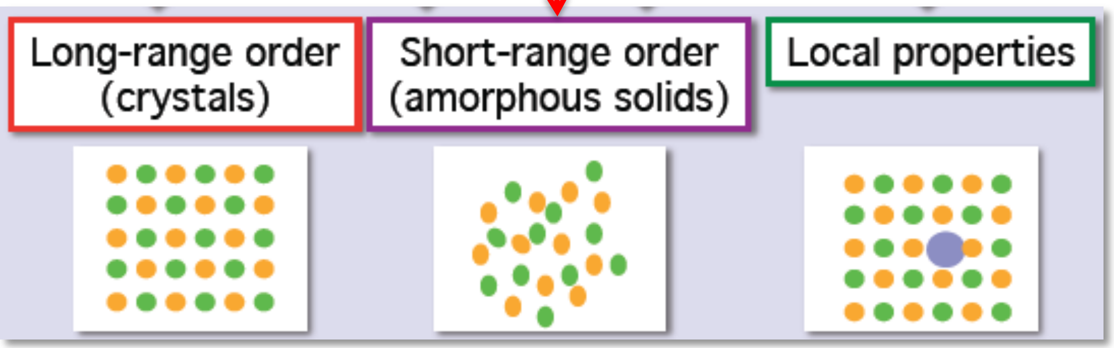
X-RAY SCATTERING METHODS



Spatial informations

Structural informations





Thank you for your attention!