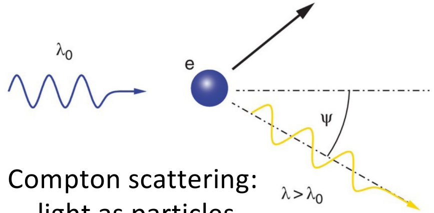
PAUL SCHERRER INSTITUT
PSI
EPFL

Steven Van Petegem – Material Science at Large Scale Facilities

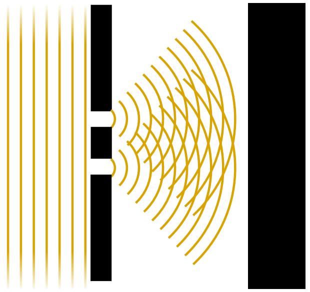
# Interaction of X-rays/Neutrons with Matter

Master Course 2024

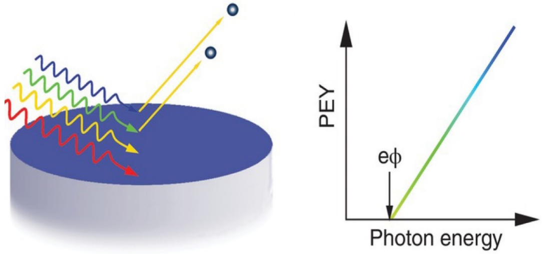
# Particle - wave duality



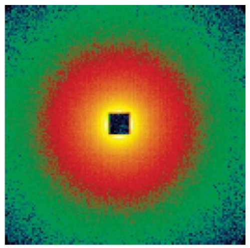

Compton scattering:
light as particles



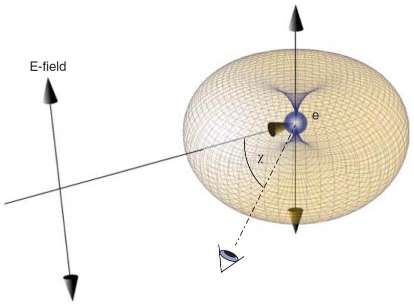
Young's slit experiment:
light as waves




Photoelectric effect: light as particles



SANS: Neutrons as waves




Dipole radiation: light as waves,
electrons as particles

## Particle-wave duality

Single model (i.e., wave *or* particle) inadequate to explain all observations of microscopic systems

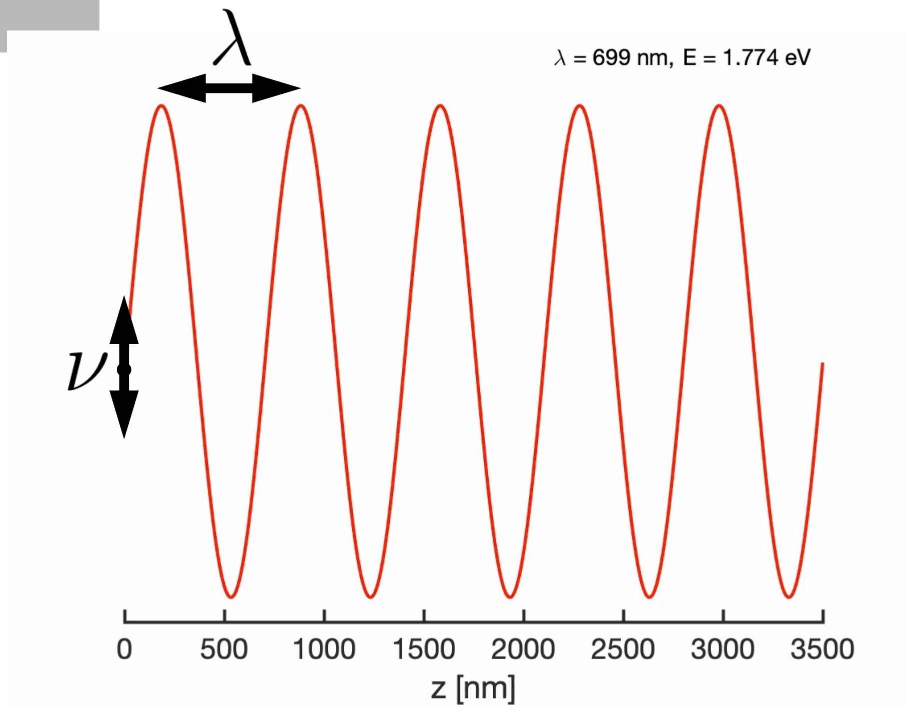
Neutron beam also has a wave character

X-rays: electromagnetic wave (as visible light is), particle of light = photon

| Phenomenon | Can be explained in terms of waves. | Can be explained in terms of particles. |
|---|---|---|
| Reflection | ✓ | ✓ |
| Refraction | ✓ | ✓ |
| Interference | ✓ | ⊗ |
| Diffraction | ✓ | ⊗ |
| Polarization | ✓ | ⊗ |
| Photoelectric effect | ⊗ | ✓ |

http://hyperphysics.phy-astr.gsu.edu/hbase/mod1.html

# Speed, wavelengths, and frequencies




Red (700 nm) to blue (400 nm)
visible light
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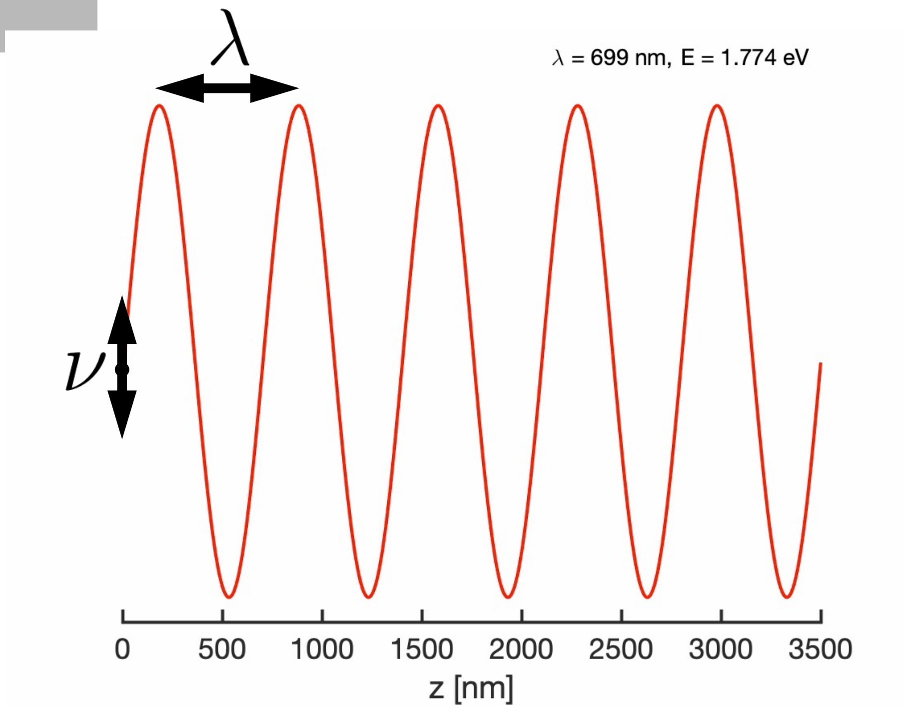
$$c = \nu\lambda$$

Velocity of light $c$ = constant in vacuum

$c$ = 2.9979 x 108 m $s^{-1}$

As wavelength $\lambda$ decreases, frequency $\nu$ increases

# Speed, wavelengths, frequencies and energy




Red (700 nm) to blue (400 nm)
visible light
Philip Willmott: Synchrotron and X-ray Free Electron Laser

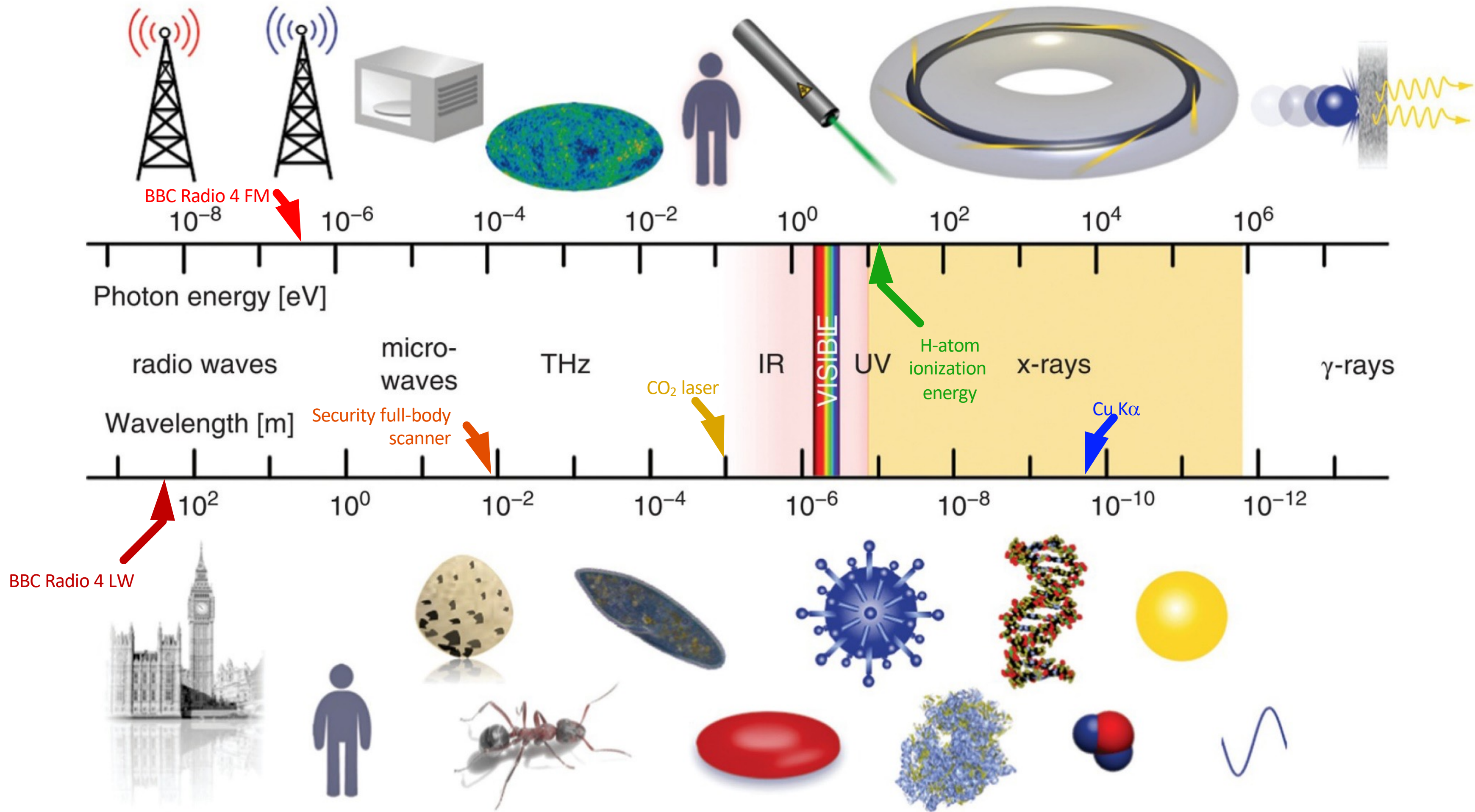
$$E = h\nu = hc/\lambda$$

h = Planck's constant
h = 6.626 x 10-34 J s
ħ = h/2p = 1.055 x 10-34 J s

Visible light
E = 1.774 eV @ 700 nm
= 3.100 eV @ 400 nm

Electronvolt = eV
Energy of an electron after being accelerated from rest in a potential of 1 V
1 eV = 1.6022 x $10^{-19}$ J

# The electromagnetic spectrum

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# Electronvolts and the atomic world

## Chemical reactions

Imagine a chemical reaction resulting in a 1 eV difference in energy per involved molecule

1 eV/molecule x 6.022 x $10^{23}$ molecules/mole
= 1.6022 x $10^{-19}$ x 6.022 x $10^{23}$ = 96.5 kJ/mol

100 kJ/mol IS TYPICAL FOR REACTION ENTHALPIES

## Chemical bonds

Graphite interplanar van-der-Waals bond = 0.05 eV

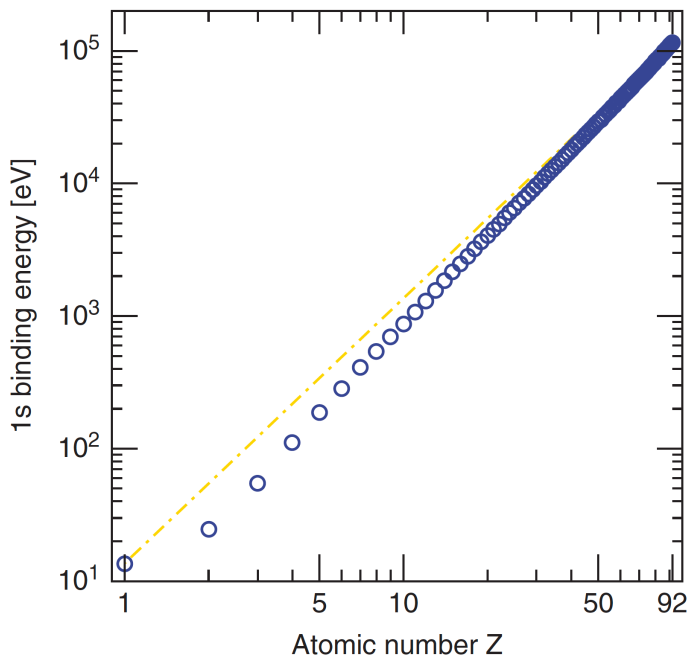
Diamond C-C bond = 3.5 eV

Ionization energy of H-atom = 13.6 eV

Thermal energy = $3k_BT/2$ = 0.04 eV @ RT

Core-electron binding energies

$0^{th}$ approximation: 1s B.E. = 13.6 x $Z^2$ eV

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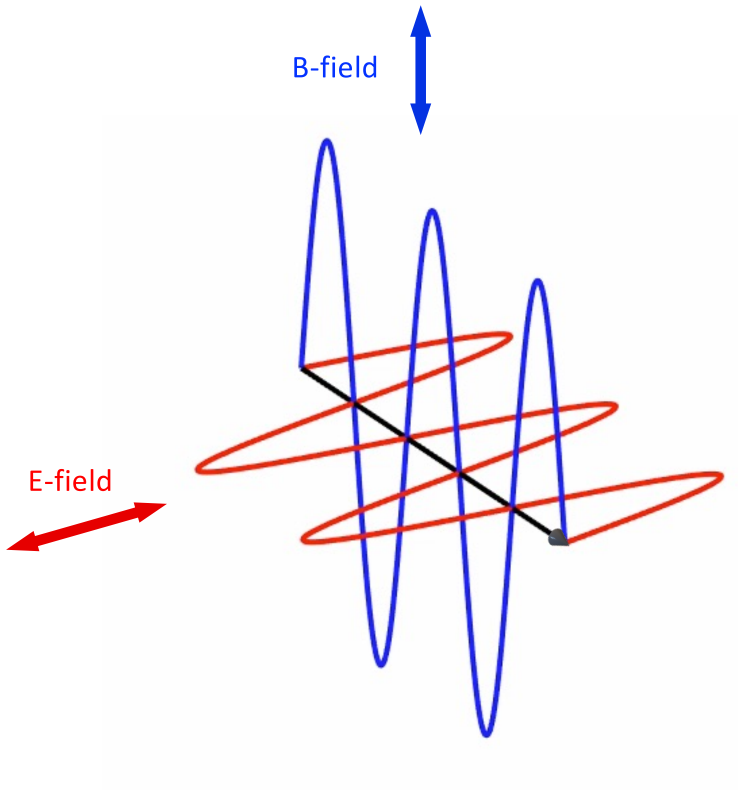
# Electromagnetic wave




Transverse E- and B-fields ⇒ displacements perpendicular to direction of propagation

E- and B-fields: amplitudes $E_0$ and $B_0$

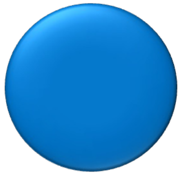
Oscillating at same frequency and phase

X-rays: $\nu \sim 10^{18}$ Hz

We can only **record the intensity** $\propto$ |amplitude|$^2$

Phase information is lost!

# Neutrons – particles and wave



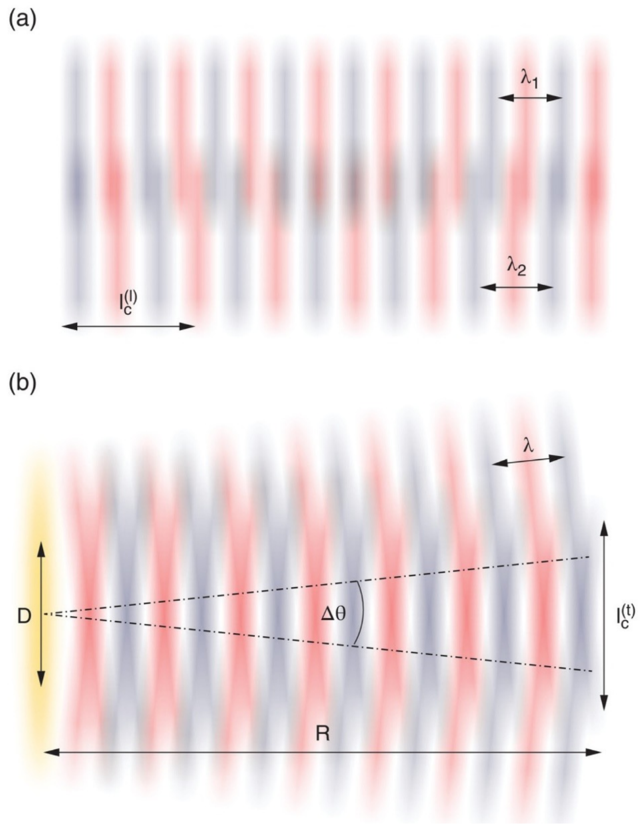
Neutron
$m$ = 1.6749 $10^{-27}$ kg

- mass is about 1840 times that of an electron
- has zero electric charge
- has a magnetic moment

$$E = \frac{mv^2}{2} = \frac{h^2}{2m} \cdot \frac{1}{\lambda^2}$$

| Neutrons | Energy range | Wavelength [Å] | Velocity [m/s] |
|---|---|---|---|
| **ultra cold** | ≤ 300 neV | ≥ 500 | ≤ 8 |
| **very cold** | 300 neV - 0.12 meV | 52.2 – 26.1 | 7.5 – 152 |
| **cold** | 0.12 meV - 12 meV | 26.1 – 2.6 | 152 – 1515 |
| **thermal** | 12 meV - 100 meV | 2.6 - 0.9 | 1515 - 4374 |
| **epithermal** | 100 meV - 1eV | 0.9 - 0.28 | 4374 - 13.8 $10^3$ |
| **intermediate** | 1eV - 0.8MeV | | |
| **fast** | > 0.8MeV | | |

# Coherence




longitudinal (temporal) coherence length

determined by monochromacy of the source

$$l_c^{(l)} = \frac{\lambda^2}{2\Delta\lambda}$$

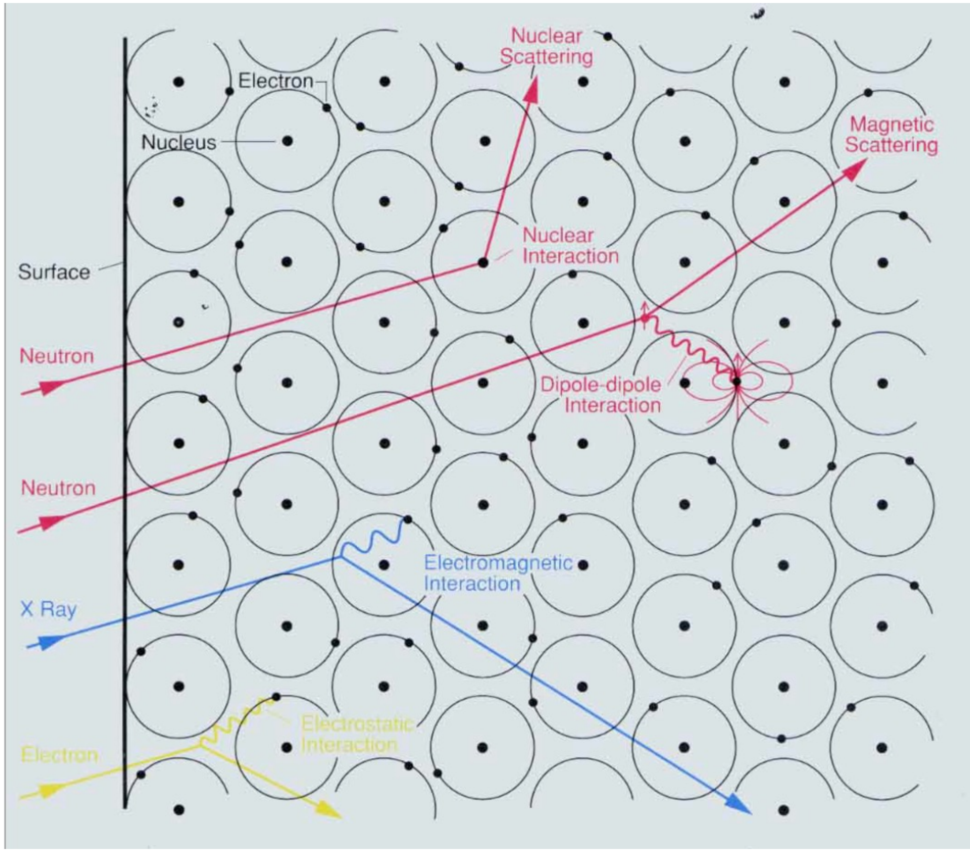
transverse (spatial) coherence length

depends on the beam divergence and source size

$$l_c^{(t)} = \lambda/2\Delta\theta = \lambda R/2D$$

Willmott, P. (2019). Scattering Techniques. An Introduction to Synchrotron Radiation, John Wiley & Sons, Ltd: 133-221.

# Interaction types X-rays vs. Neutrons




https://www.ncnr.nist.gov/summerschool/ss16/pdf/NeutronScatteringPrimer.pdf

X-rays and electron-beam interact with electrons in the materials, neutrons with the atomic nuclei

**electron beam**: electrostatic, strong interaction, very low penetration depth
**X-ray**: electromagnetic, rather strong, intermediate penetration depth
**Neutrons**: short-range strong nuclear interaction, large penetration depth, for unpaired electrons: magnetic scattering

# Strength of Interaction: Cross-sections


(1) Hard spheres

# Strength of Interaction: Cross-sections

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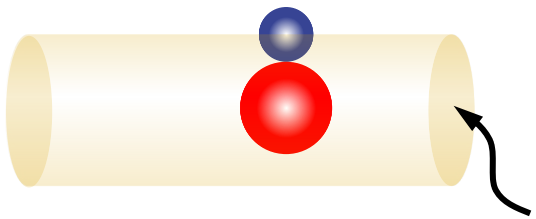
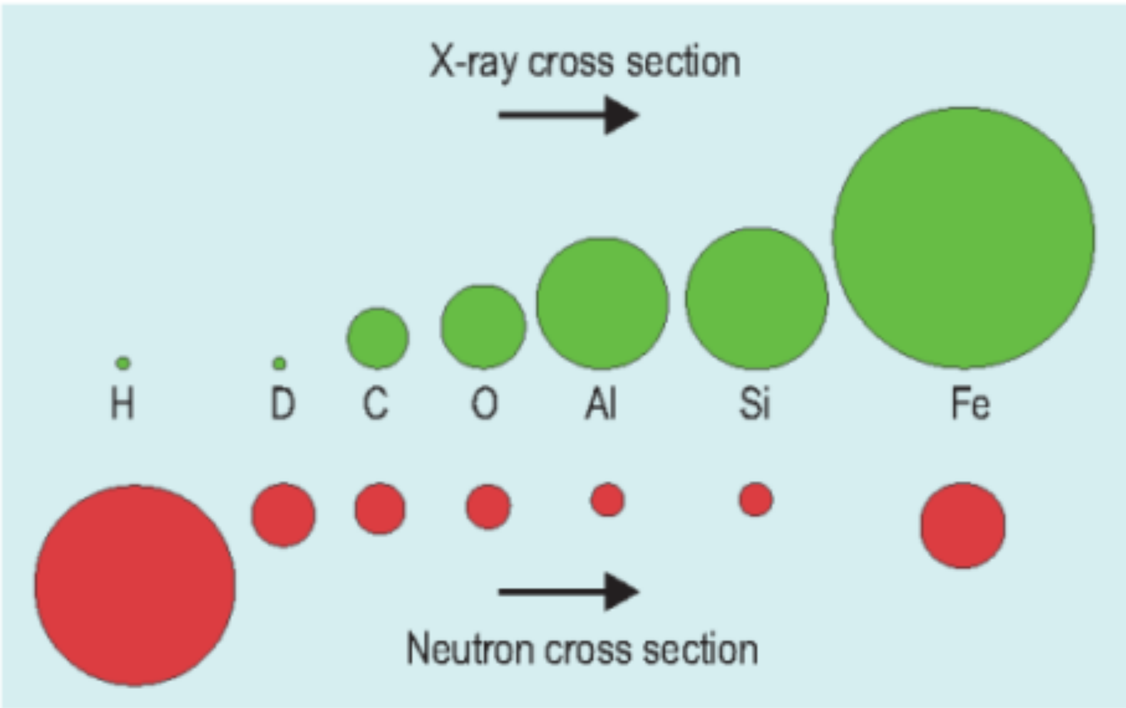


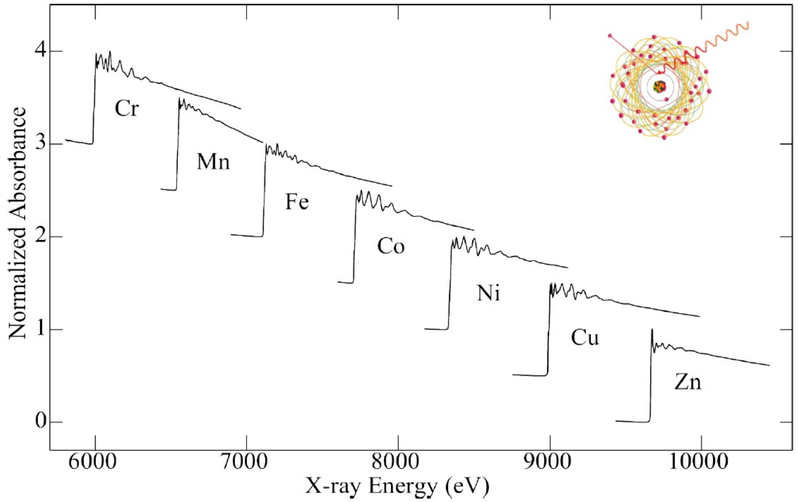
$$\sigma = \pi(r_1 + r_2)^2$$

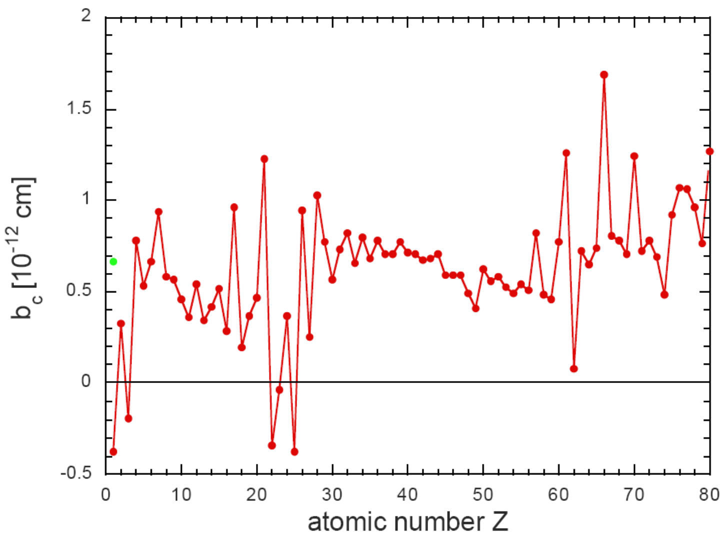
# Strength of Interaction: Cross-sections


Action at a distance (e.g. electromagnetic radiation interacting with atoms/matter)

# Cross section for different elements



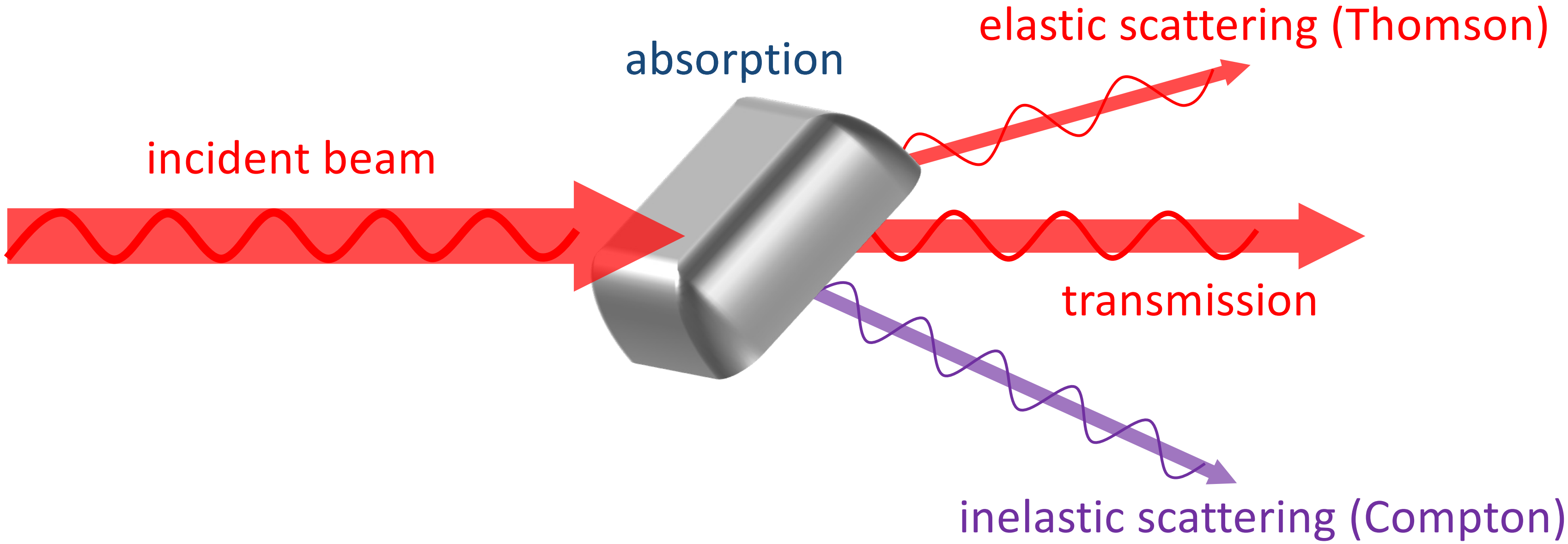




Scattering length of atoms are documented in table which can be found e.g. on the internet: http://www.ncnr.nist.gov/resources/n-lengths/

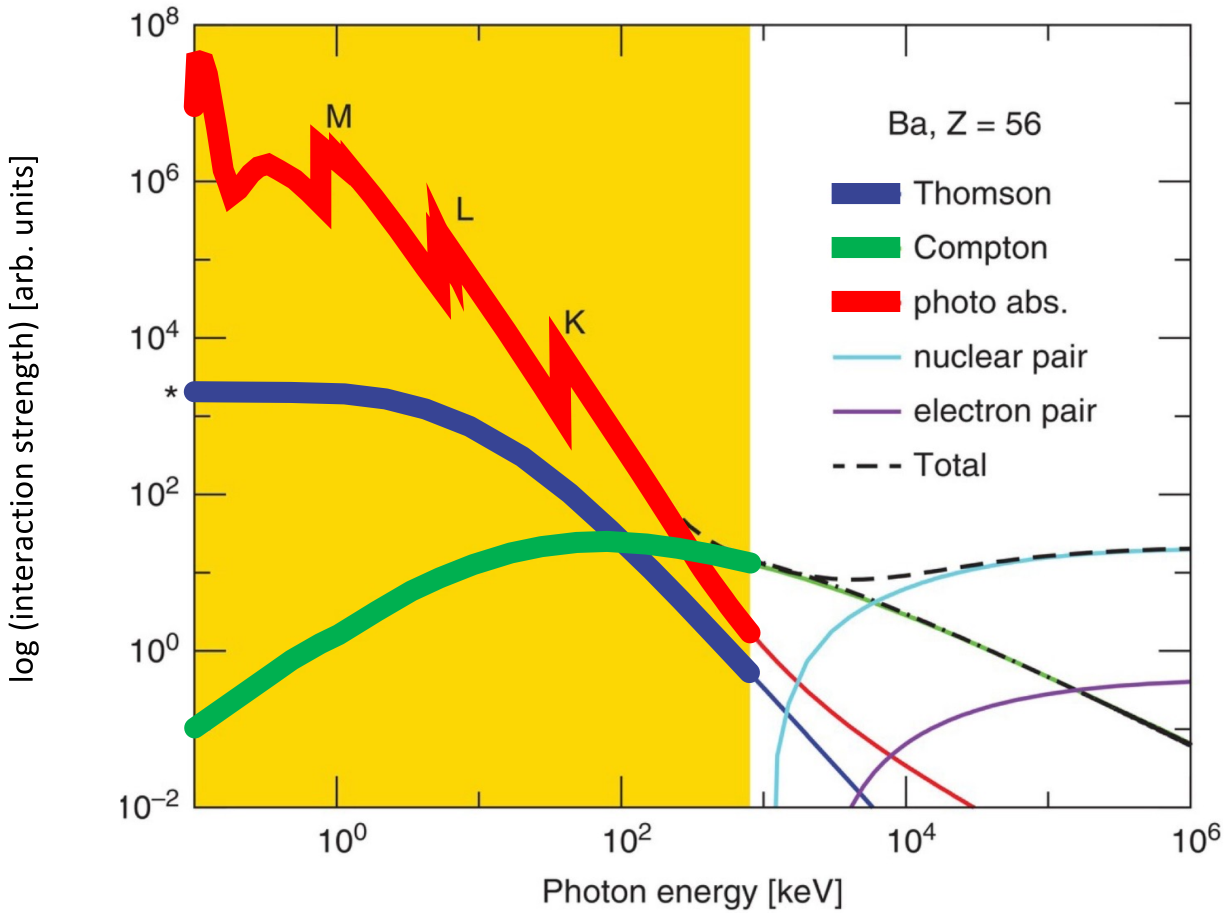
# Neutrons: metals are transparent, water absorbs

# Interaction of X-rays with matter

interaction with electrons



# Interaction strengths of x-rays with matter

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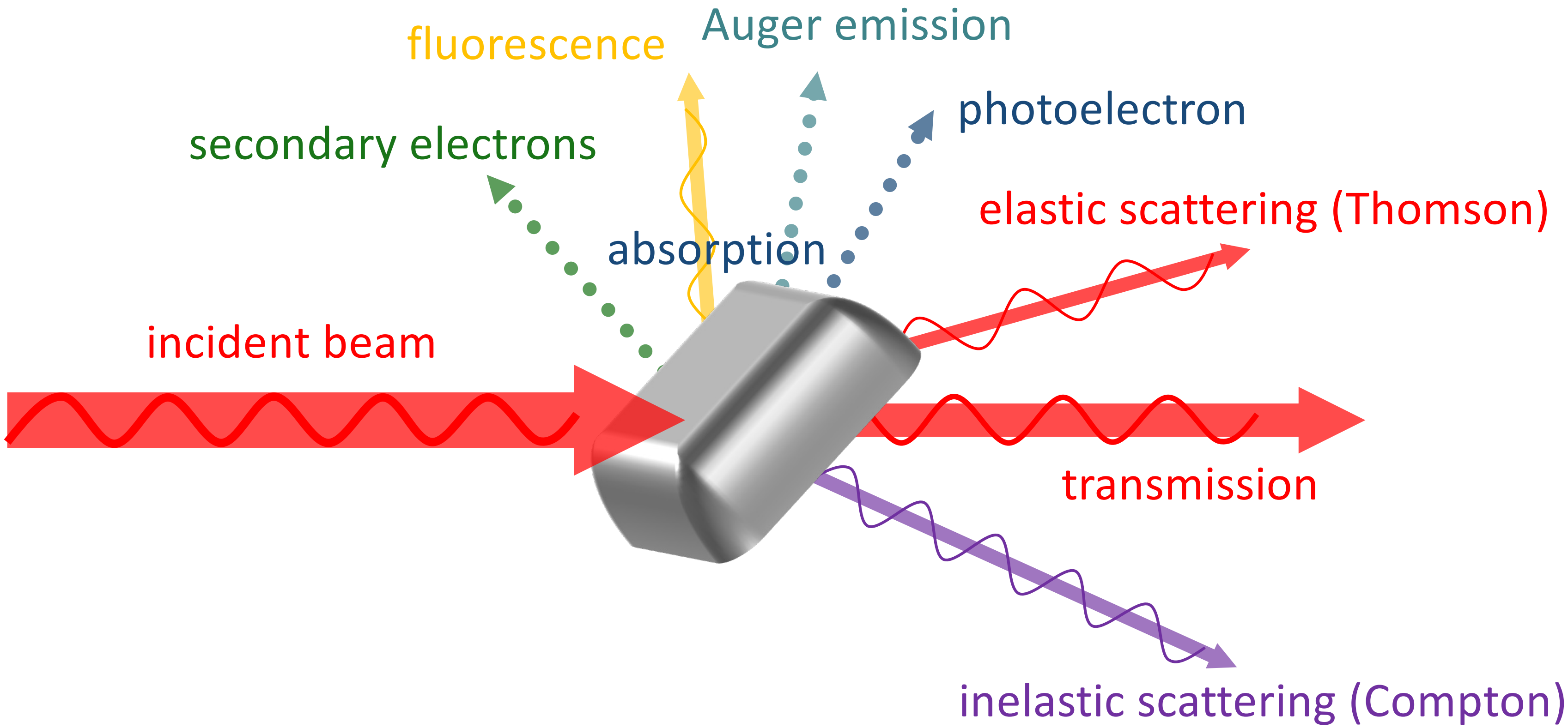
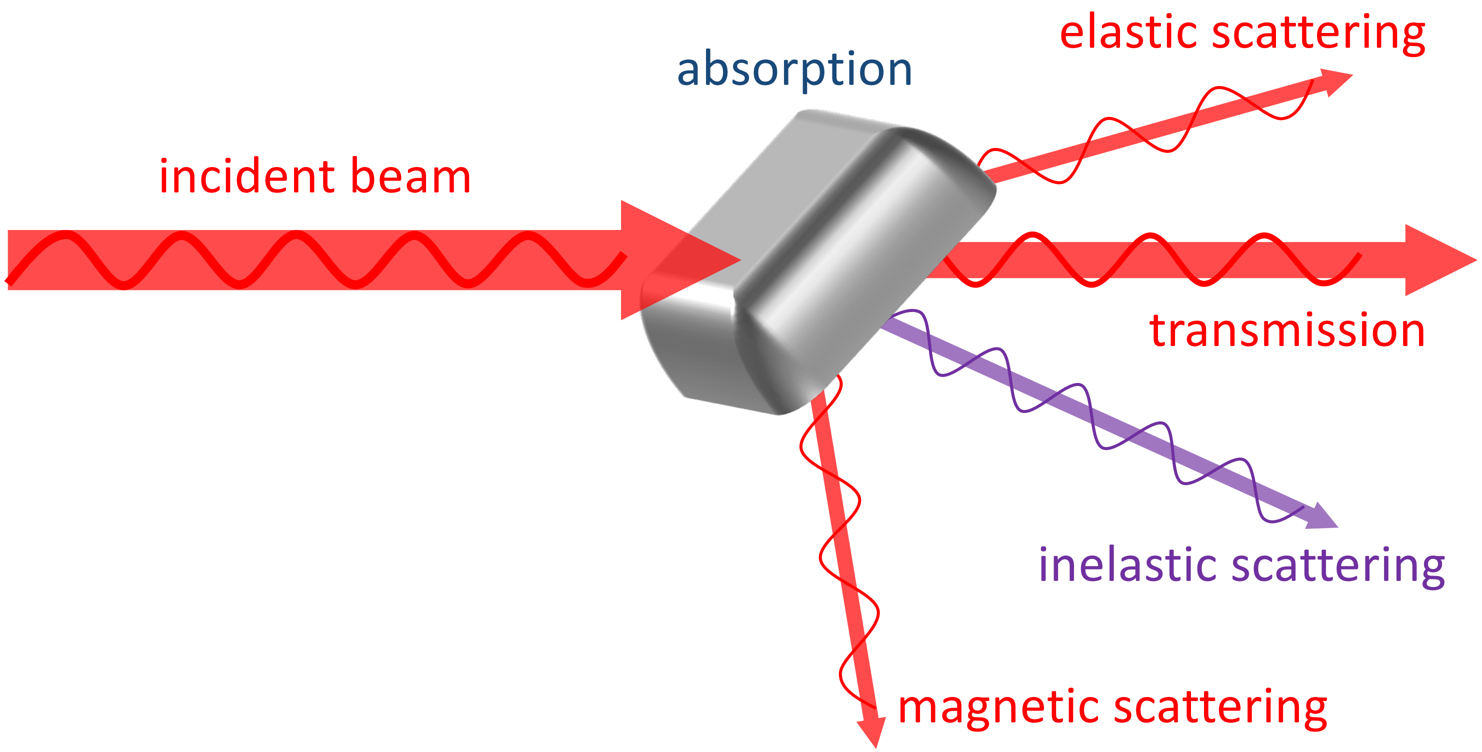
# Interaction of X-ray with matter



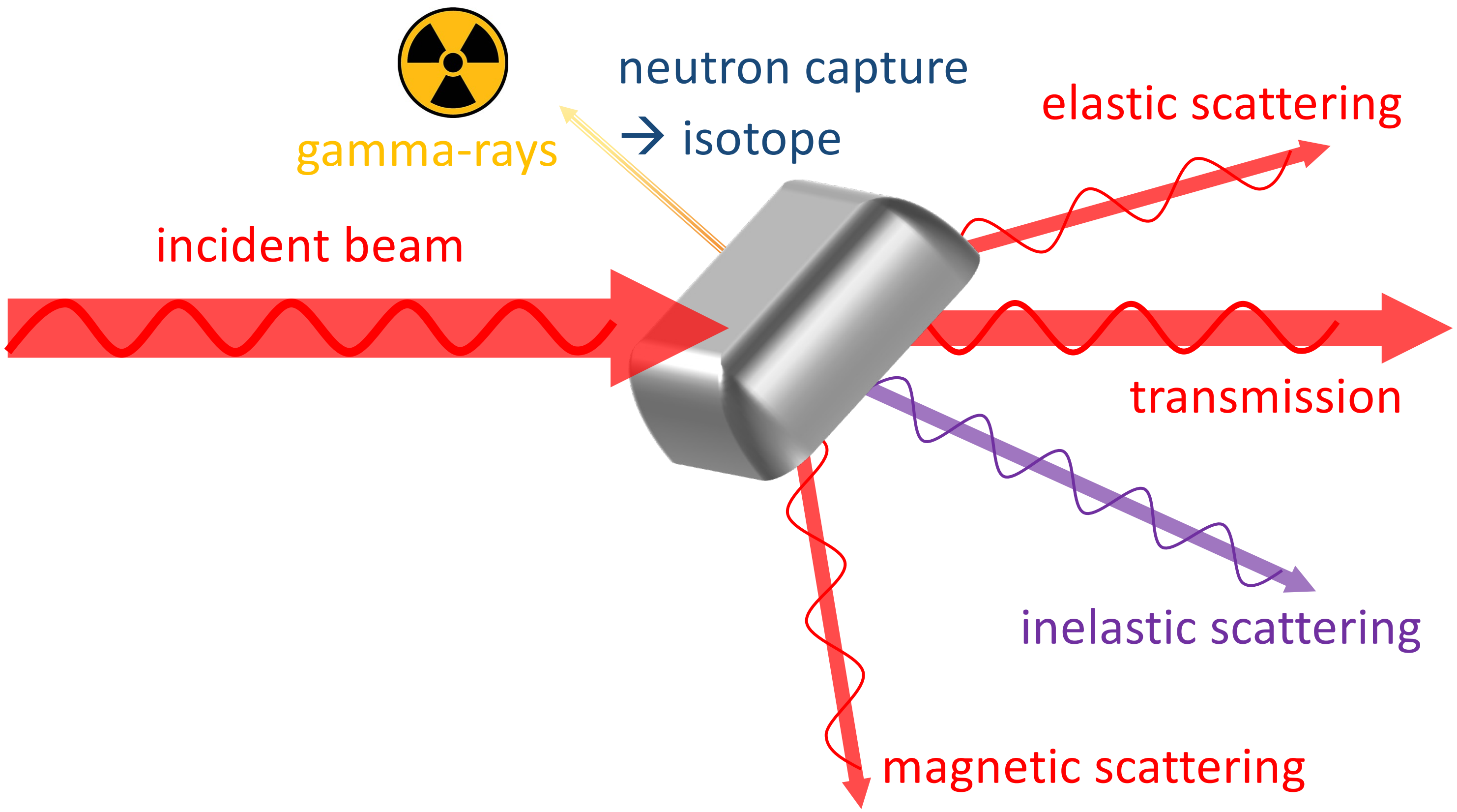
# Interaction of neutrons with matter

interaction with nuclei (& magnetic moment)

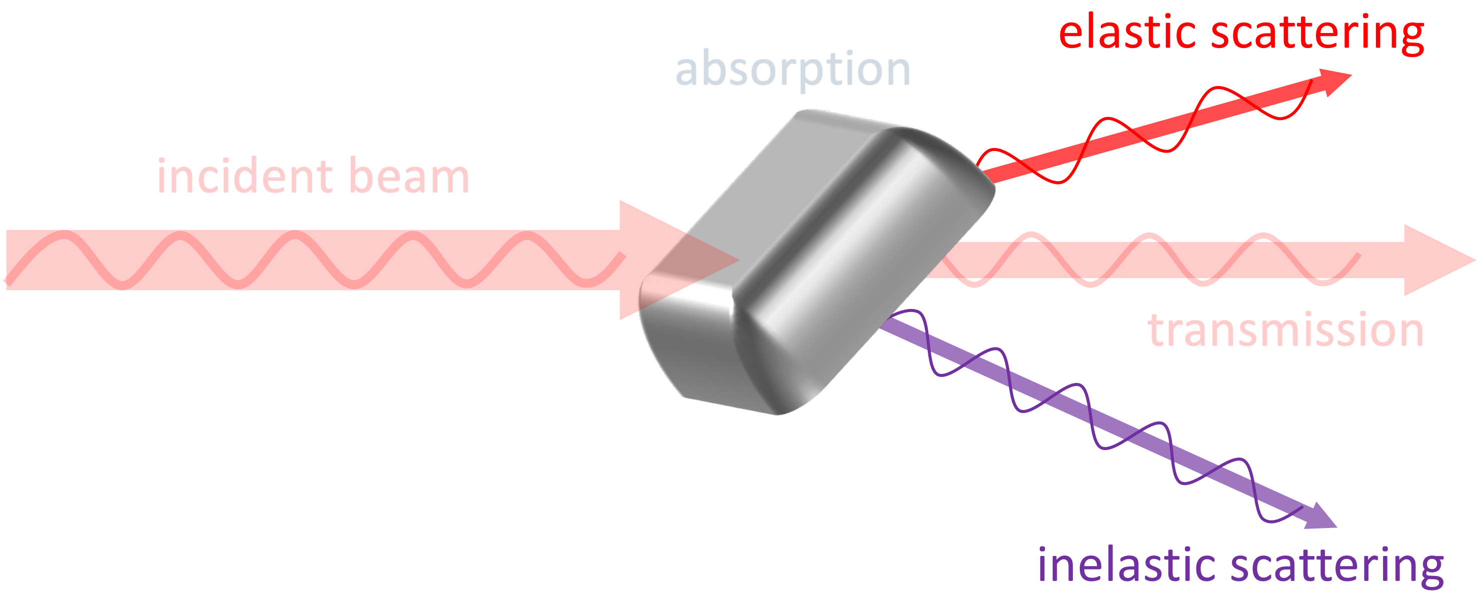


# Interaction of neutrons with matter

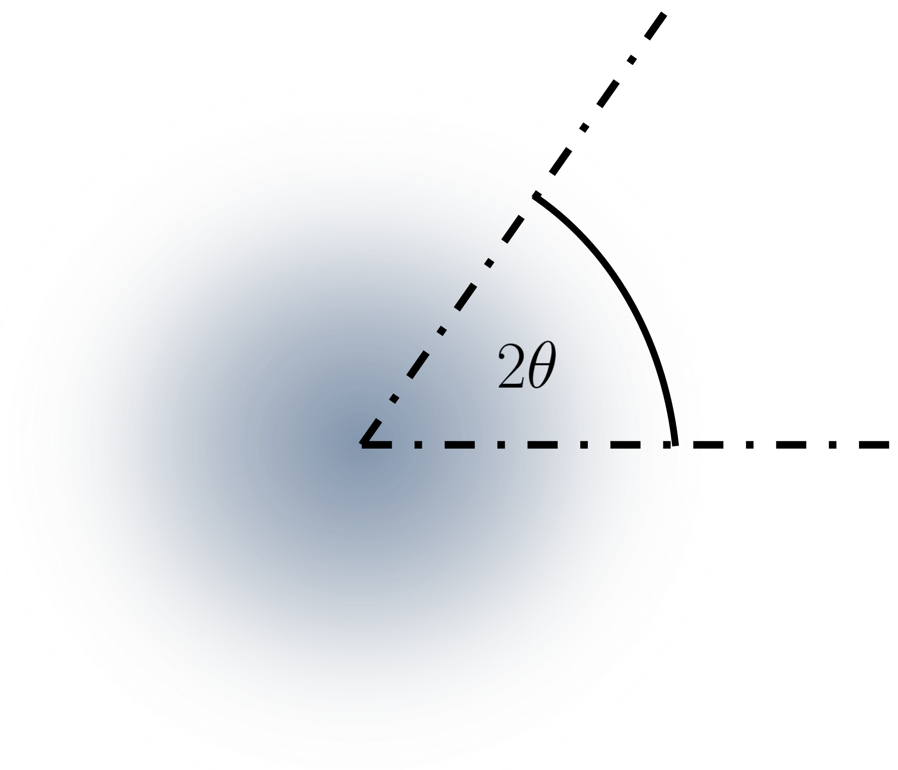
interaction with nuclei (& magnetic moment)



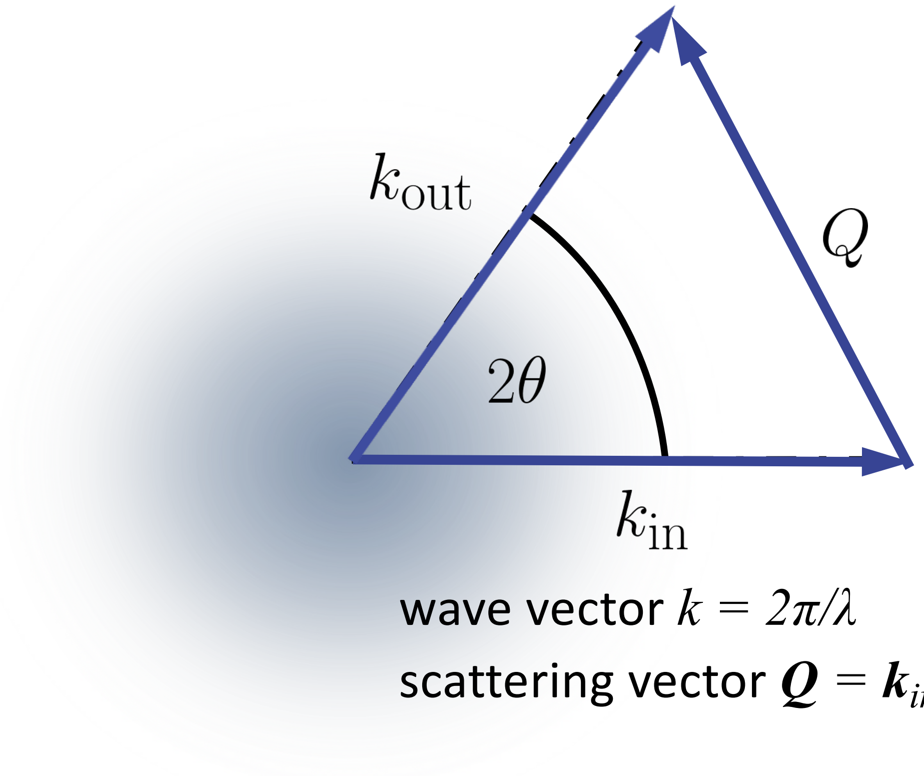
# Interaction of X-rays and neutrons with matter



# Scattering and Q-vector



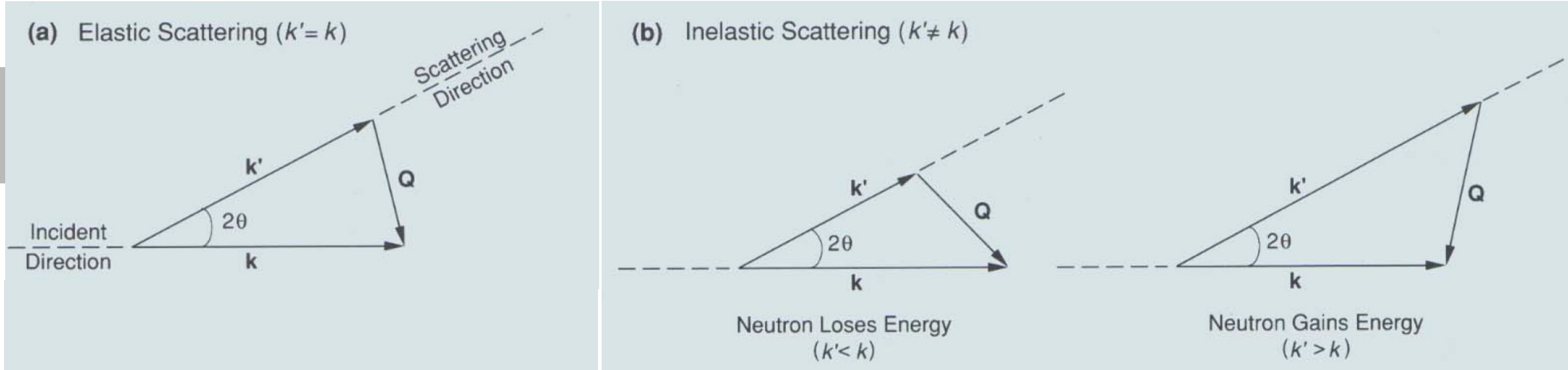
# Scattering and Q-vector




wave vector $k = 2\pi/\lambda$

scattering vector $\boldsymbol{Q} = \boldsymbol{k}_{in} - \boldsymbol{k}_{out}$

# Elastic scattering vs. inelastic scattering

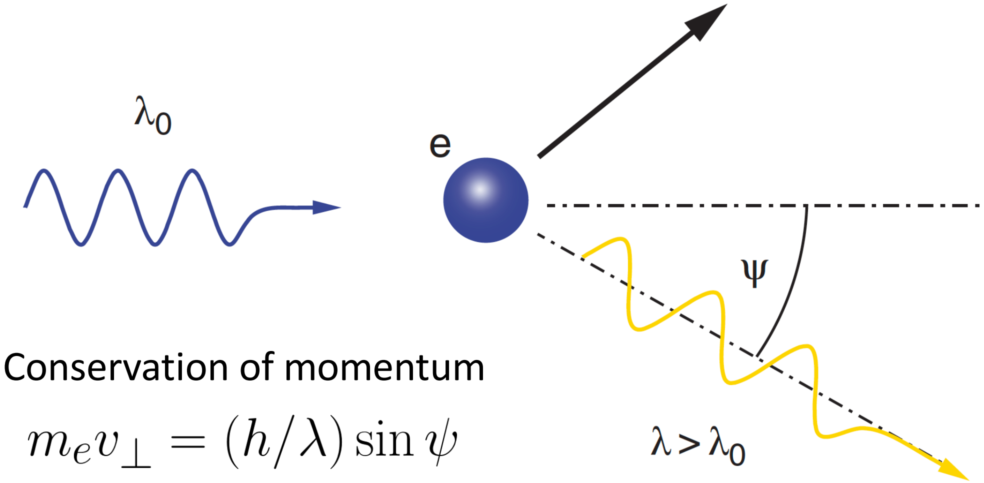



**elastic scattering**: scattering with no change in the energy of the incident neutron/photon, the direction of the vector changes but not its magnitude $|k_{in}| = |k_{out}|$

**inelastic scattering**: scattering in which exchange of energy and momentum between the incident neutron/photon and the sample causes both the direction and the magnitude of the wave vector to change $|k_{in}| \neq |k_{out}|$

https://www.ncnr.nist.gov/summerschool/ss16/pdf/NeutronScatteringPrimer.pdf

# Inelastic X-ray scattering: Compton scattering




Conservation of energy

$$hc/\lambda_0 + m_e c^2 = hc/\lambda + E_e$$

Conservation of momentum

$$m_e v_\perp = (h/\lambda)\sin\psi$$

$$h/\lambda_0 = m_e v_\parallel + (h/\lambda)\cos\psi$$

Compton scattering equation

$$\lambda = \lambda_0 + \underbrace{\left[\frac{h}{m_e c}\right]}_{\lambda_C}(1 - \cos\psi)$$

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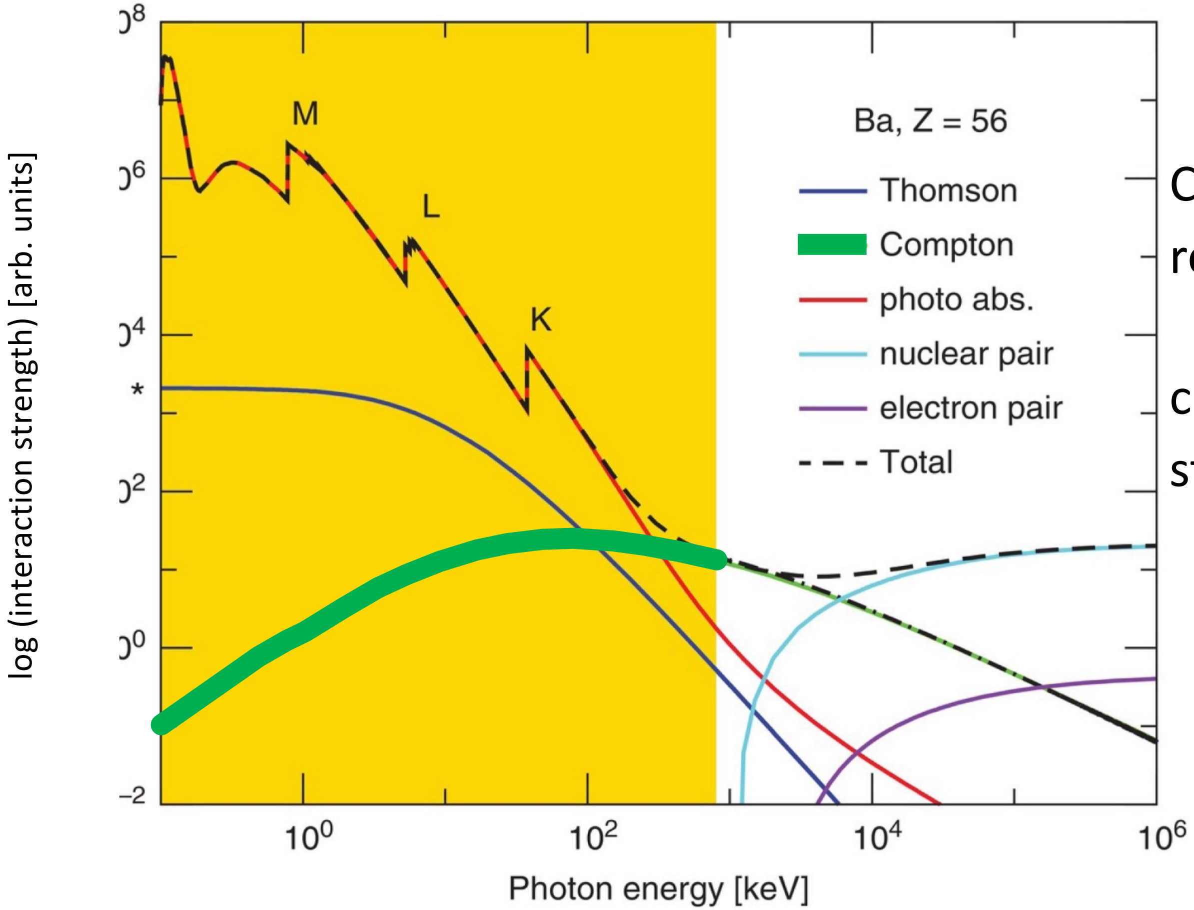
# Interaction strengths of x-rays with matter
# Compton scattering




Compton Scattering is only relevant above approx. 100 keV

can give information on electronic structure

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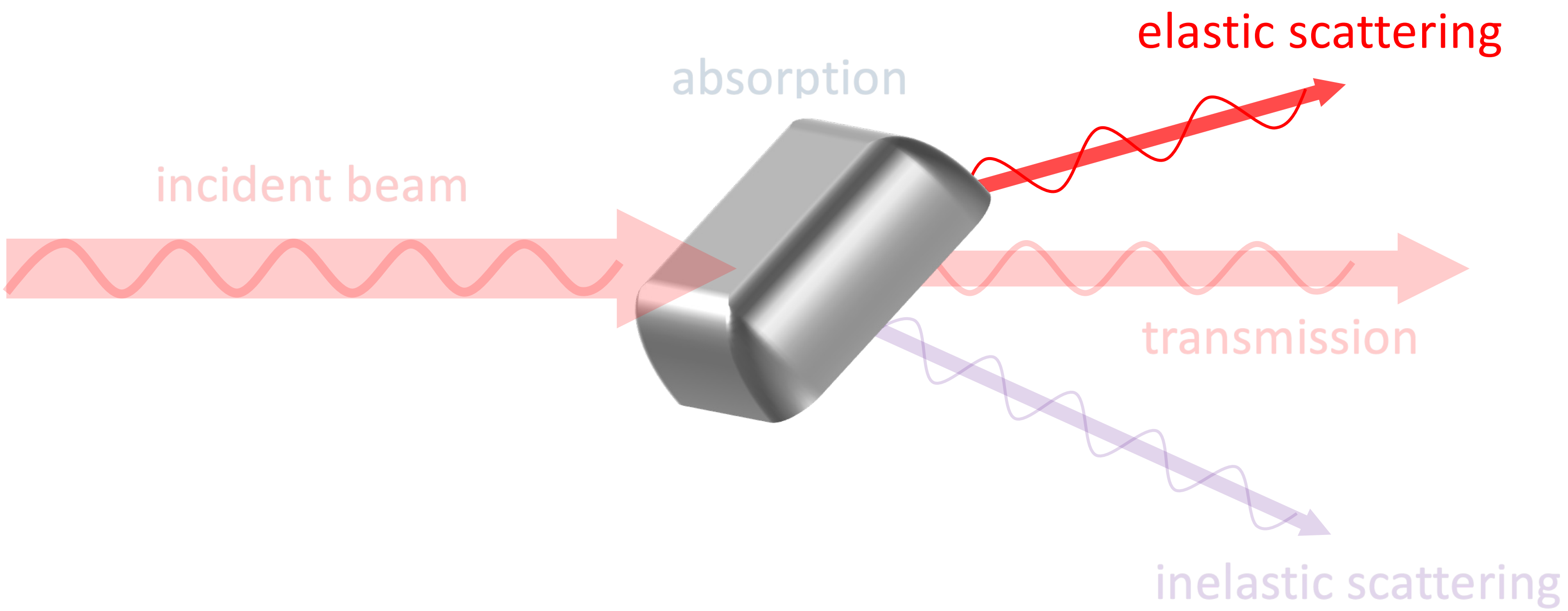
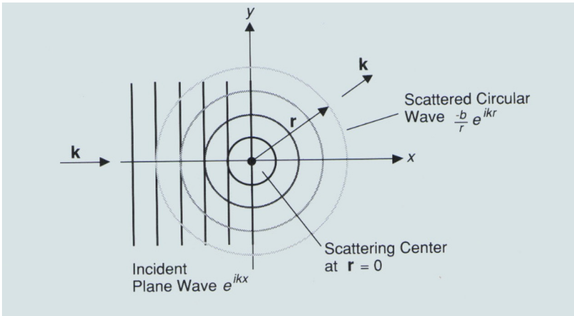
# Interaction of X-rays and neutrons with matter

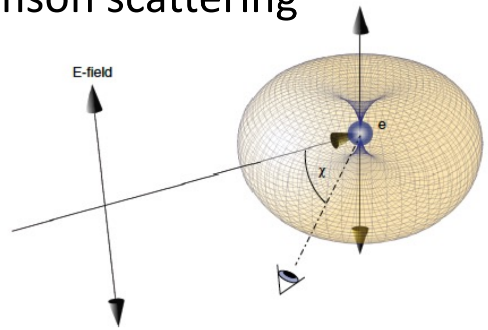


# Elastic scattering from a single scatterer

- neutron scattering from a single nuclei



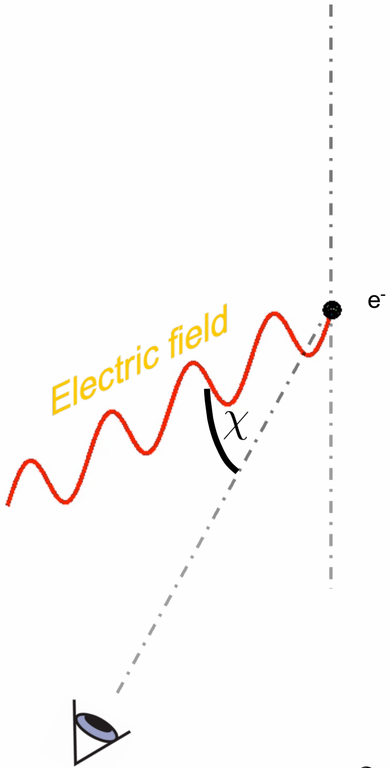

- X-ray scattering from a single electron
  Thomson scattering




- point scatterer, i.e. isotropic scattering, since the nuclei is very small compared to the wavelength

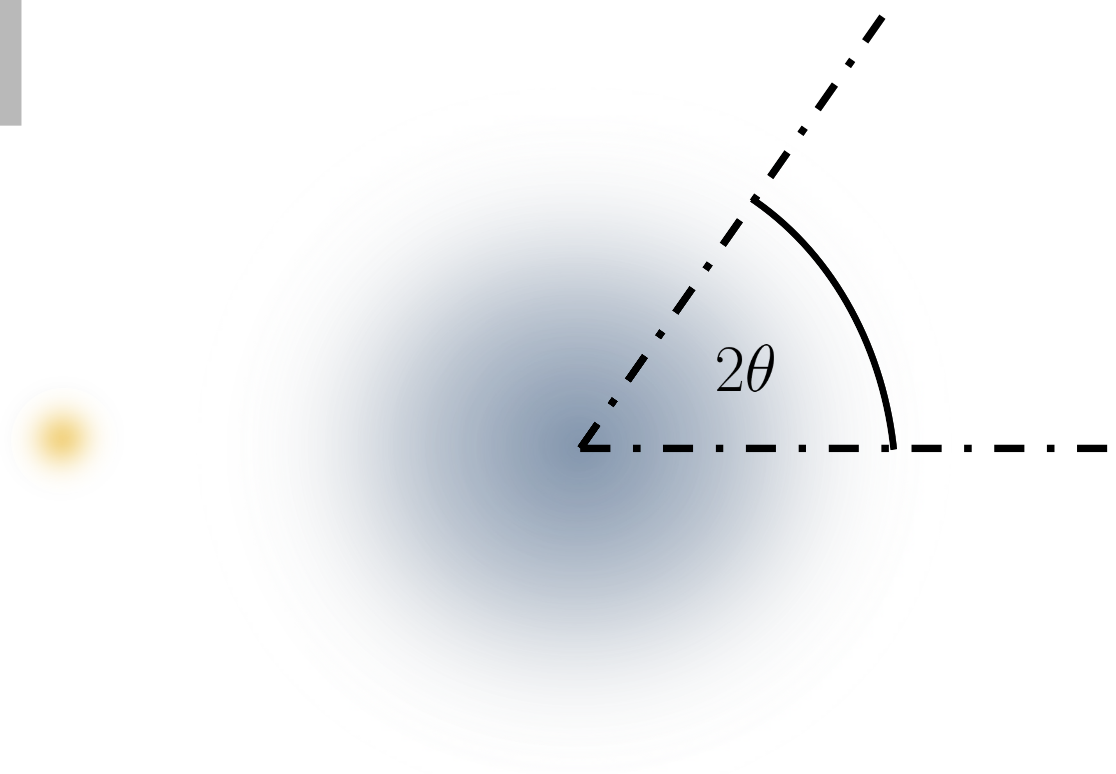
- electromagnetic dipole radiation (non-isotropic)

# X-ray scattering from a single electron: Dipole radiation

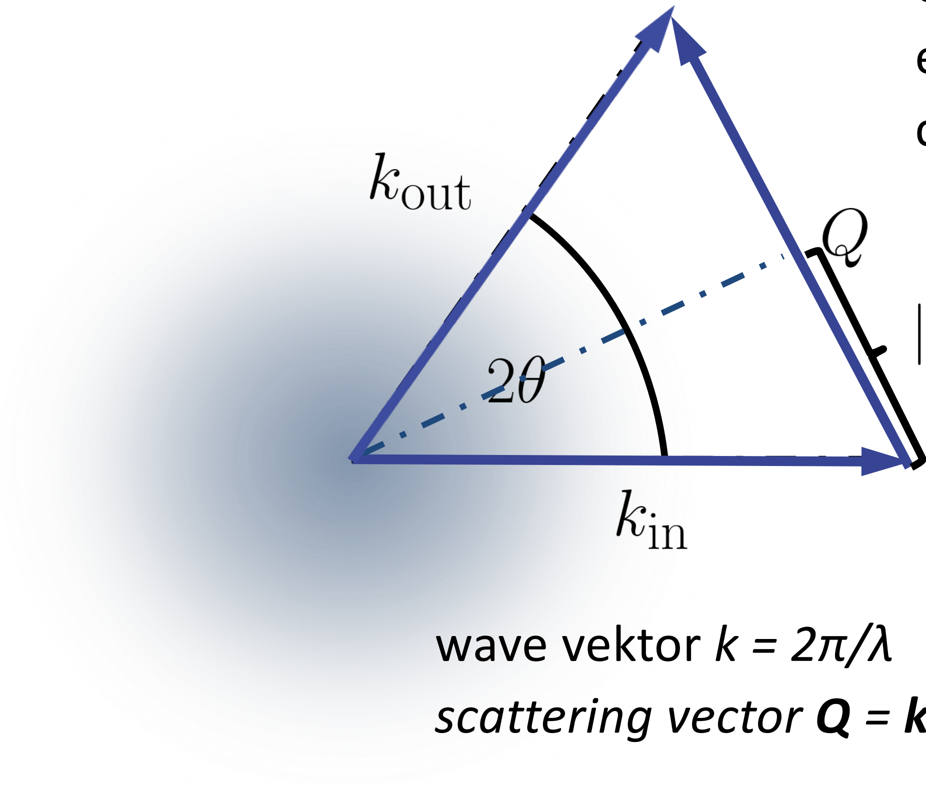



$$I(\chi) = E_0^2 \cos^2 \chi$$

# Elastic scattering of photons: Thompson Scattering



# Elastic scattering of photons




elastic scattering: no loss in photon energy but direction or of the photon can change: scattering angle 2θ

$$Q = 2|k| \sin\theta = (4\pi/\lambda) \sin\theta$$

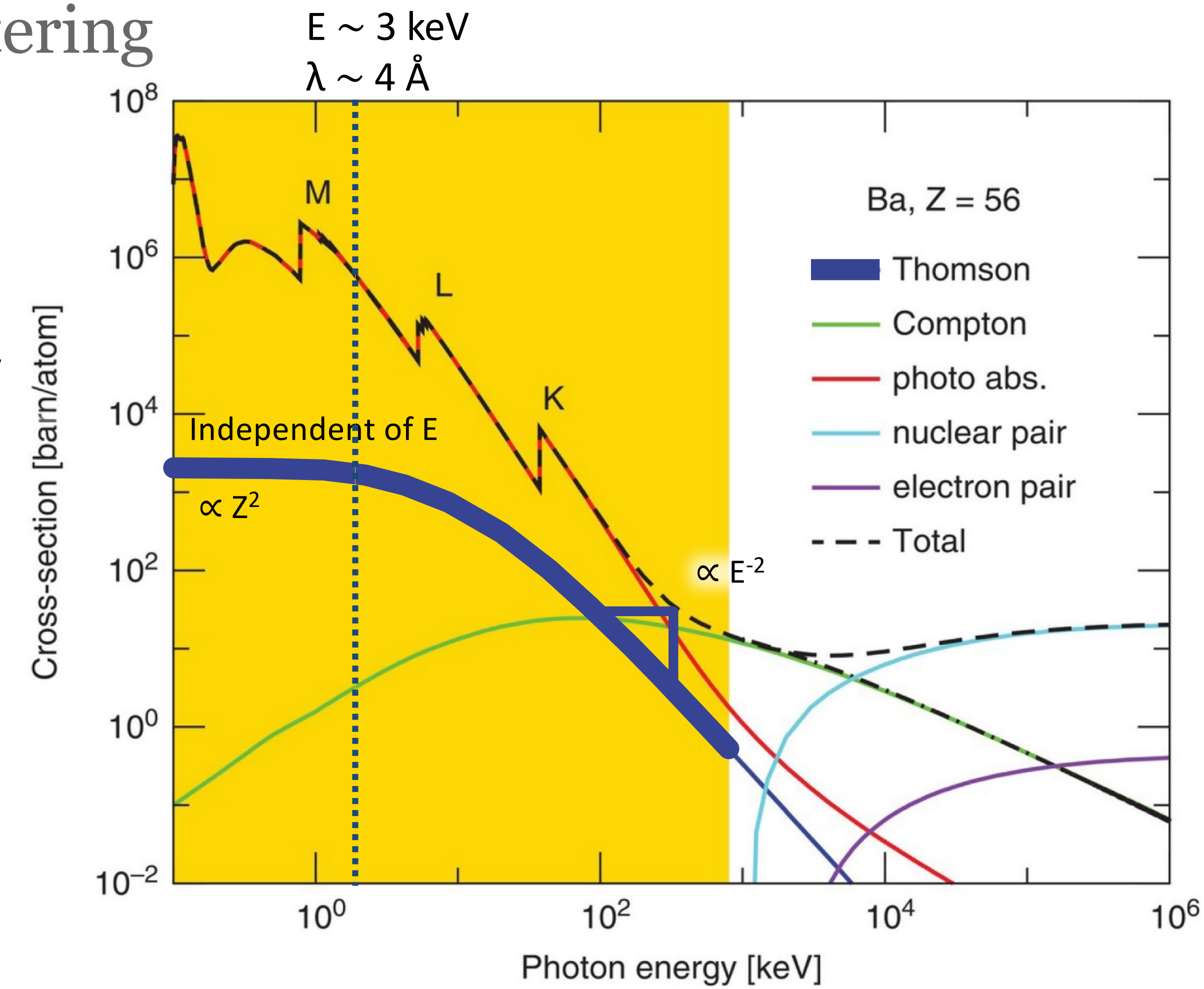
wave vektor $k = 2\pi/\lambda$

*scattering vector* $\mathbf{Q} = \mathbf{k}_{in} - \mathbf{k}_{out}$

# Interaction strengths of x-rays with matter
# Thomson scattering

energies below ~ 3 keV: $\propto Z^2$
wavelength is large compared to the size of the electron cloud: all scattering elements scatter coherently

energies above ~ 3 keV $\propto E^{-2}$
smaller wavelength than size of atom: partially destructive interference reduces cross-section → drop off determined by **atomic form factor**

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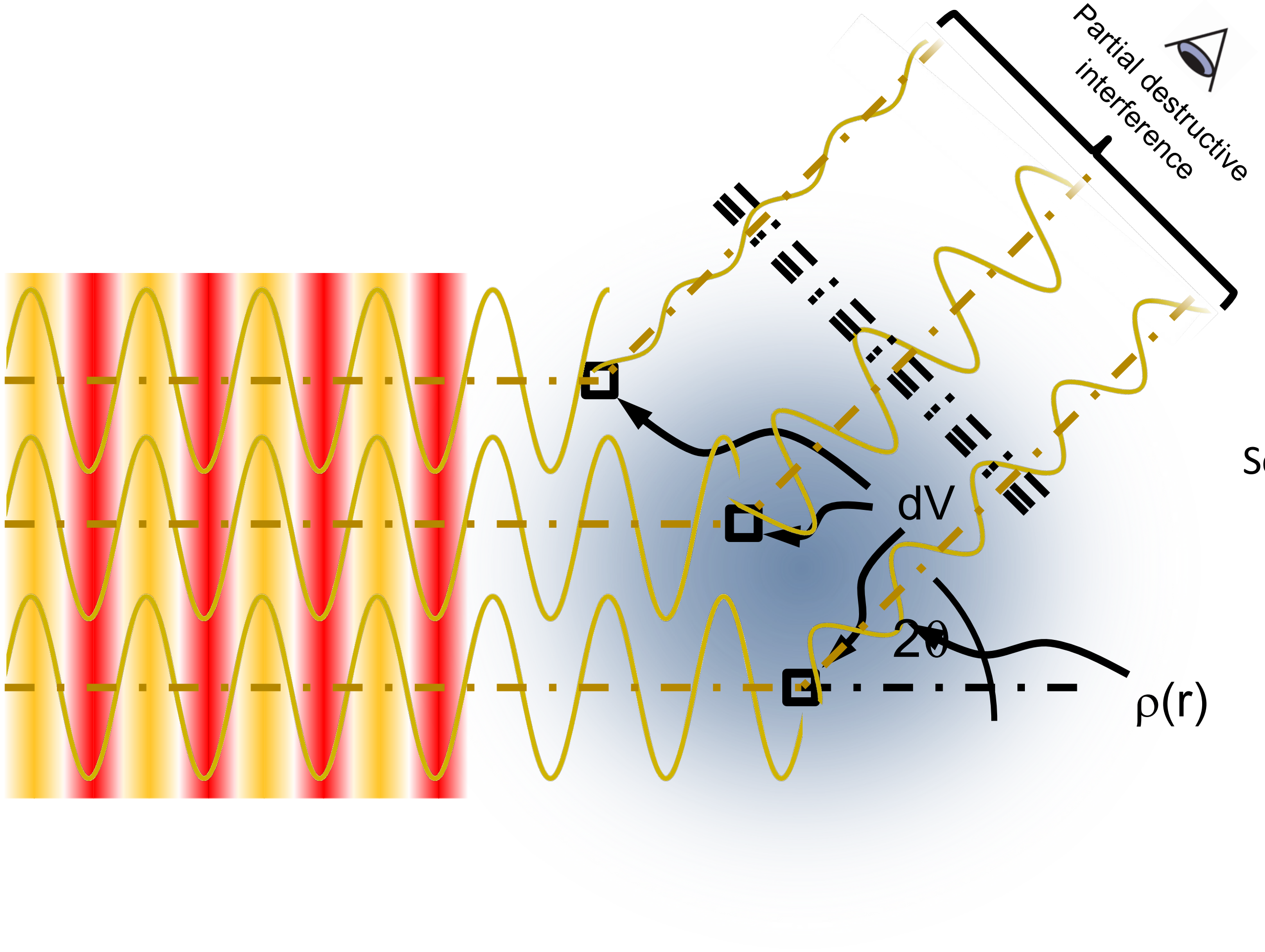
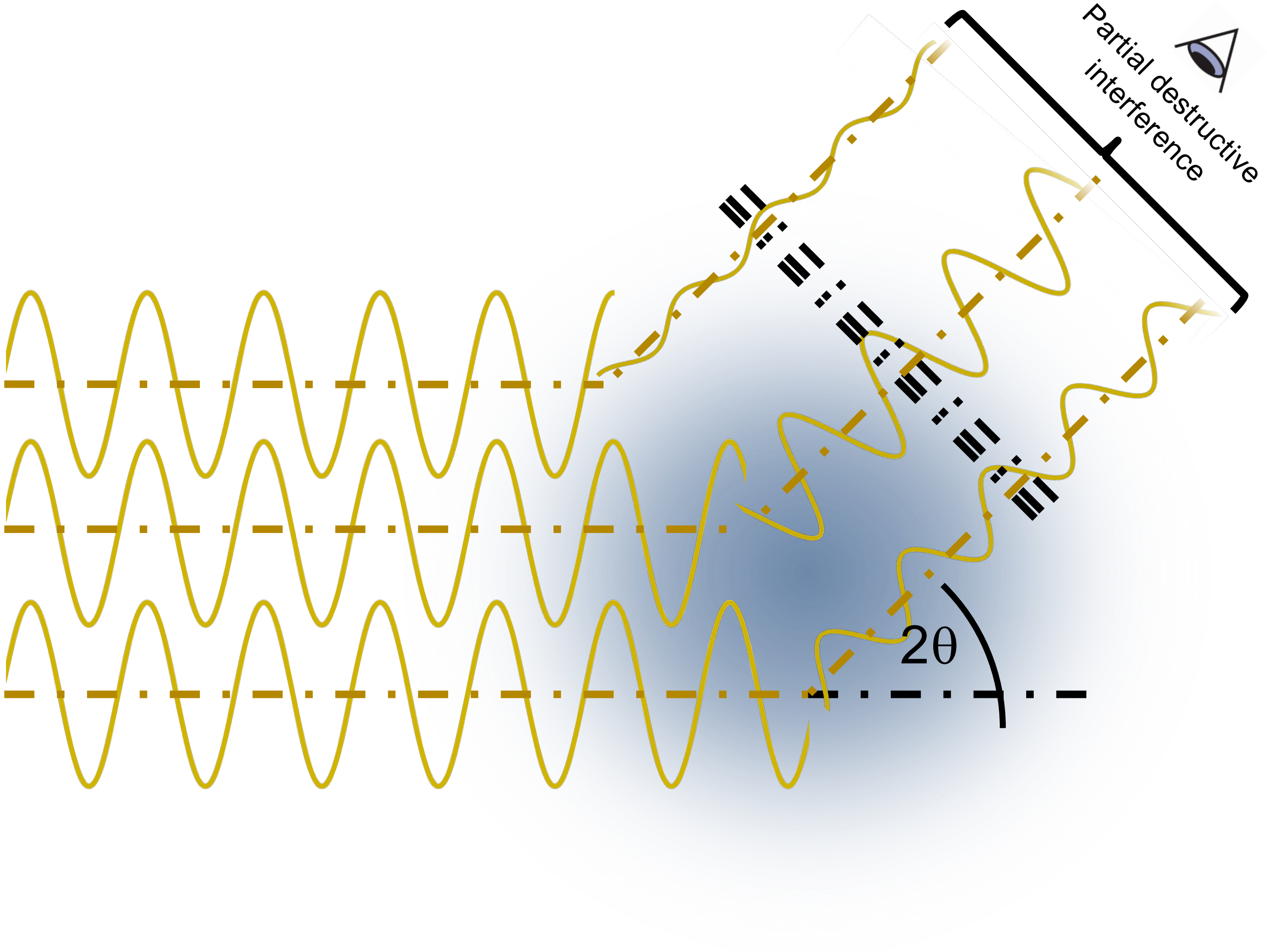
# X-ray scattering from an atom




Scattering amplitude decreases with increasing angle 2θ

# X-ray scattering from an atom



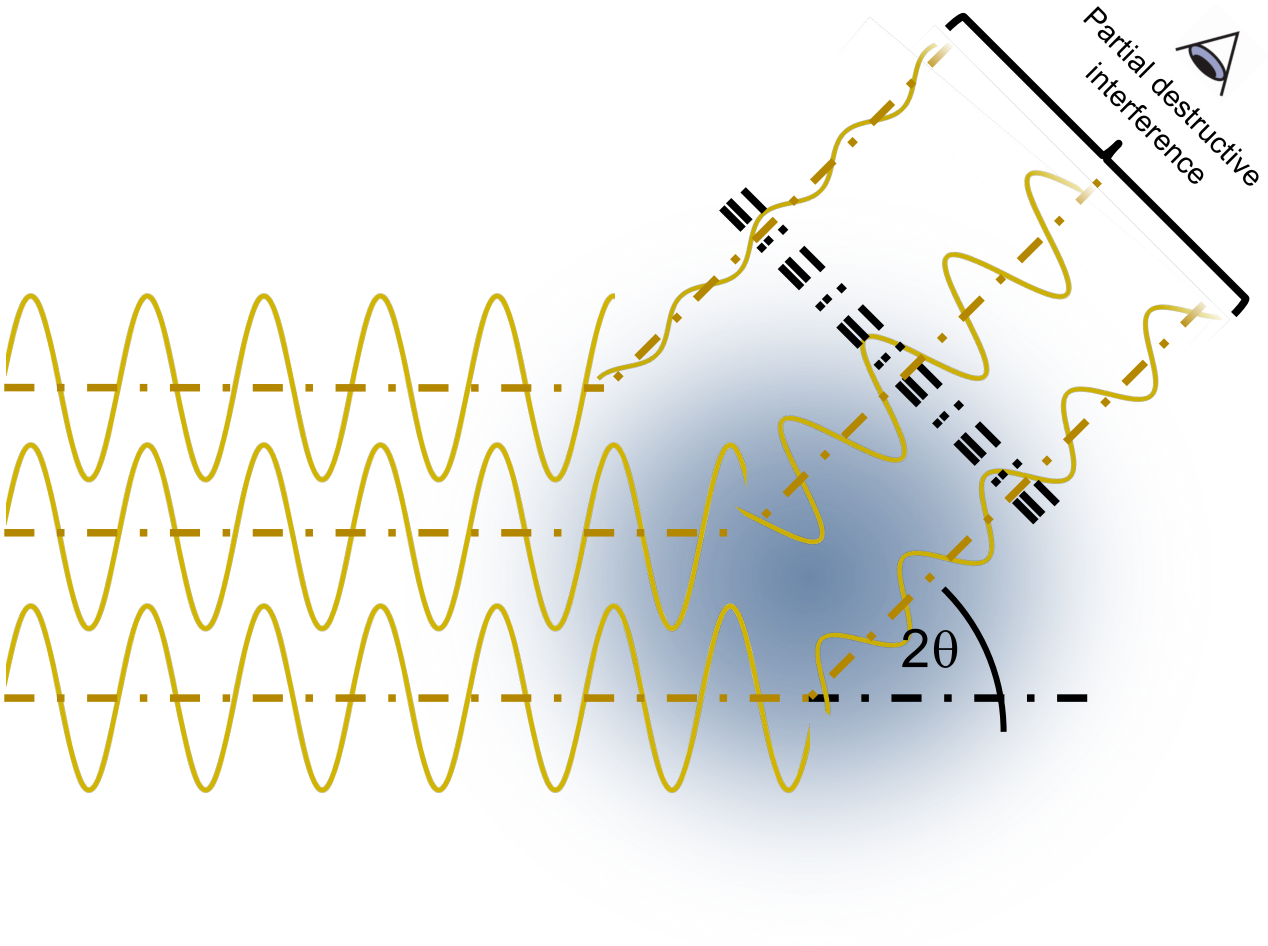

quantify phase difference between scattered radiation from any two dV and integrate contributions from all the volume elements

→ scattering amplitude of an atom as a function of the scattering angle and photon energy

→ **atomic form/scattering factor**

→ Fourier transform of electron density distribution ρ(r)

# X-ray scattering from an atom




First approximation: assume electrons in cloud around atom are free i.e. unbound to nuclear core (far away from absorption edges)

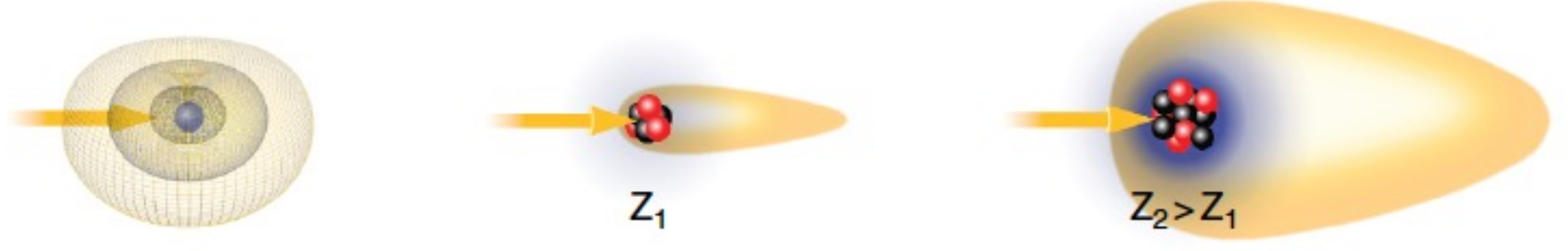
Second approximation: Fraunhofer approximation: observer (= detector) is far from sample relative to distance within the sample (scattering/diffraction)

Third approximation: Kinematic approximation: sample is a weak scatterer, every photon only scatters once

# Elastic scattering and atomic form factor

photon wave length < electron cloud

(a) single electron (b) light atom (c) heavy atom




forward direction $f^0(0)$: integral of the electron density over the atom's electron cloud: atomic number Z

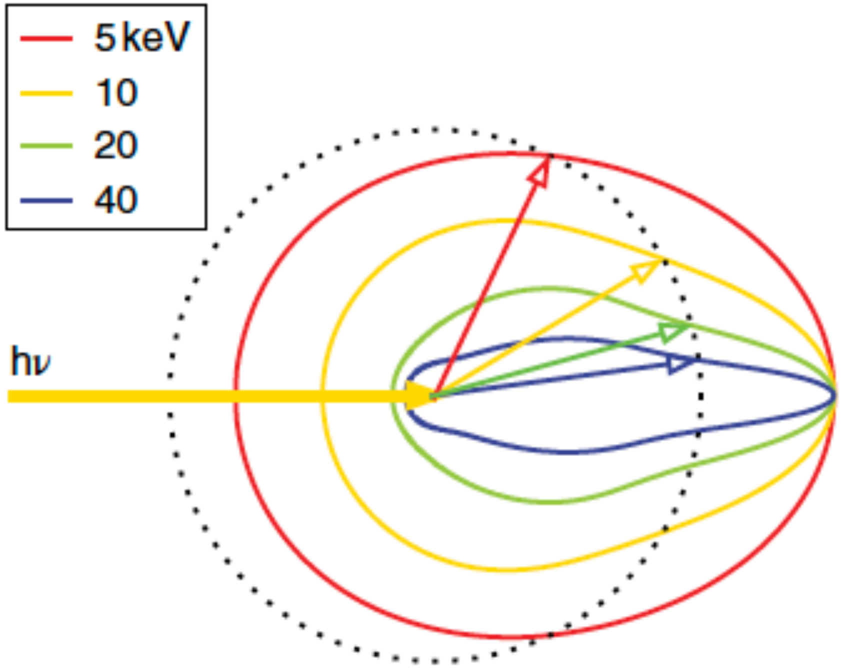
for Q≠0 scattering amplitude decreases with increasing 2θ

drop off is steeper for $Z_1$: core electrons are closer to nuclear core, heavy atoms have electron density concentrated in a smaller central volume

Willmott, P. (2019). Scattering Techniques. An Introduction to Synchrotron Radiation, John Wiley & Sons, Ltd: 133-221.

# Elastic scattering and atomic form factor

atomic form factor $f^0(Q)$ of Phosphorus at different X-ray energies




atomic form factors can be found in the International Tables for Crystallography

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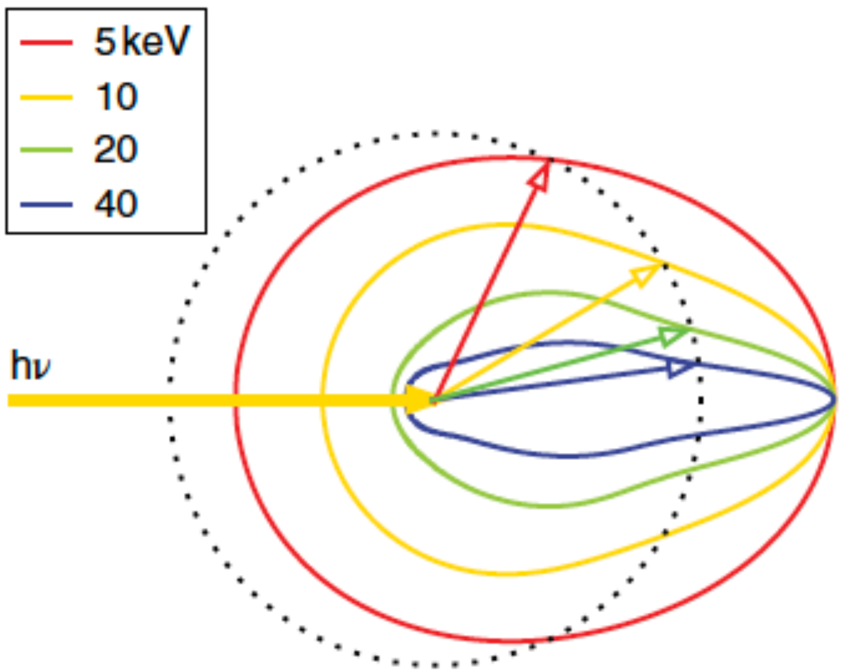
# Elastic scattering and atomic form factor

atomic form factor $f^0(Q)$ of Phosphorus at different X-ray energies




First approximation: assume electrons in cloud around atom are free i.e. unbound to nuclear core

→ valid if photon energy is much larger than the electron binding energy

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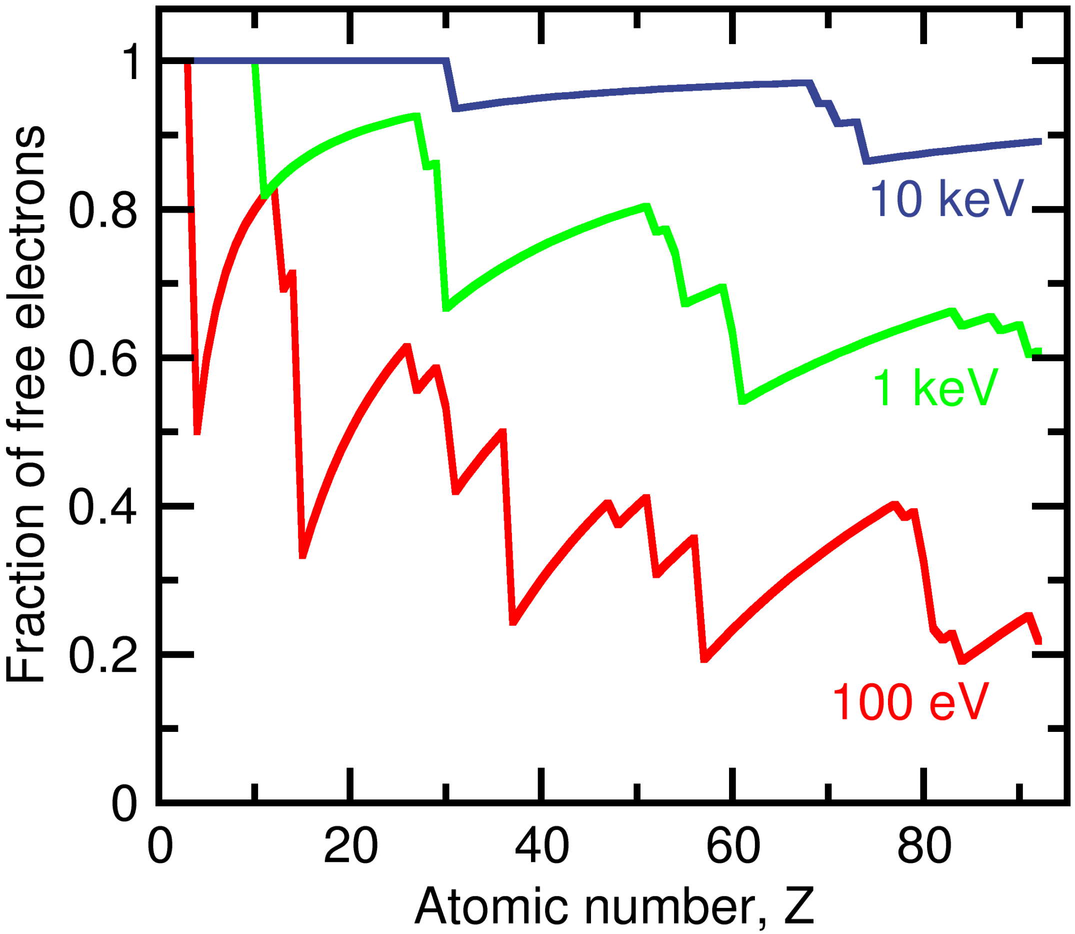
# Atomic response to x-rays

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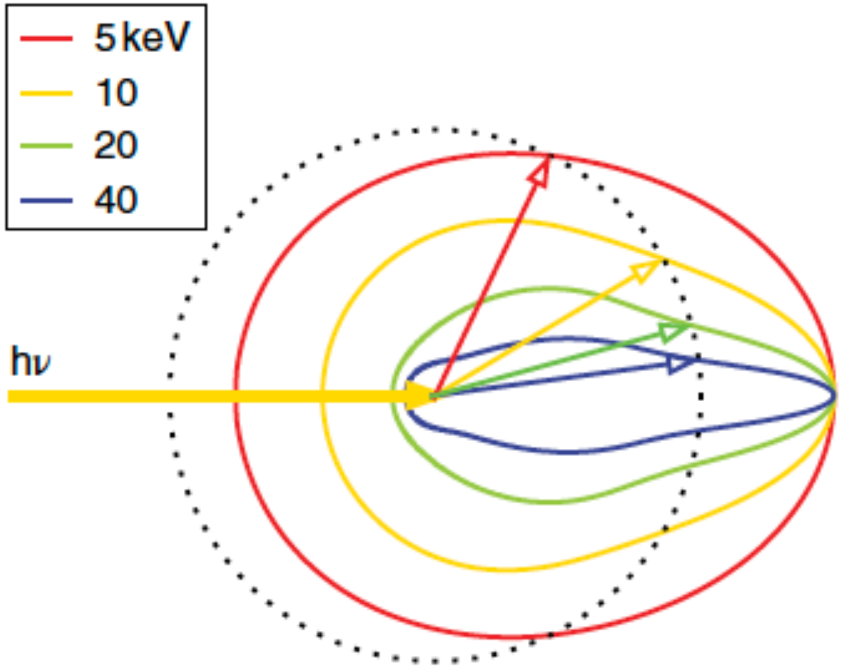
Most electrons in atoms can be considered to be quasi “free” for photon energy > 1 keV

# Elastic scattering and atomic form factor

atomic form factor $f^0(Q)$ of Phosphorus at different X-ray energies




First approximation: assume electrons in cloud around atom are free i.e. unbound to nuclear core

→ valid if photon energy is much larger than the electron binding energy

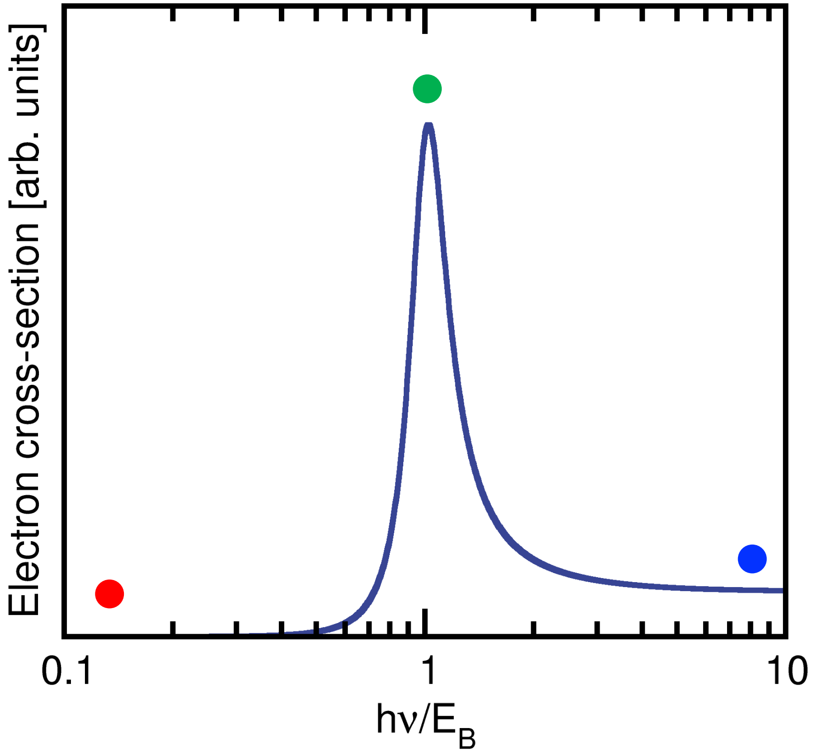
to account for electrons being bount adding of energy-dependent terms to the atomic form factor:

$$f(Q, \hbar\omega) = f^0(Q) + f'(\hbar\omega) + if''(\hbar\omega)$$

Willmott, P. (2019). Scattering Techniques. An Introduction to Synchrotron Radiation, John Wiley & Sons, Ltd: 133-221.

# Bound electrons' response to x-rays

$\omega_0 = E_B/\hbar$ natural osciallation frequency for a defined binding energy

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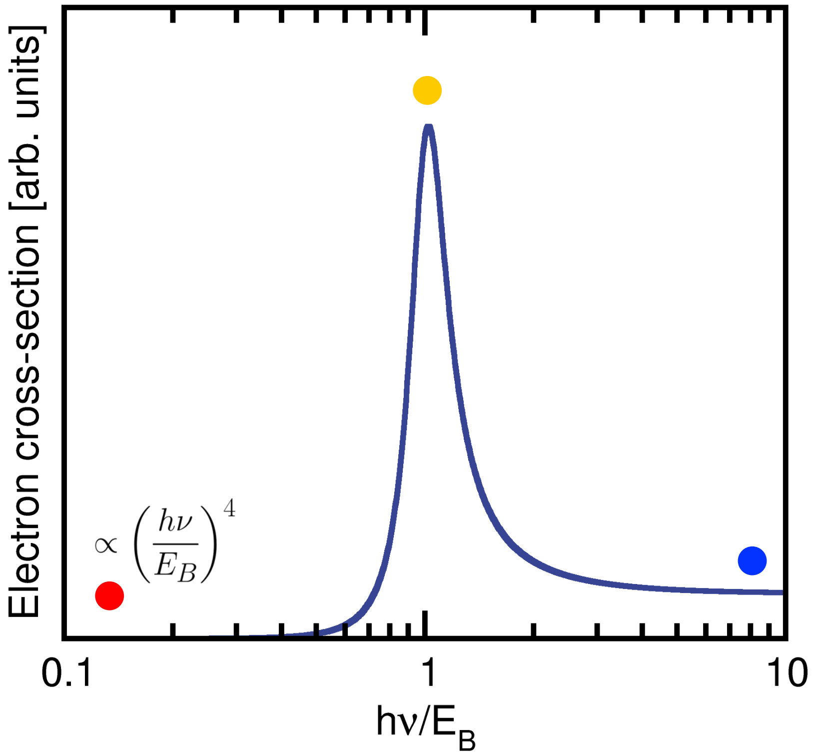
$\hbar\omega \gg E_B$

Electron quasi "free"

# Bound electrons' response to x-rays

$\omega_0 = E_B/\hbar$ natural osciallation frequency for a defined binding energy

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$\hbar\omega \ll E_B$

Response strongly suppressed ~ 0

"Rayleigh scattering"

$\hbar\omega \gg E_B$

Electron quasi "free"

$\hbar\omega \simeq E_B$

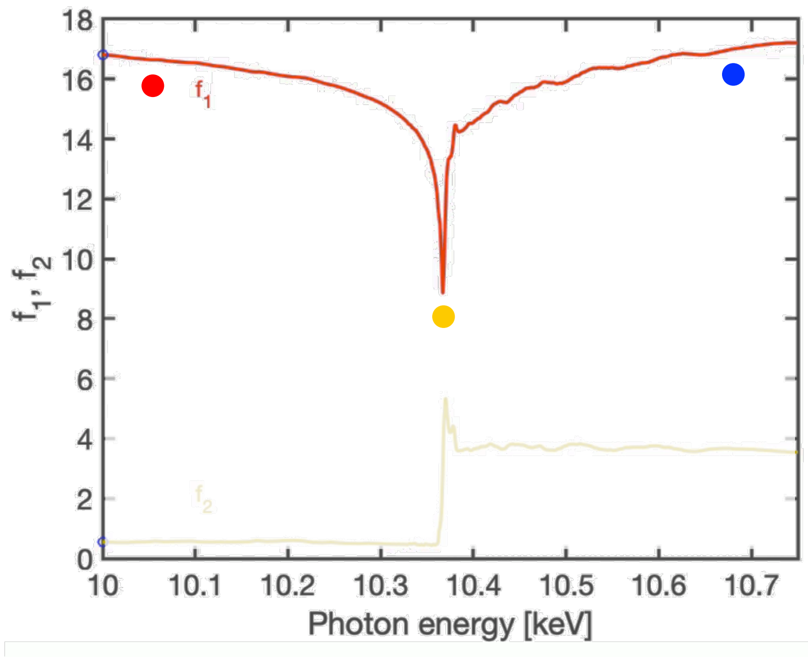
Resonance

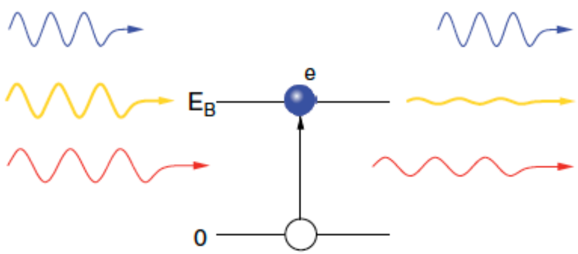
Enhanced response

dissipation (absorption)

# Correction terms to the atomic form factor: f'

$$f_1(Q,\hbar\omega) = f^0(Q) + f'(\hbar\omega) \qquad f'(\hbar\omega) < 0$$




$\hbar\omega < E_B$

Reduced response from those electrons that are bound ⇒ small reduction in scattering factor

Add negative component f'

f' a function of $\hbar\omega$

$\hbar\omega \gg E_B$

**Electron quasi "free"**

f' ⇒ 0

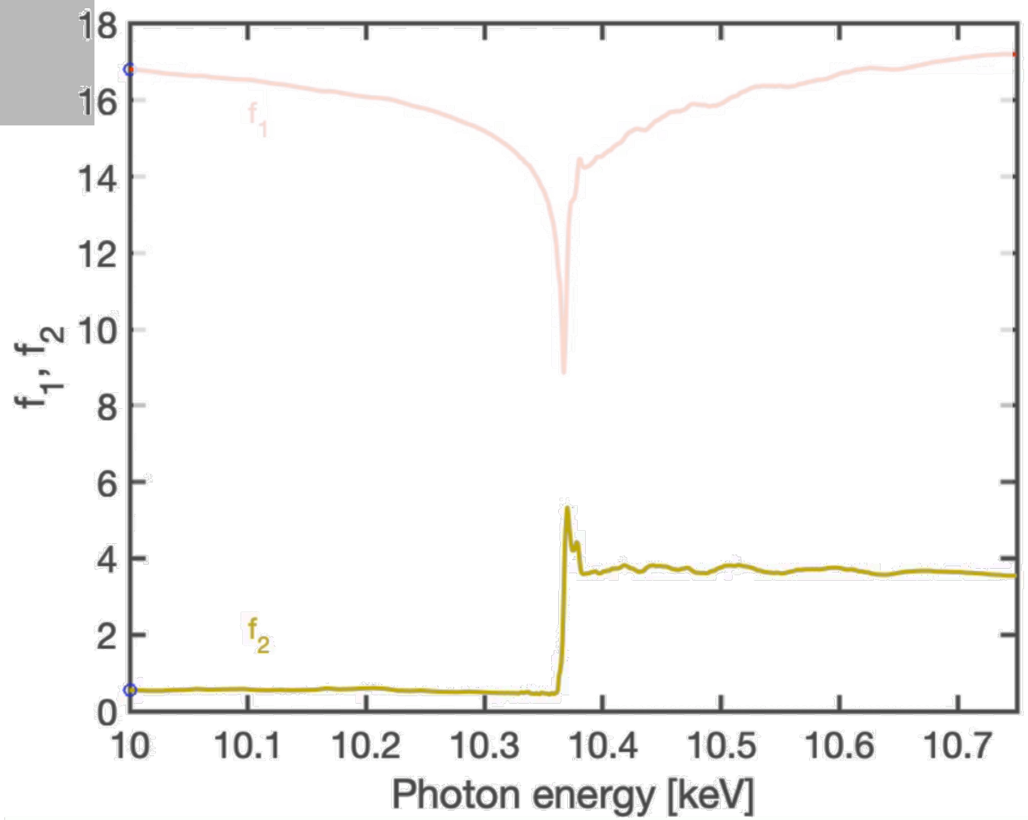
$\hbar\omega \simeq E_B$

Resonance

Enhanced response ⇒ maximal |f'|

→ **decreased scattering strength**

# Correction terms to the atomic form factor: f''




the absorption cross-section

$$f_2 = f'' = \frac{\sigma_a}{2\lambda r_0}$$

$\hbar\omega \simeq E_B$

Resonance

Enhanced response ⇒ maximal |f'|

Phase shift @ resonance = $\pi/2$

Express as imaginary component if''

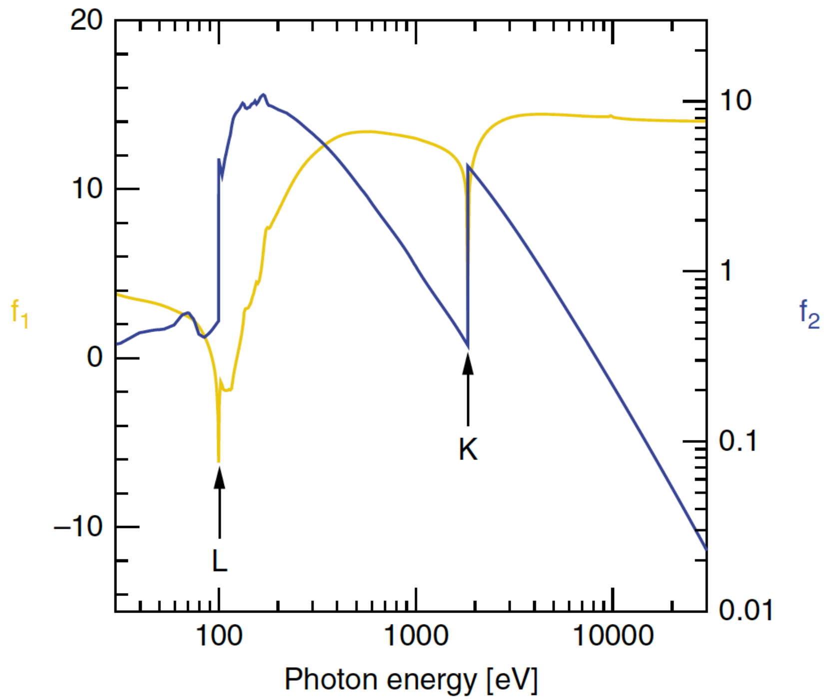
Results in energy dissipation (absorption)

# complex atomic form factor

$$f(Q, \hbar\omega) = f^0(Q) + f'(\hbar\omega) + if''(\hbar\omega)$$

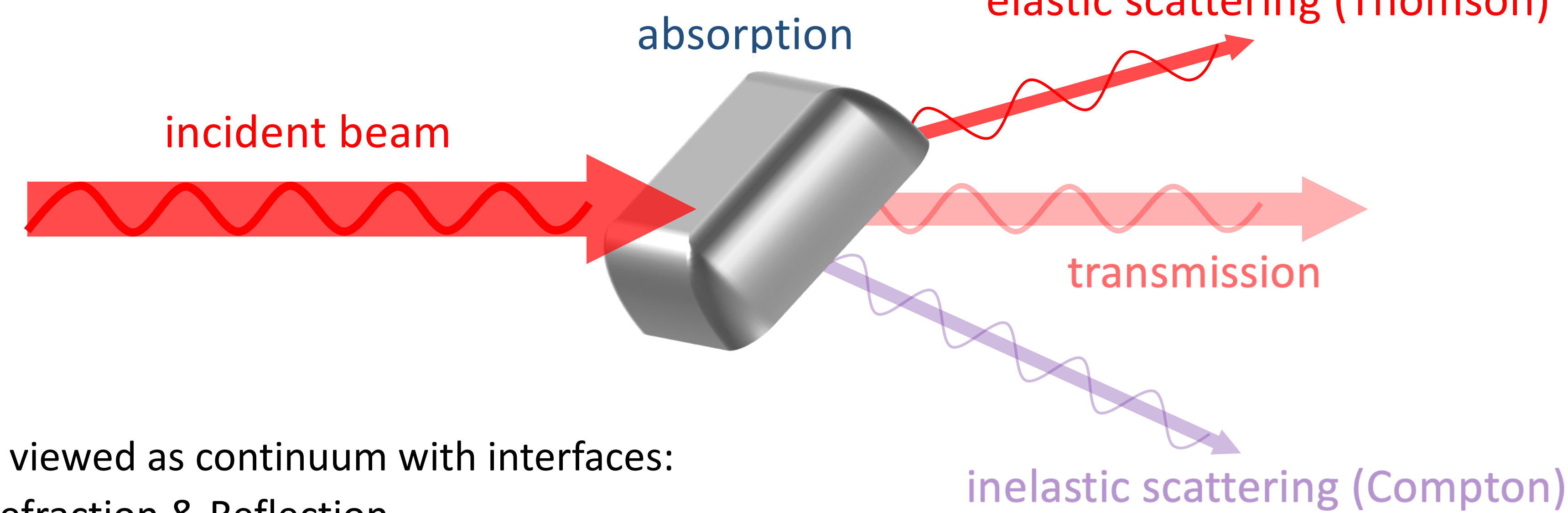
$f_1(Q,\hbar\omega)$ = $f^0(Q) + f'(\hbar\omega)$; $f_2(\hbar\omega)$ = $f''(\hbar\omega)$

complex atomic form factor for Si



# Interaction of X-rays with matter

interaction with electrons



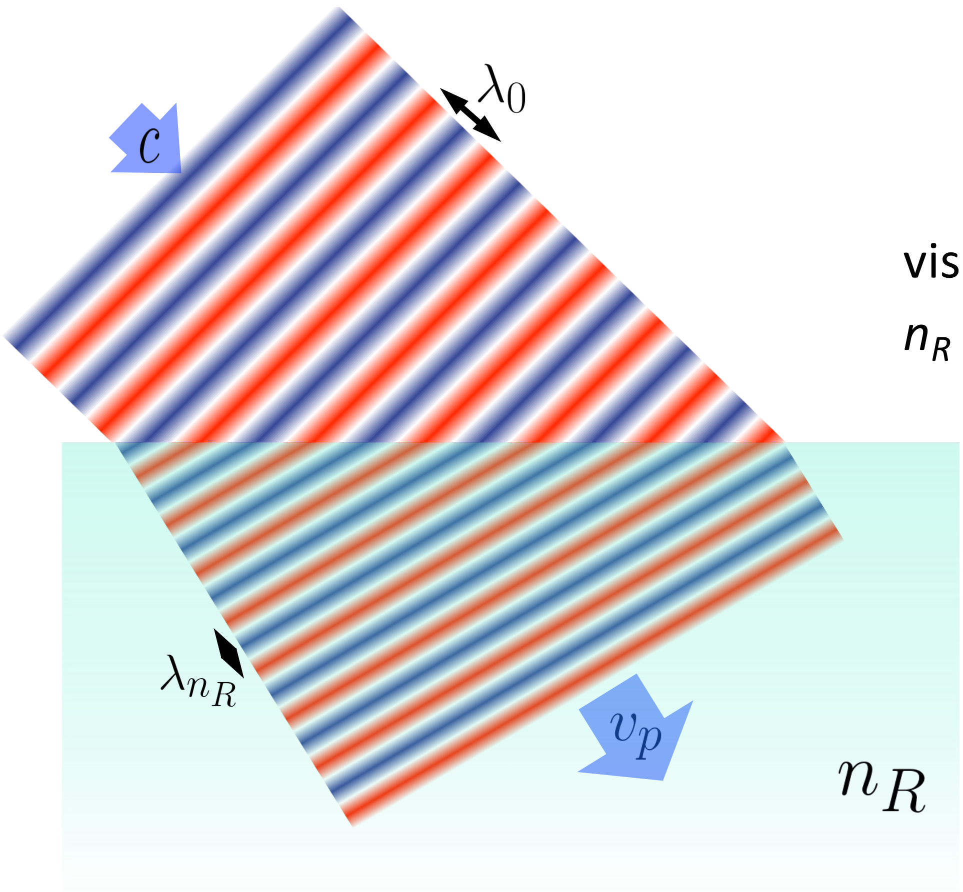

if viewed as continuum with interfaces:
Refraction & Reflection

scattering and refraction descriptions are equivalent

# Refraction

$$n_R = \frac{c}{v_p}$$

$$\lambda_{n_R} = \lambda_0 / n_R$$




visible range

$n_R$ water ~ 1.33

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# Change in n with photon energy

# Complex refractive index for X-rays

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

Refraction – the bending of light as it passes from one medium to another.

Reflectivity

Absorption – attenuation of light by photoexcitation of electrons

refractive-index decrament

absorption index

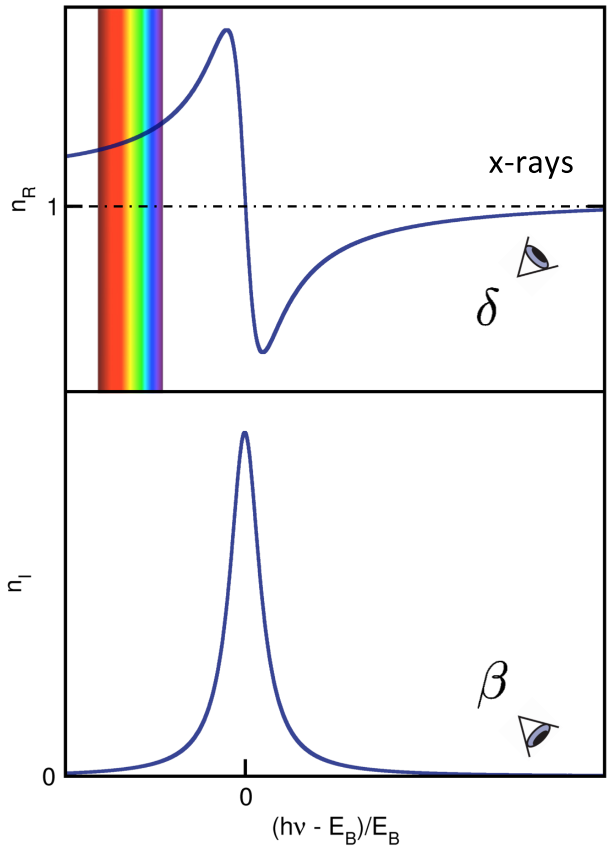
$$n = 1 - \frac{r_0}{2\pi} \lambda^2 \sum_i N_i f_i(0)$$

related to the complex atomic form factor !

far away from an absorption edge (ignoring f')

= ρ average density of electrons

# Refractive index in the x-ray regime




well above resonance:

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

refractive-index decrement

absorption index

$n_R$ for X-rays < 1

deviation from 1 (= δ) in the order of $10^{-4}$ to $10^{-6}$

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# refractive index for neutrons

we consider here only the interaction with nuclei, and skip the magnetic part

$$n = \sqrt{1 - \frac{\lambda^2 \rho}{\pi}}$$

$n < 1$ for almost all materials the refractive index for thermal neutrons deviation from 1 in the order of $10^{-5}$

scattering length density of neutrons

$$\rho = \frac{1}{V} \sum_j b_j$$

$b_j$: coherent scattering length of all atoms (nuclei) in one unit of volume $V$

complex scattering length $b$

$$b = b' - ib''$$

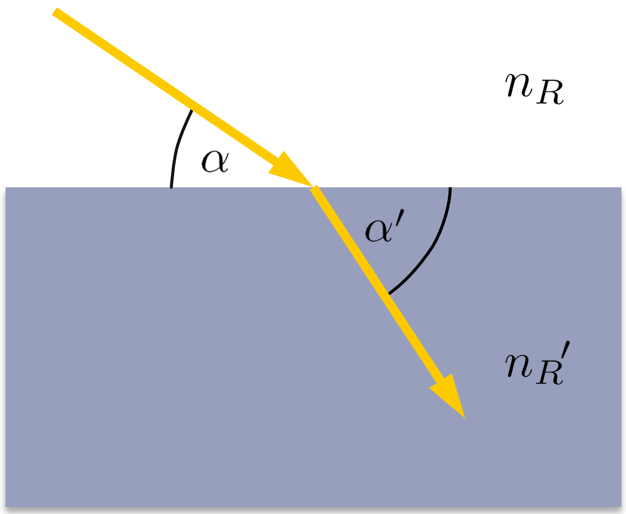
$b''$ imaginary part of the scattering length for Neutron absorption (can be mostly neglected)

$b'' = \left(\frac{k}{4\pi}\right) \sigma_a(k)$ with $\sigma_a$ the absorption cross section

Torikai, N. (2011). Neutron Reflectometry. 115–145.

# Snell's law

$$\frac{\cos\alpha}{\cos\alpha'} = \frac{n_R{}'}{n_R}$$



# Refractive index: visible light, x-rays, neutrons

**Visible**

$n_R > 1.0$

Light bent to **steeper** angles when entering denser medium

at angles smaller than the critical angle → **total internal reflection**

**X-rays**

$n_R = 1 - \delta < 1.0$

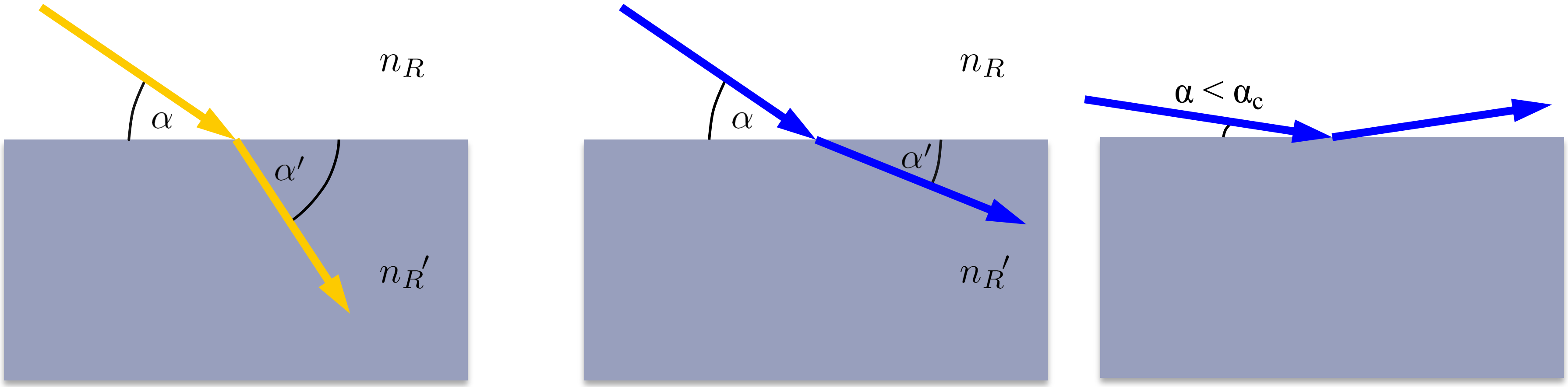
**neutrons**

$n_R < 1.0$

X-rays and neutron bent to **shallower** angles when entering denser medium

at angles smaller than the critical angle → **total external reflection**

deviation from 1 is very small ($10^{-4}$-$10^{-6}$) the critical angle is very small

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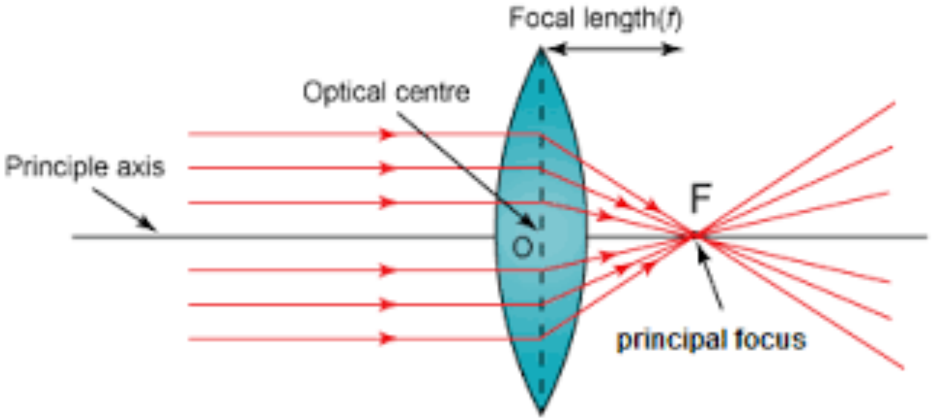
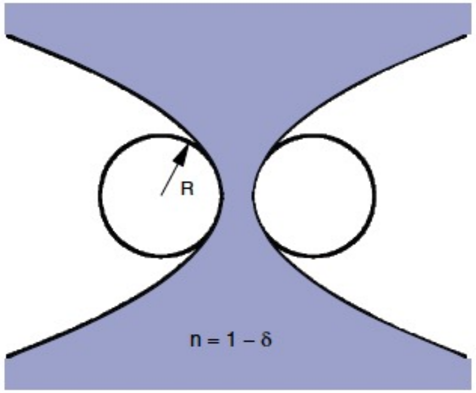
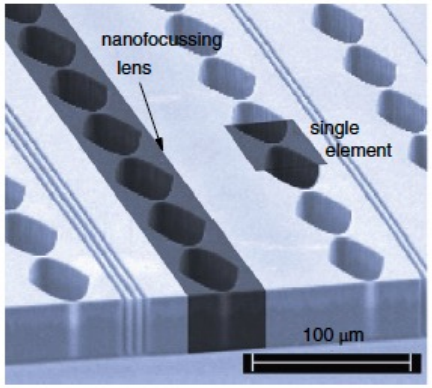
# Refractive index: visible light vs x-rays

focusing lenses



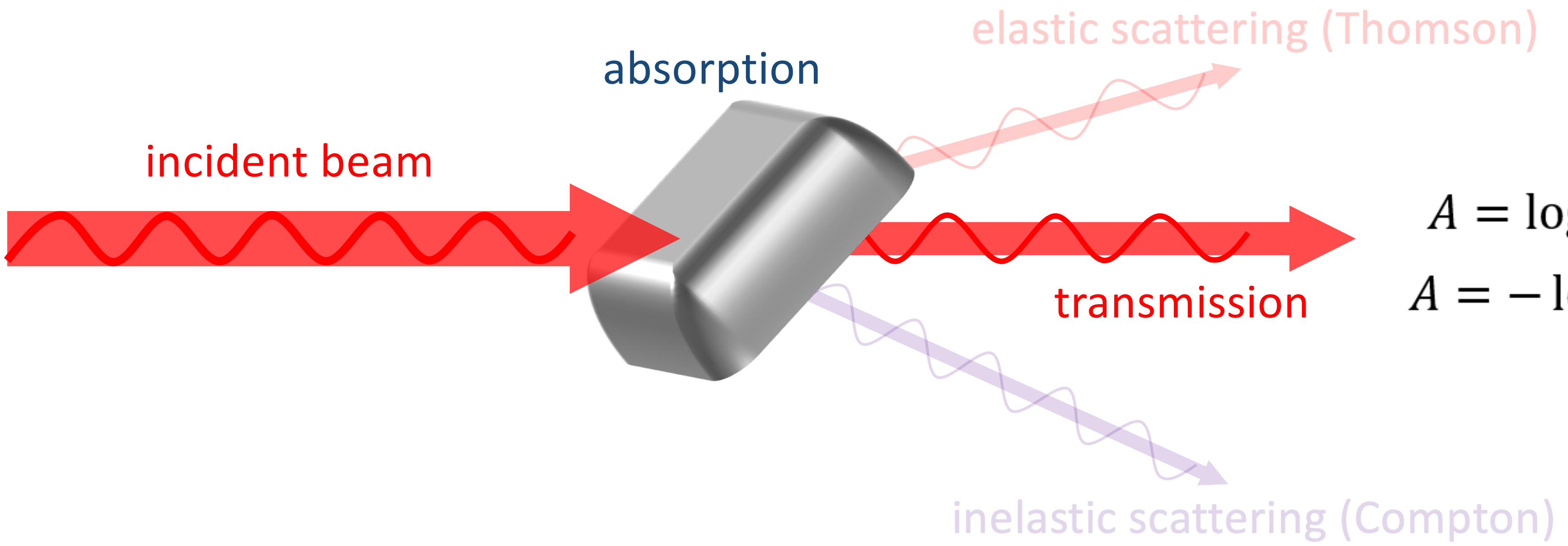

convex lense for focusing in the visible




nanofocussing parabolic compund refractive lenses

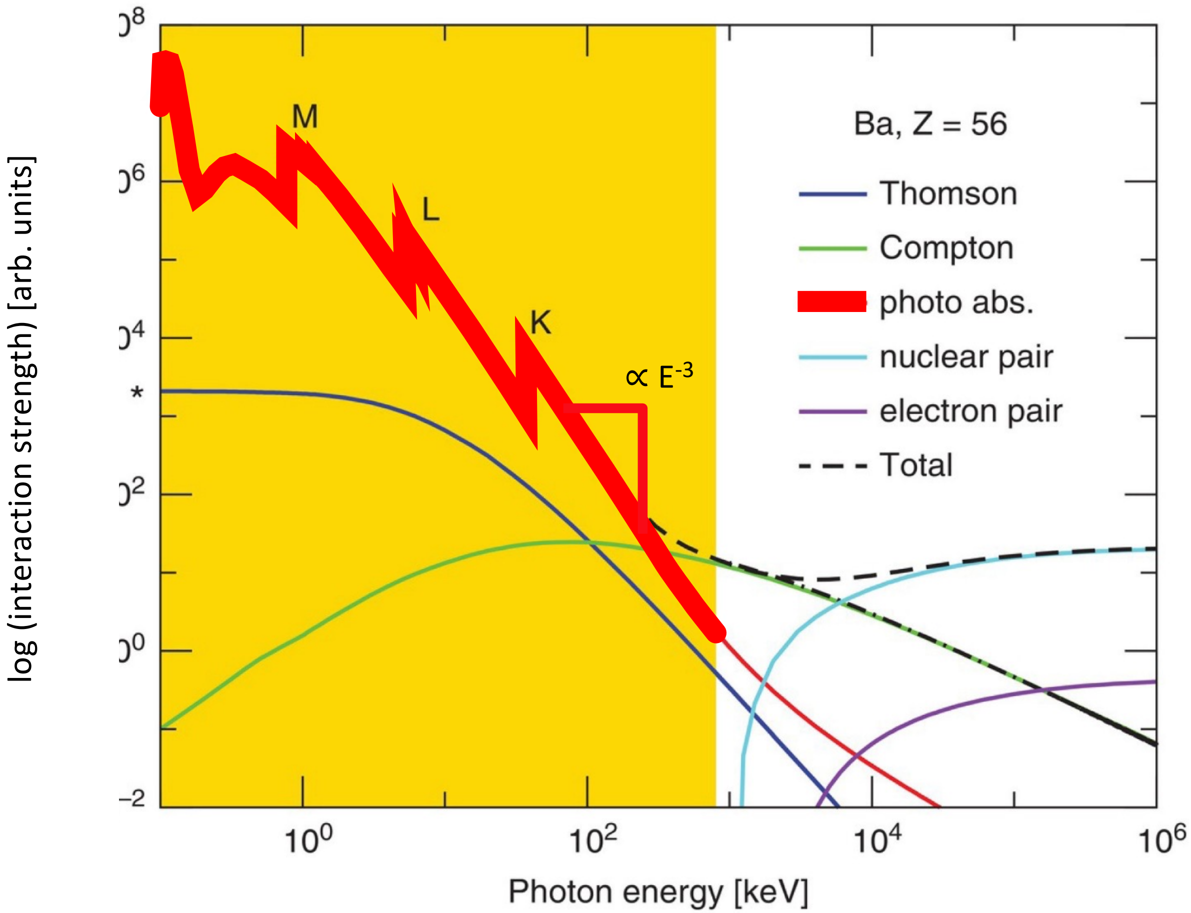
# Interaction of X-ray with matter




$$A = \log_{10} \frac{I_0}{I}$$

$$A = -\log_{10} T$$

# Interaction strengths of x-rays with matter

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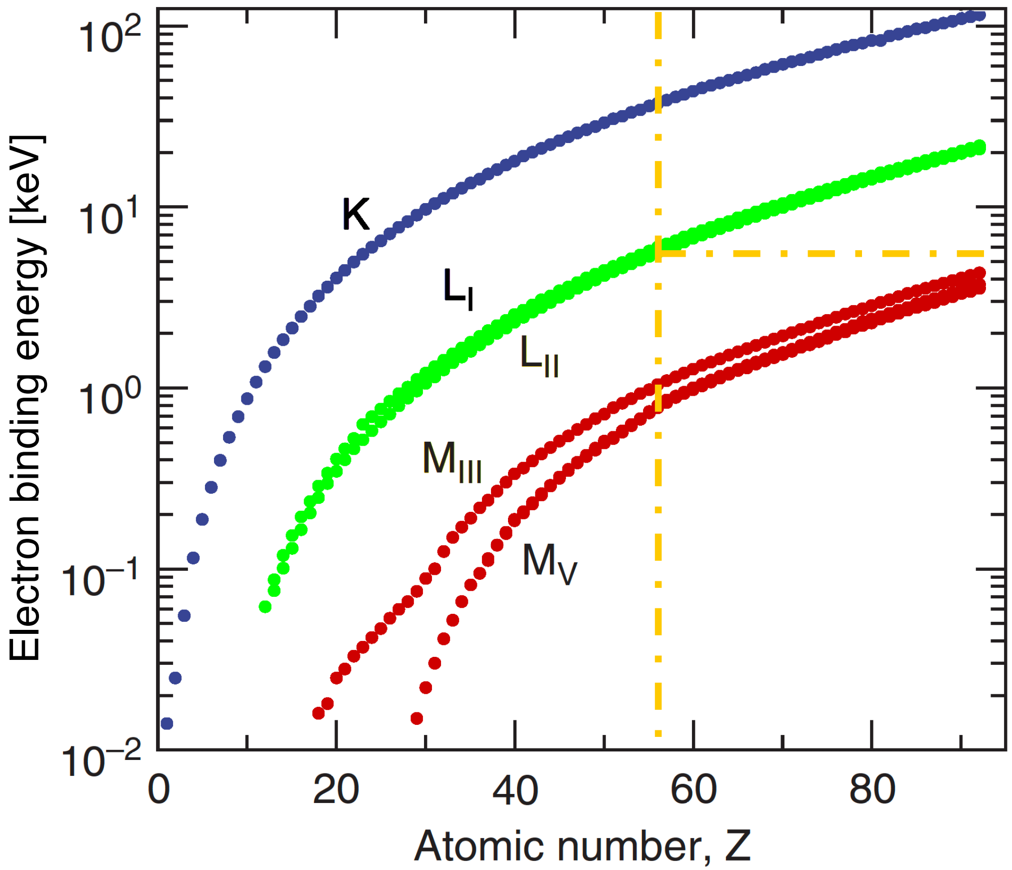
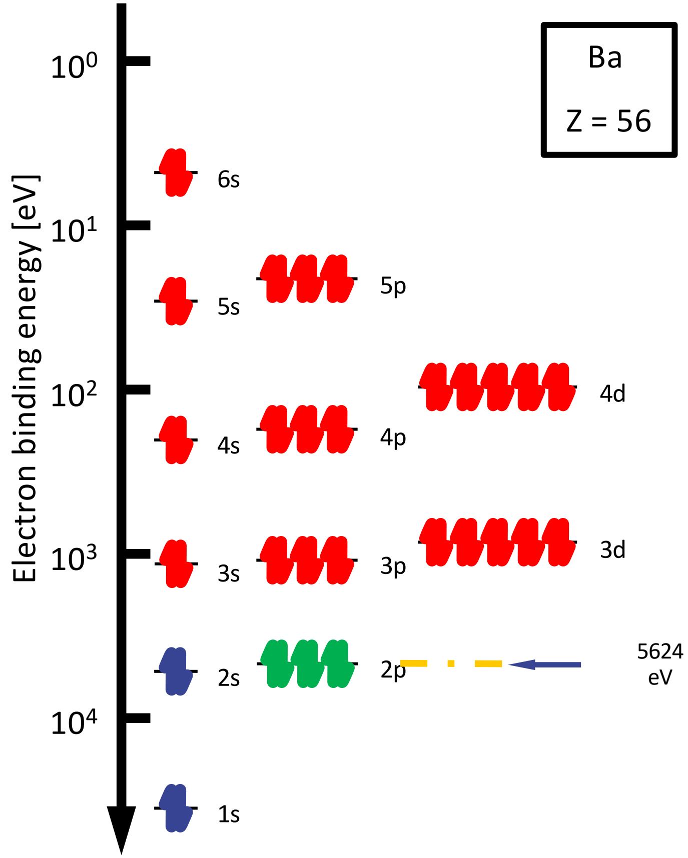
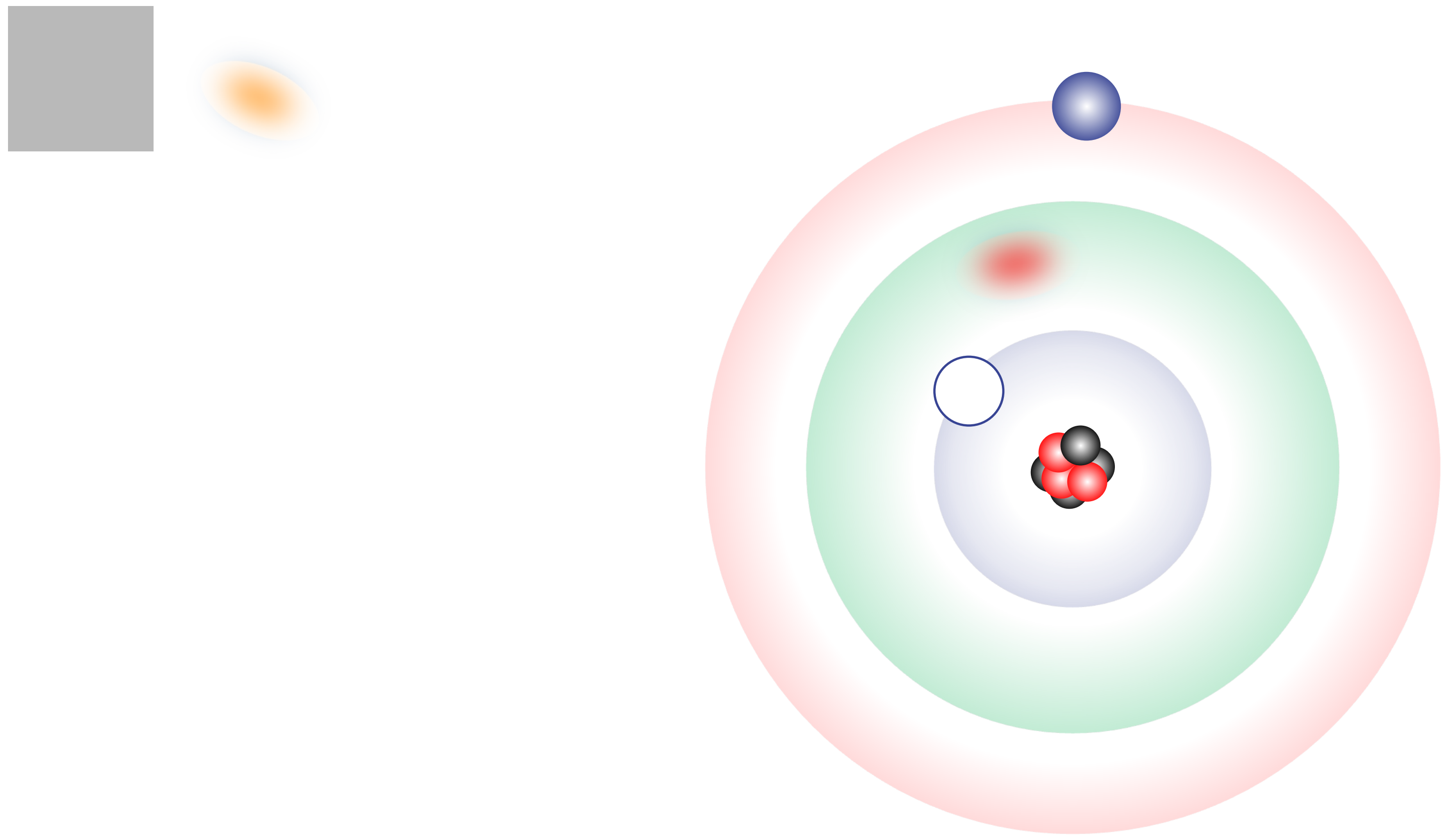
# Electron binding energies of the elements



# Photoelectrons and fluorescence



Photoelectron

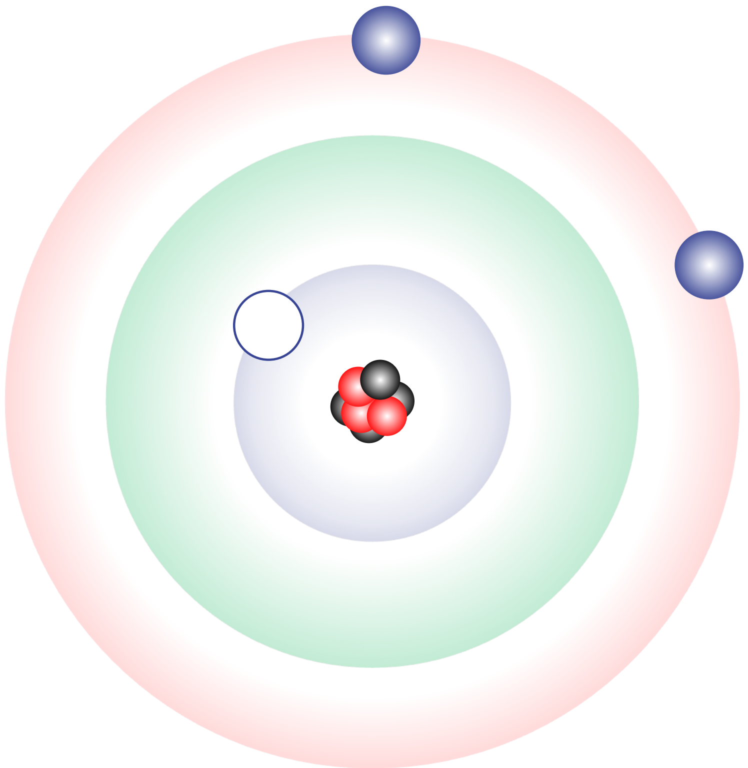
$KE = h\nu_{in} - E_B$

Fluorescence

$h\nu_{in} > h\nu_{out}$

$h\nu_{out} = E_{B,1} - E_{B,2}$

# Auger electrons



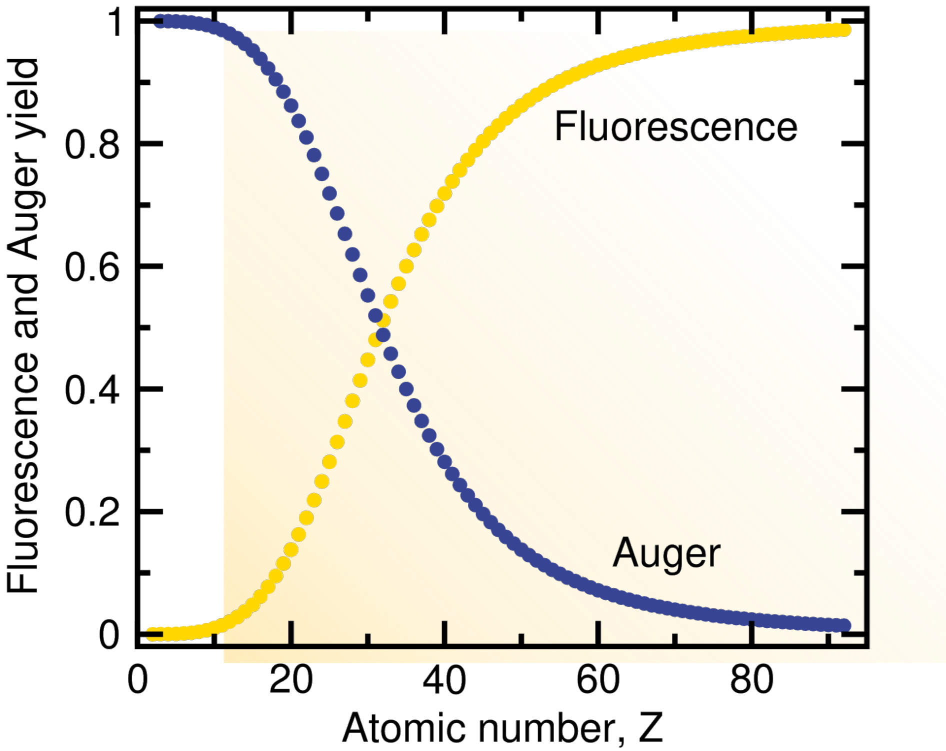
Photoelectron

$KE = h\nu_{in} - E_B$

Auger-electron

KE independent of $h\nu$

# Fluorescence or Auger?



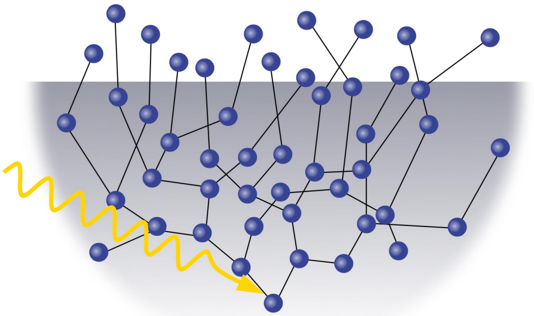

probability for fluorescence depends on relaxation energy

$$p_{\text{fl}} \propto (h\nu)^3$$

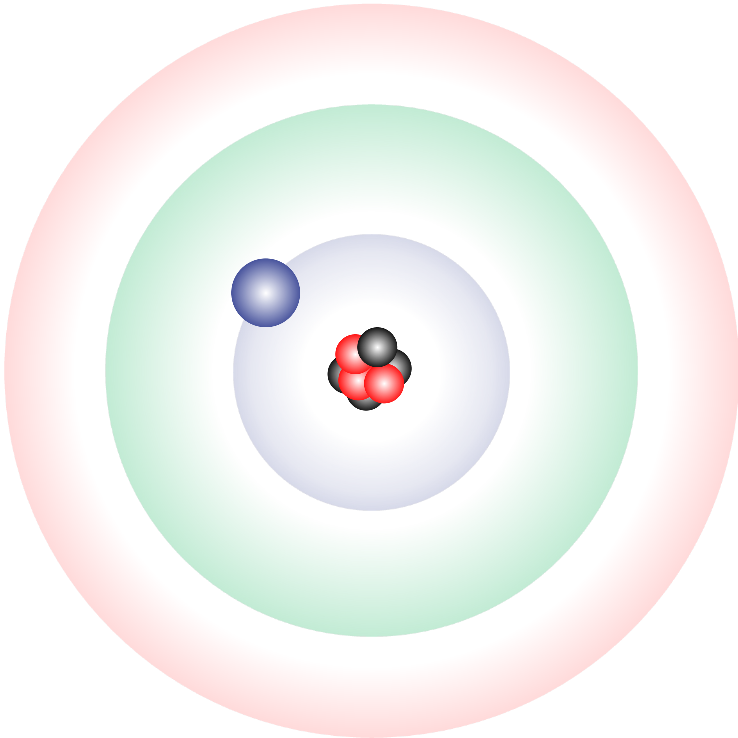
yield for K-shell fluorescence (empirically):

$$Y_K = \frac{Z^4}{10^6 + Z^4}$$

# Secondary electrons



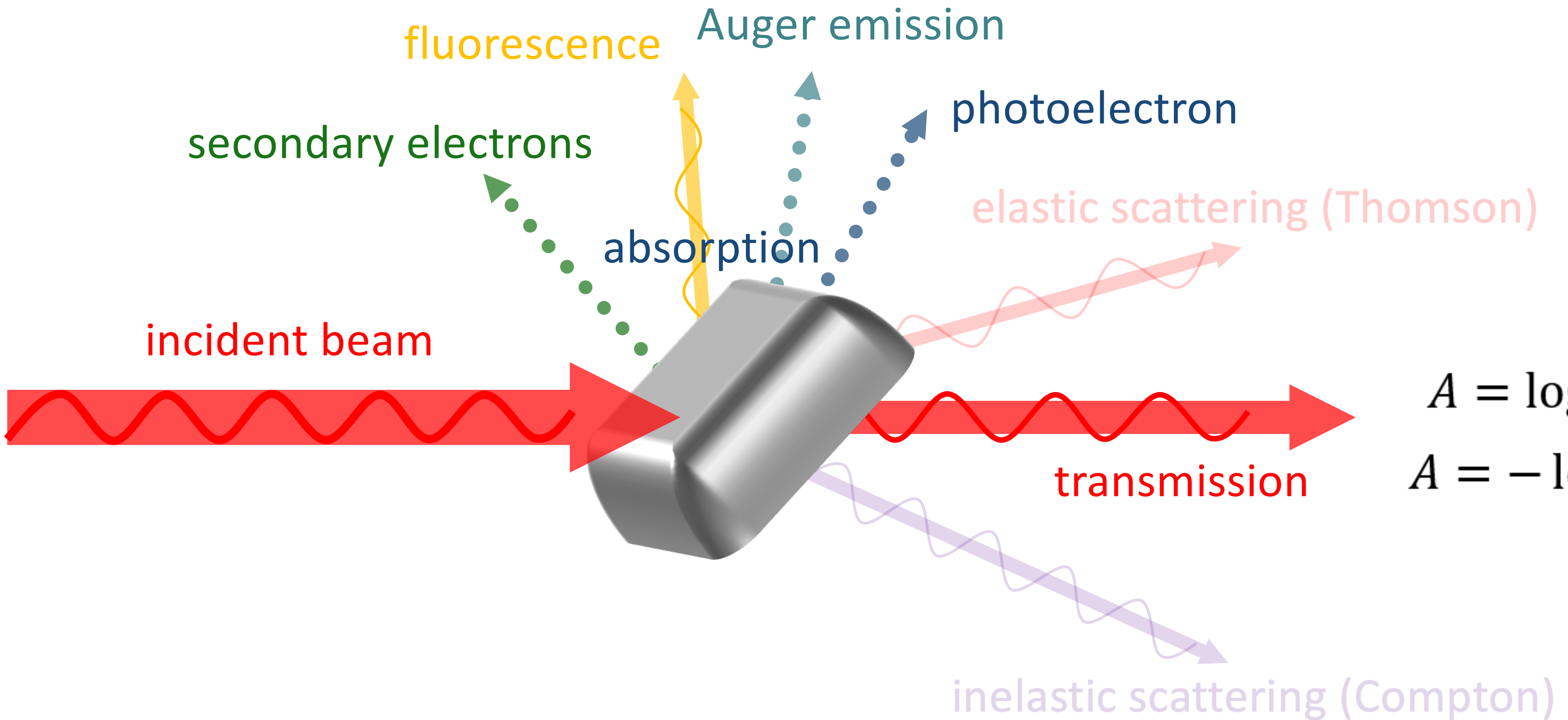
Cascade
process



Thermalization

KE ~ 1 eV or smaller

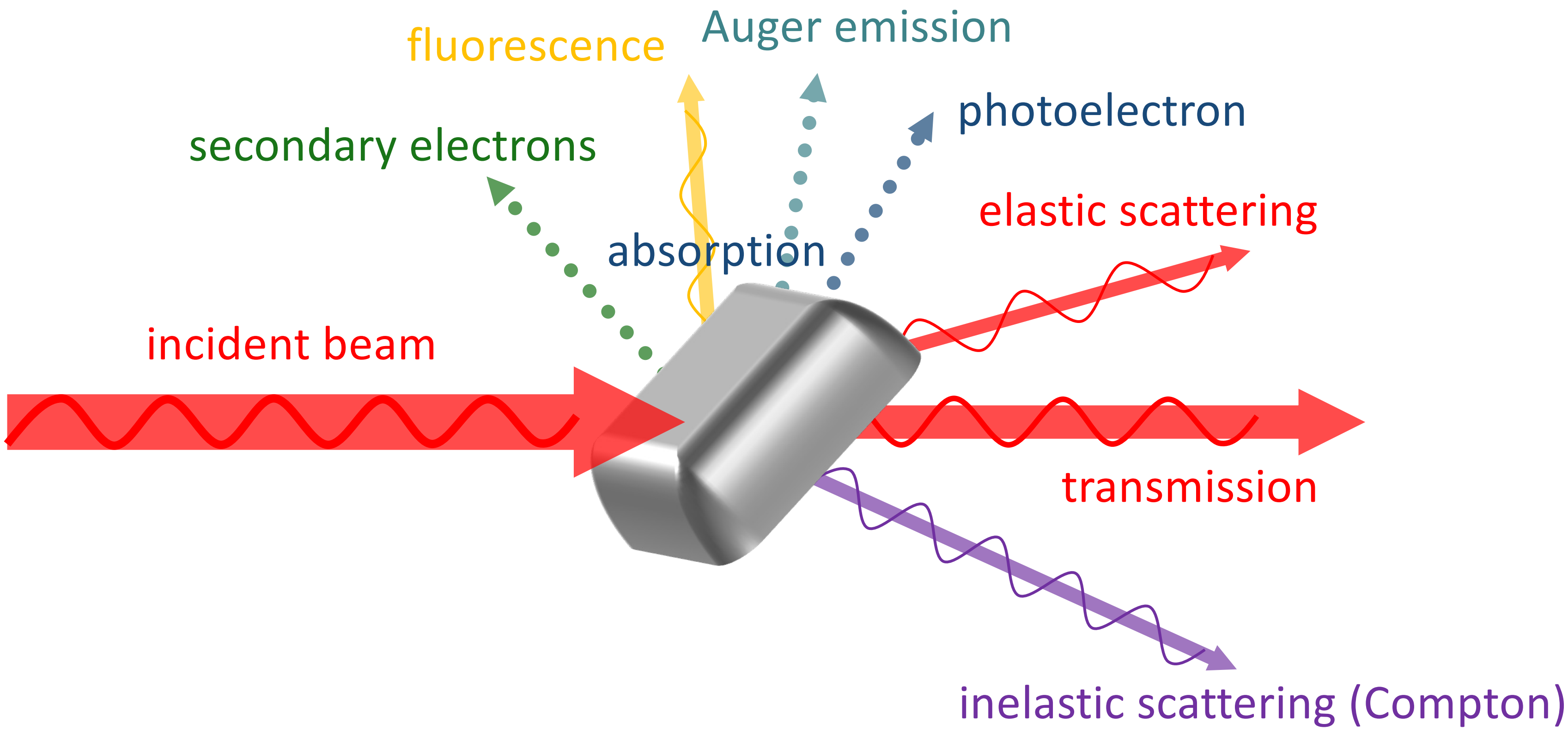
# Interaction of X-ray with matter



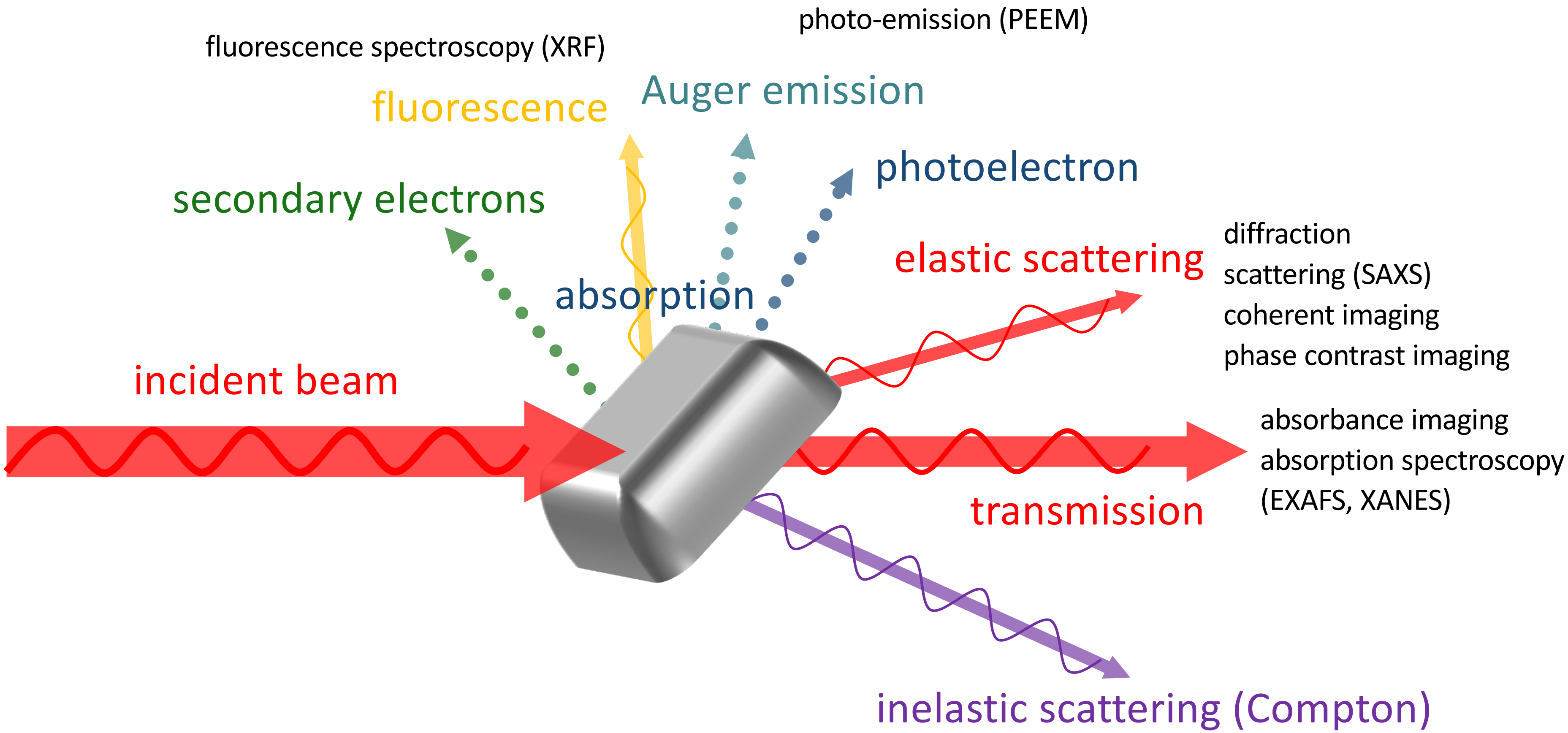

$$A = \log_{10}\frac{I_0}{I}$$

$$A = -\log_{10} T$$

# Interaction of X-ray with matter



# Interaction of X-ray with matter



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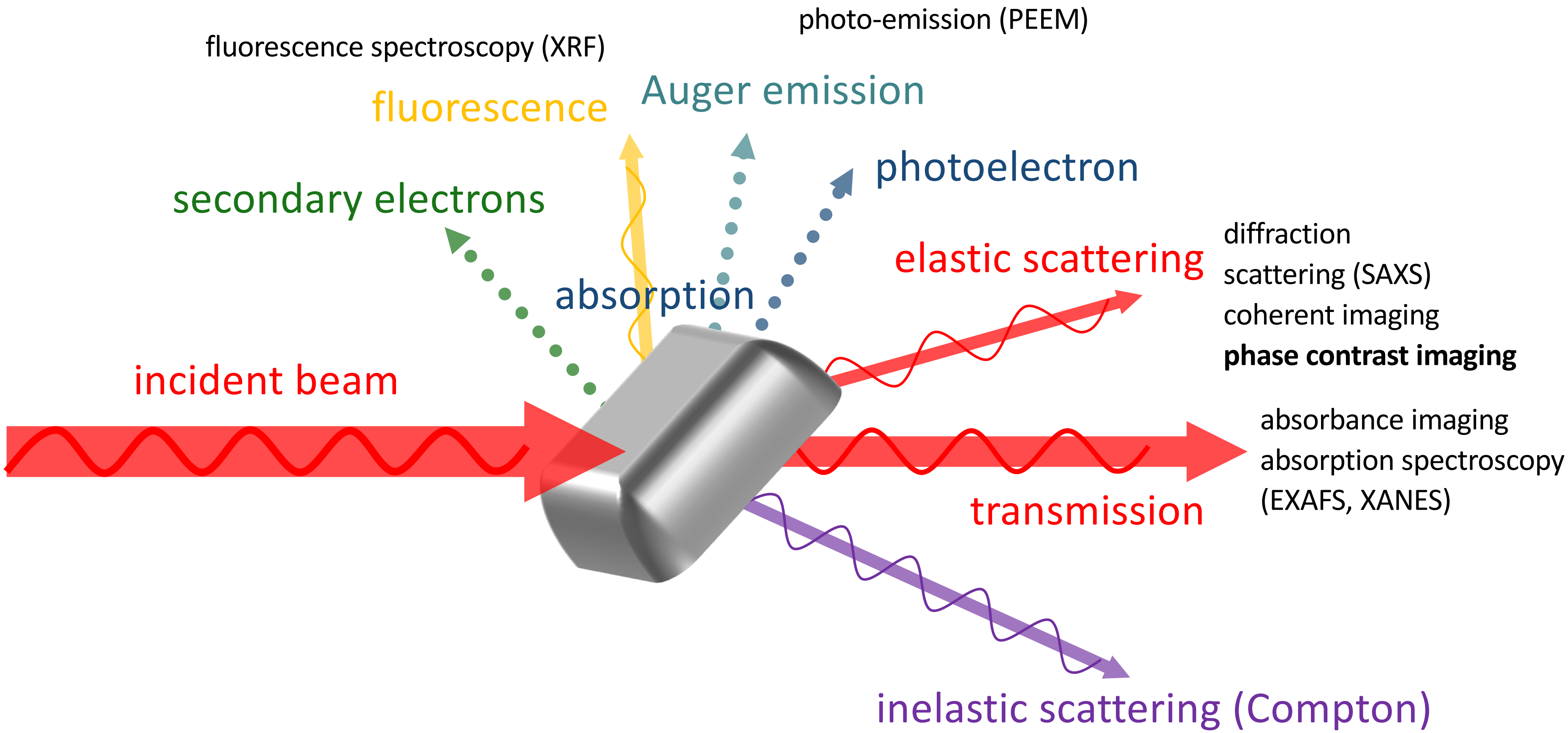
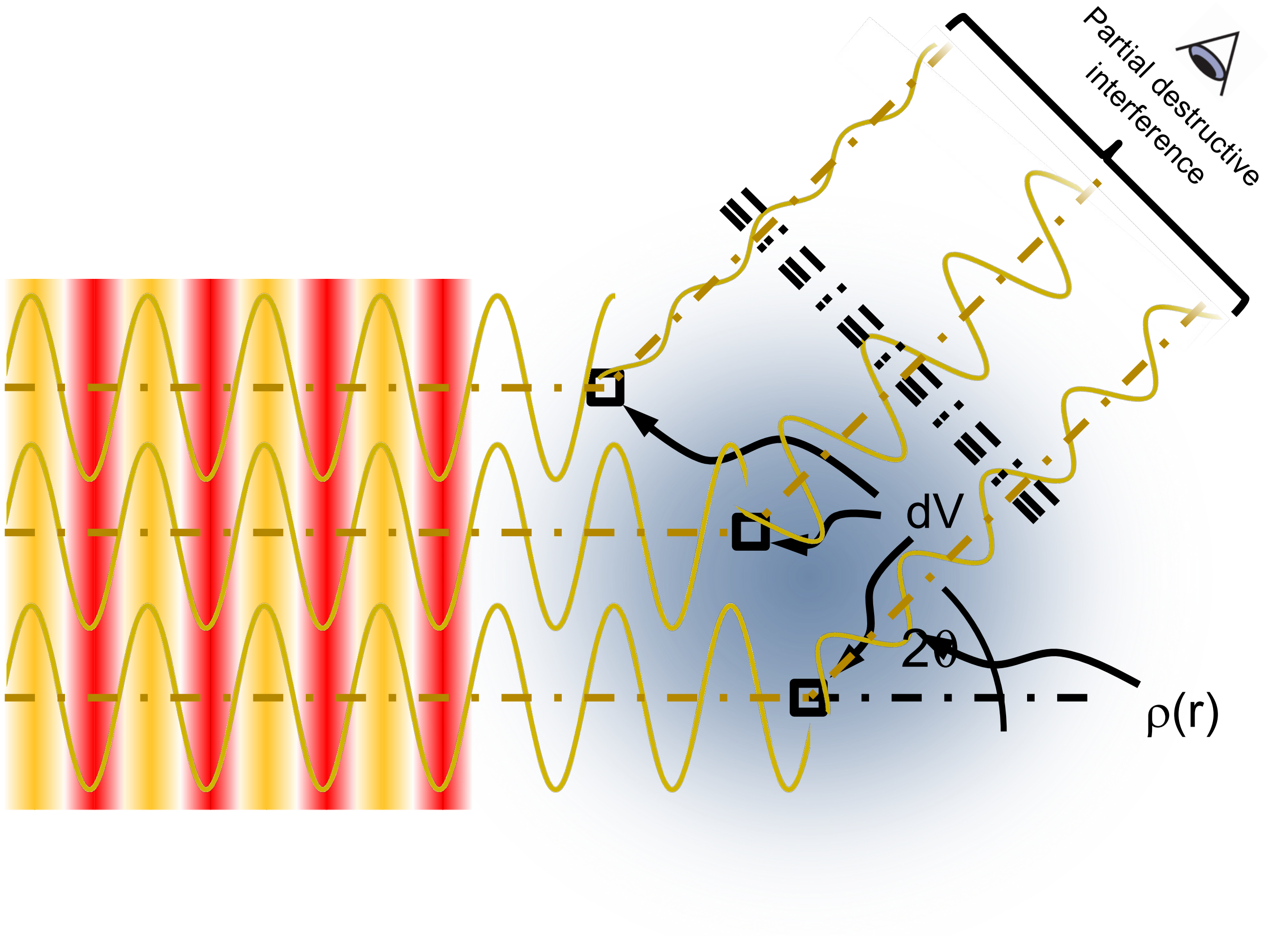
# Interaction of X-ray with matter



# Scattering from an atom



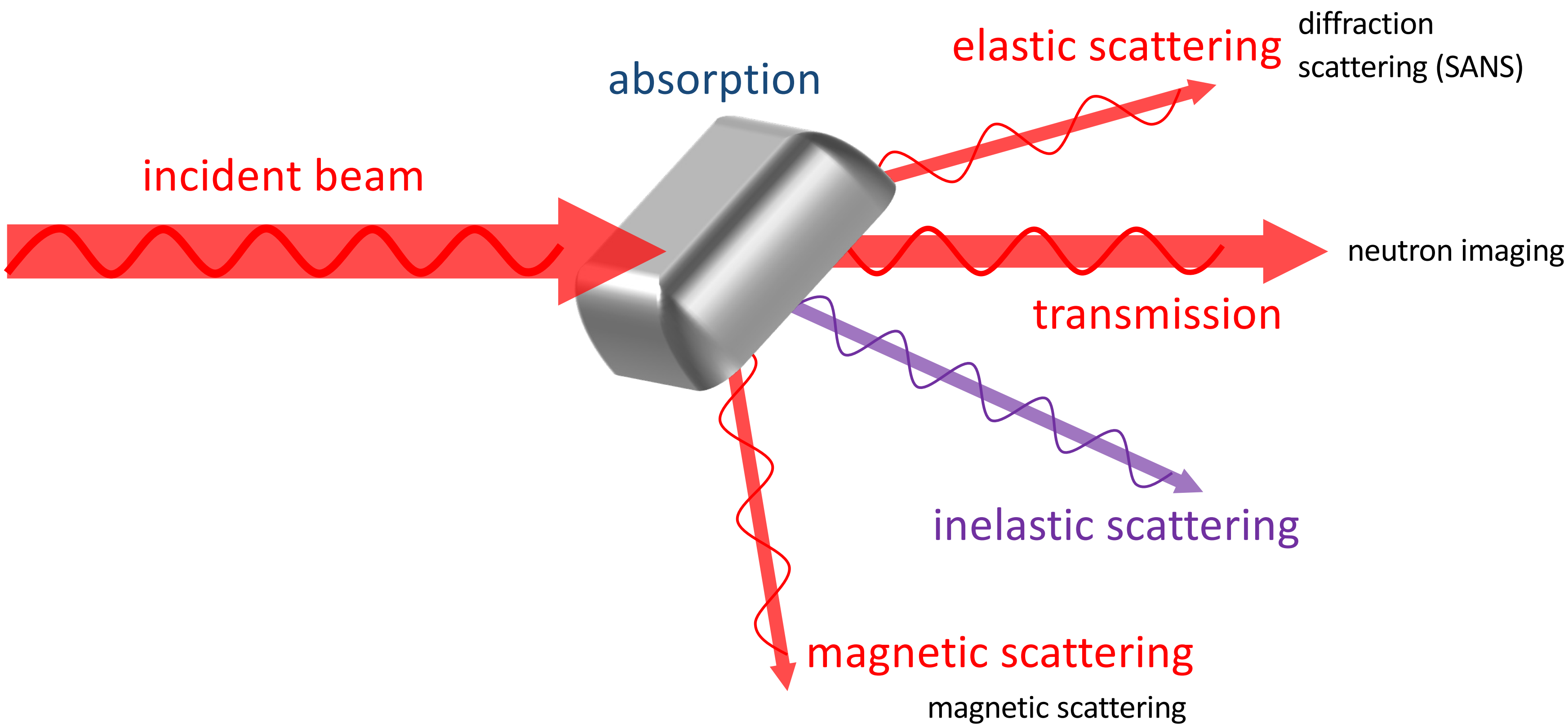

First approximation: assume electrons in cloud around atom are free i.e. unbound to nuclear core (far away from absorption edges)

**Second approximation: Fraunhofer approximation: observer (= detector) is far from sample relative to distance within the sample (scattering/diffraction)**

Third approximation: Kinematic approximation: sample is a weak scatterer, every photon only scatters once

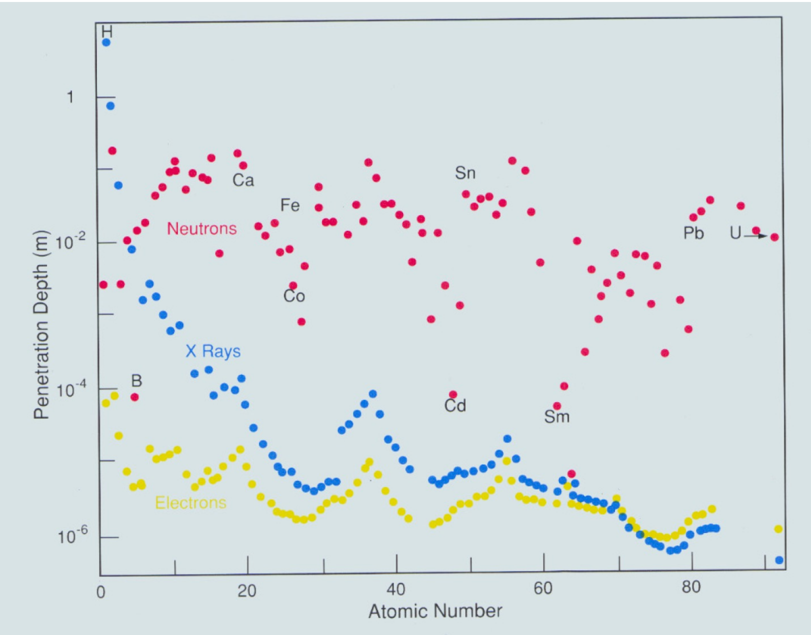
# Interaction of neutrons with matter

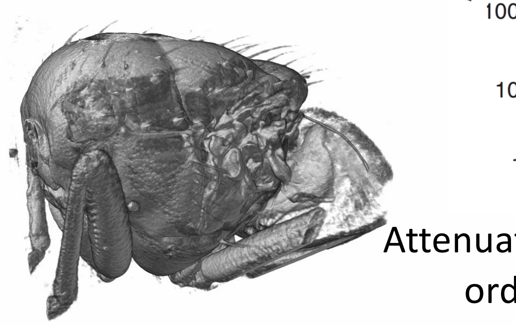
interaction with nuclei (& magnetic moment)

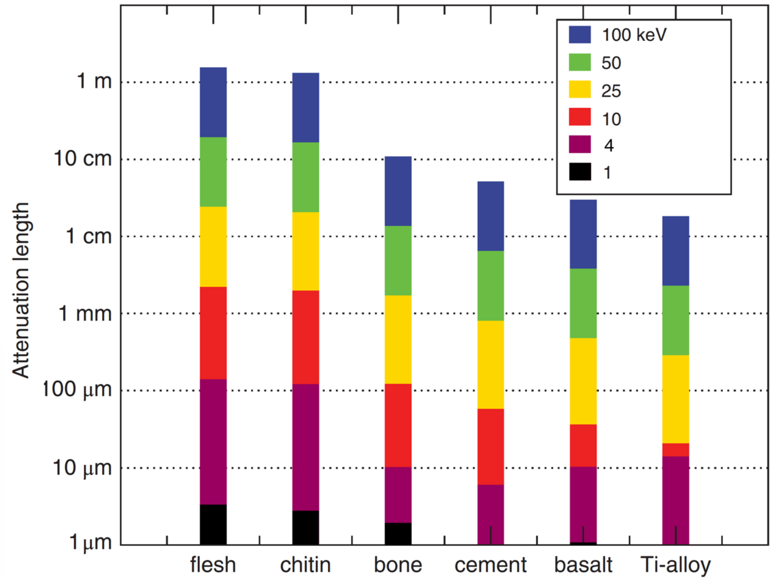


# Why X-rays and Neutrons: Transparency

→ investigate nondestructively internal 3D structure of heterogenous samples



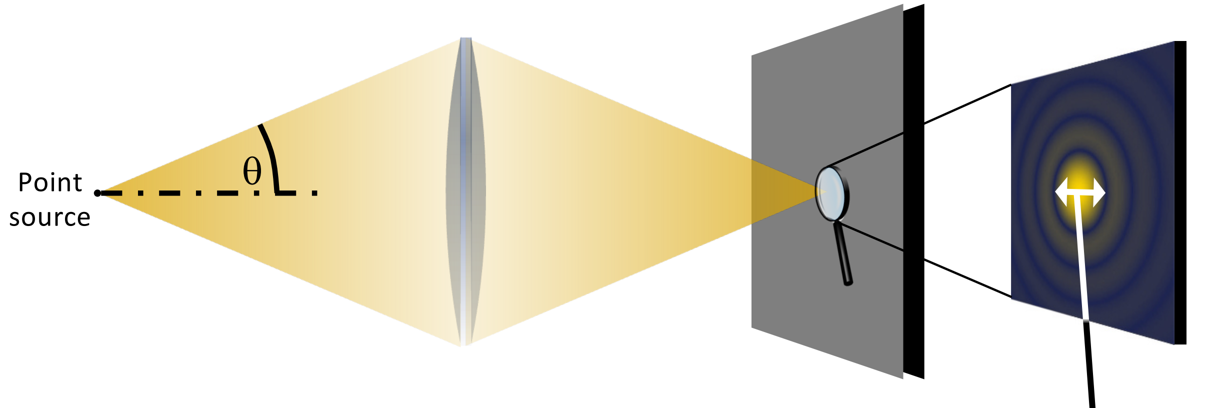



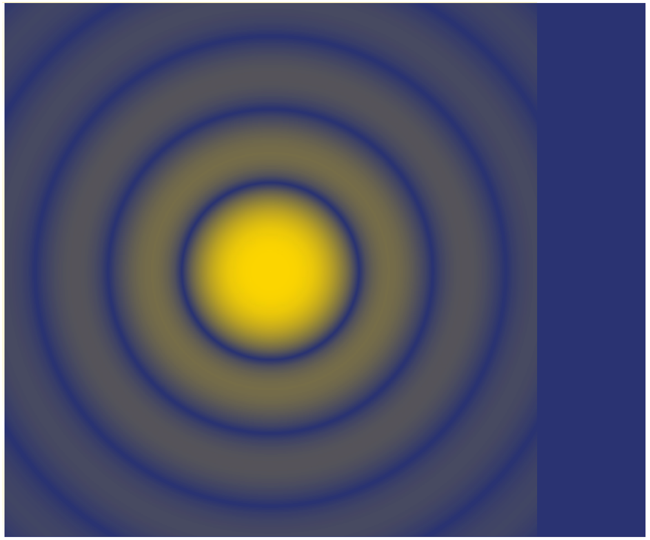



Attenuation lengths of different materials over two orders of magnitude x-ray photon energy

https://www.ncnr.nist.gov/summerschool/ss16/pdf/NeutronScatteringPrimer.pdf

# Why X-rays and neutrons: Abbe-limit



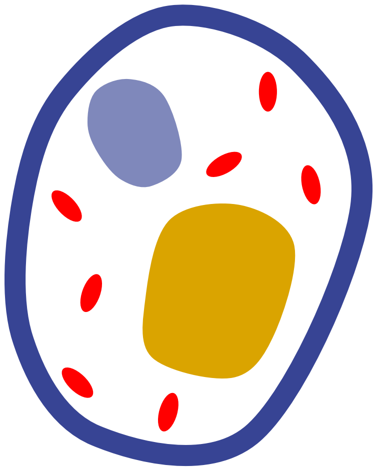
$$d = \frac{\lambda}{2n\sin\theta}$$

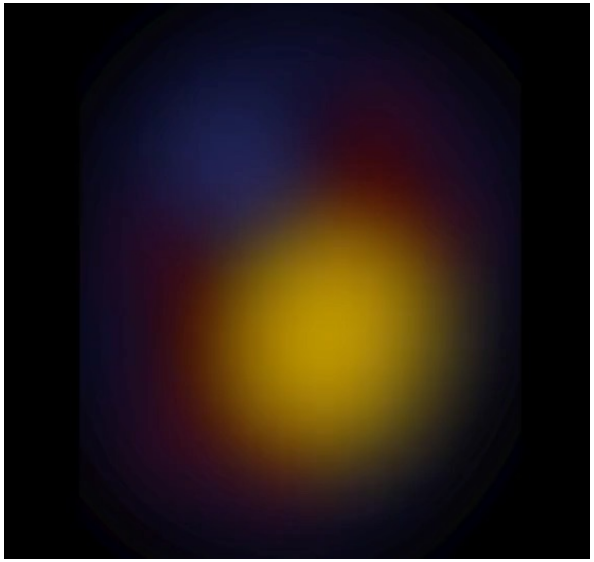
$$\text{visible}: \; d \sim \lambda/2$$

$$\text{x-rays}: \; d \sim 20\,\lambda \quad (\because \sin\theta \text{ is small})$$

# Why X-rays and neutrons

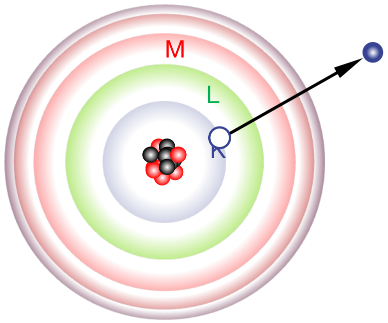
smaller wavelength → higher resolution

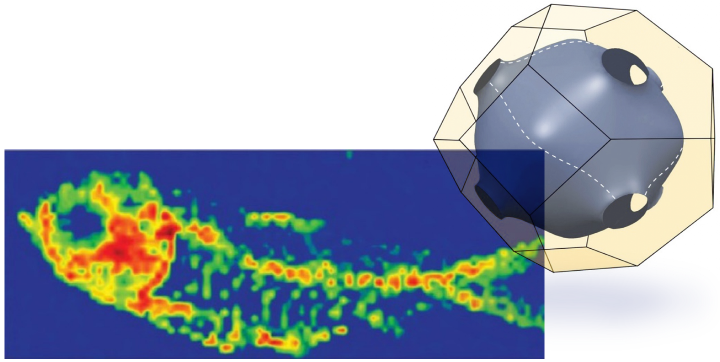




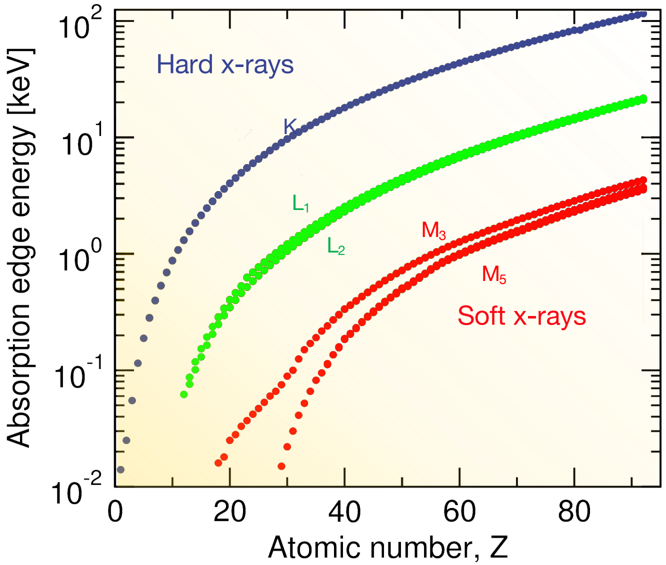
Decreasing wavelength

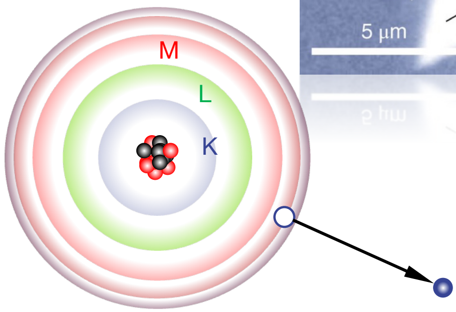
# Why x-rays: interactions with specific electrons

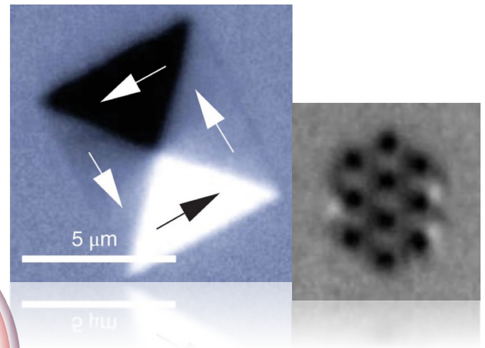


- chemical and elemental composition
- electronic properties
- magnetic domains



# Why Neutrons: Magnetic scattering and isotope specific interaction

- magnetic structures, magnetic moment distributions, and mangetic excitations
- contrast variation with different isotopes for example $H_2O$ vs. $D_2O$