Interaction: atomic approach (IR to vis/UV)

Incident beam
Intensity I_0 (photons/s)
Photon energy $\hbar\omega$
Wave vector $\vec{k}$

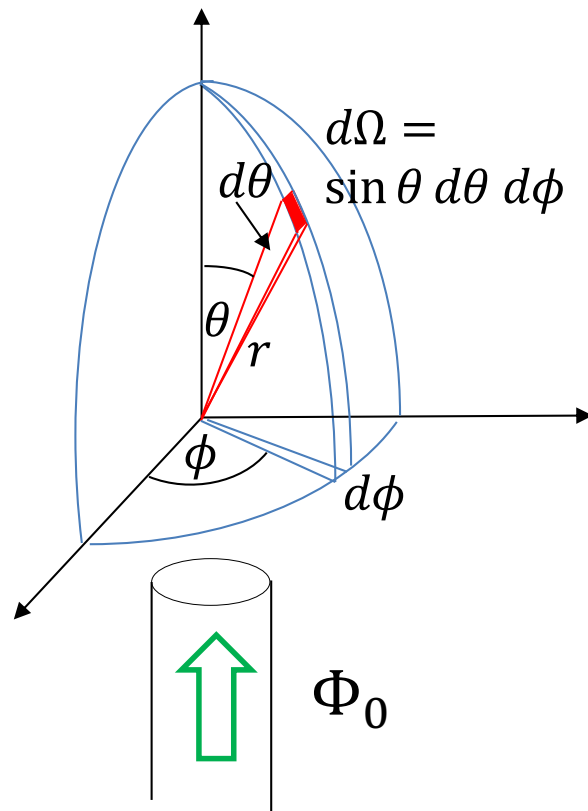## Absorption processes

- IR: vibrations/phonons
- VIS/UV: electronic transitions

Scattering

Transmitted beam
Intensity $I_T < I_0$
Energy $\hbar\omega$
Wave vector $\vec{k}$

Inelastic
$\hbar\omega' \neq \hbar\omega \quad \vec{k}' \neq \vec{k}$

Elastic
$\hbar\omega' = \hbar\omega \quad \vec{k}' \neq \vec{k}$
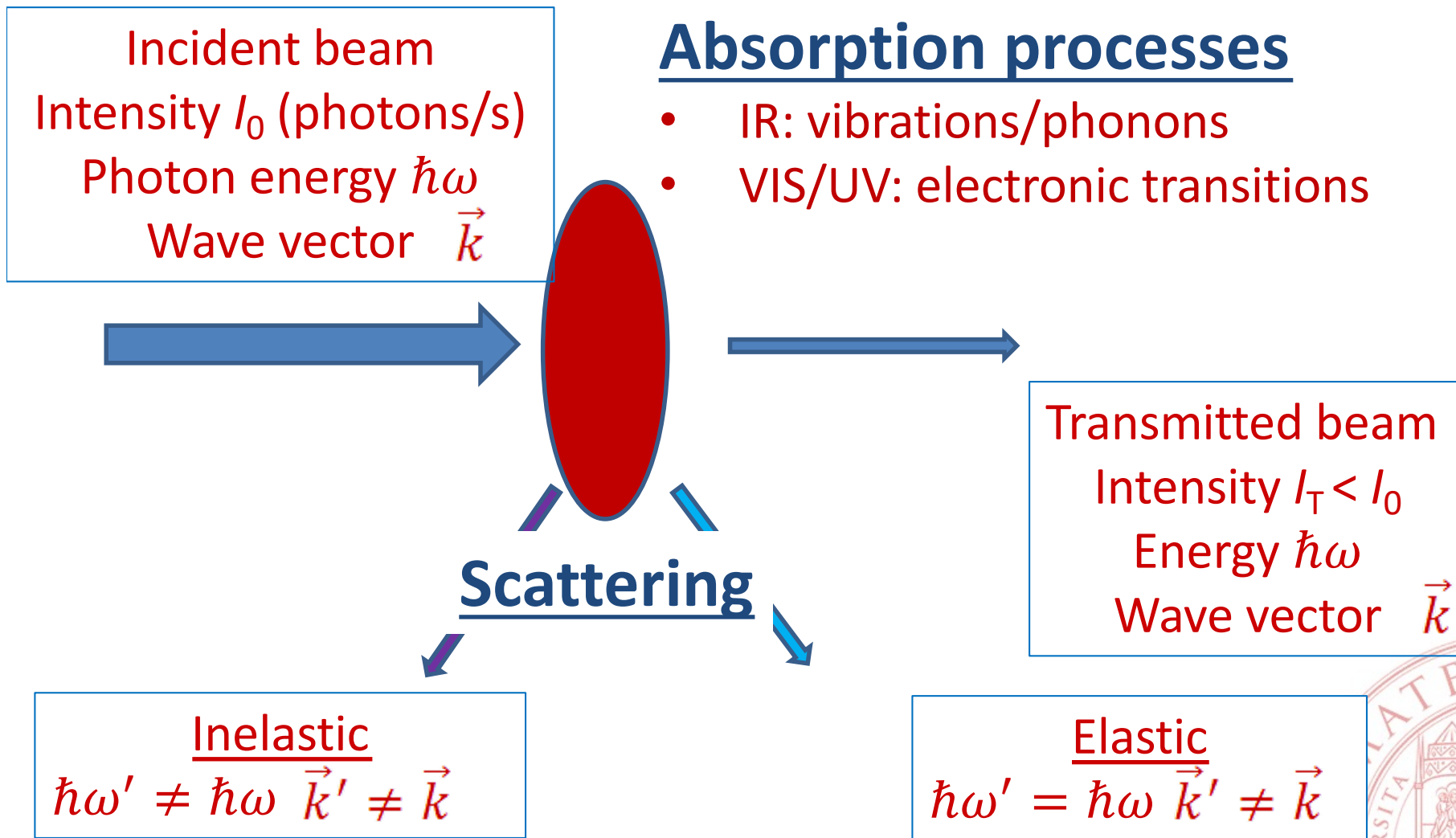
Interaction: atomic approach (UV to X-rays)

Incident beam
Intensity I_0 (photons/s)
Photon energy $\hbar\omega$
Wave vector $\vec{k}$

Photoelectric absorption

Electrons
$K = \hbar\omega - E_B$
Momentum $\vec{p}_e$

Transmitted beam
Intensity $I_T < I_0$
Energy $\hbar\omega$
Wave vector $\vec{k}$

Scattering

Inelastic
$\hbar\omega' \neq \hbar\omega$ $\vec{k}' \neq \vec{k}$

Elastic
$\hbar\omega' = \hbar\omega$ $\vec{k}' \neq \vec{k}$

Cross section

$$d\Omega = \sin\theta\, d\theta\, d\phi$$

Φ_0

Impinging beam of monochromatic photons, flux Φ_0
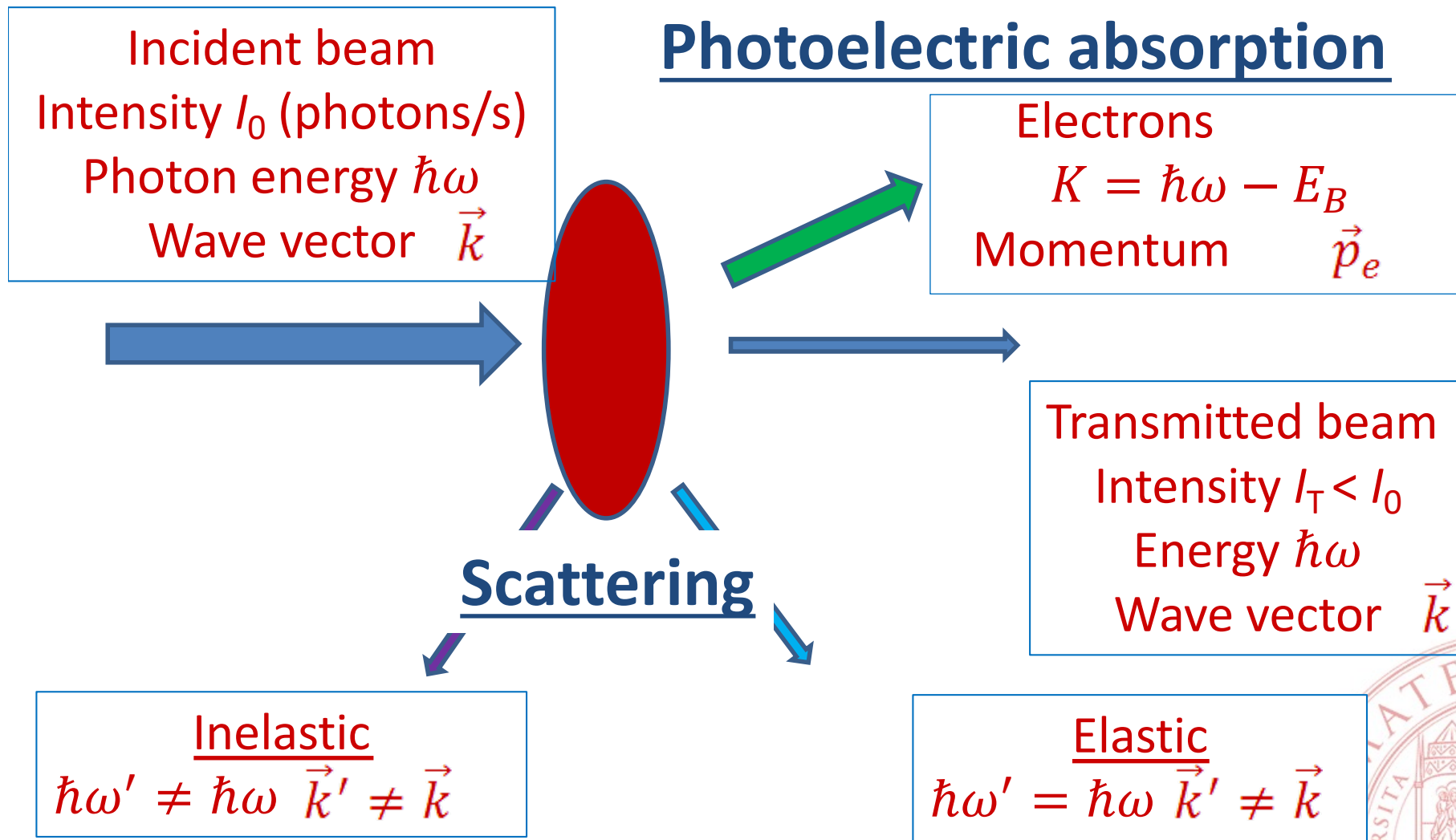
Φ_0 = photons/(s cm^2)

- A single atom in the origin
- Interaction produces dN particles per unit time in the solid angle $d\Omega$

$$dN = \Phi_0 d\sigma = \Phi_0 \left(\frac{d\sigma}{d\Omega}\right) d\Omega$$

$$\sigma = \int_{4\pi} \left(\frac{d\sigma}{d\Omega}\right) d\Omega$$

$[\sigma]$ = cm^2

1 barn = 10^{-24} cm^2

Ge, Z = 32, $\hbar\omega$ = 10 keV

σ_{photo} = 4 × 10^3 barn

σ_{el} = 2 × 10^2 barn

σ_{inel} = 1 × 10^1 barn

Cross section & linear attenuation coefficient
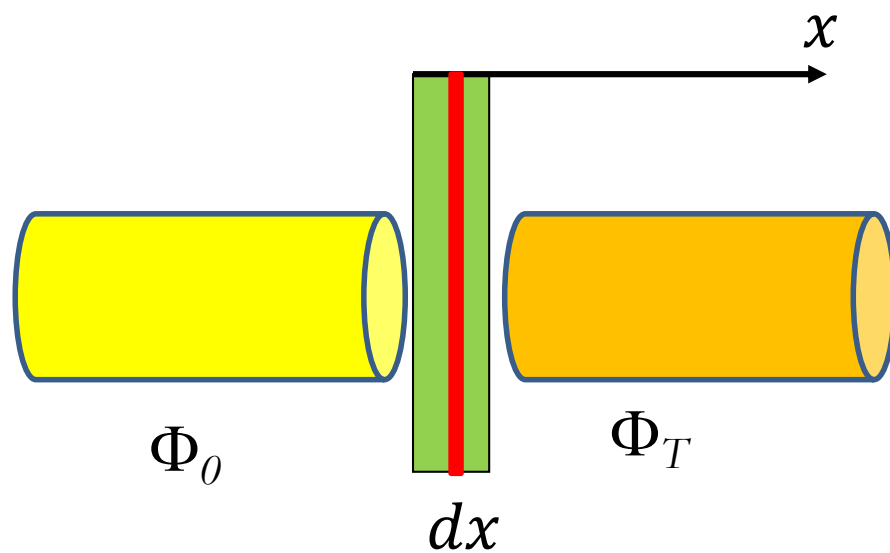

x

Φ_0 Φ_T

dx
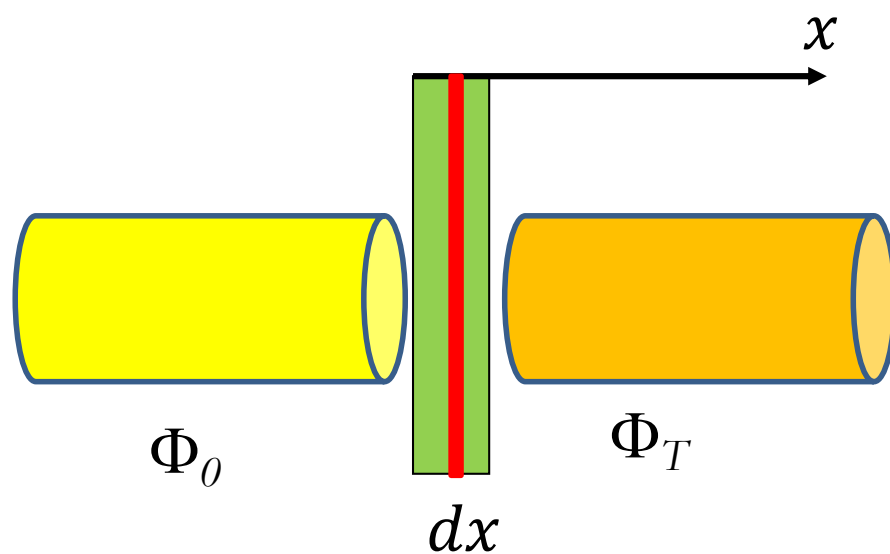
A homogeneous sample composed by identical atoms with density ρ (atoms/cm³)

- Single scattering approximation: the number of particles created by the interaction is $\propto$ number of atoms involved

- The number of particles created by a slab of thickness dx at position x in the full solid angle is

$$dN = \Phi \, \sigma \, dn$$
$$= \Phi \, \sigma \, \rho A \, dx$$
$$= I \, \sigma \rho \, dx$$

Cross section & linear attenuation coefficient

Φ_0

Φ_T

x

dx

A homogeneous sample composed by identical atoms with density ρ

- $dN = I\,\sigma\rho\,dx$
- Single particle approximation: an impinging photon can create only one particle. Therefore
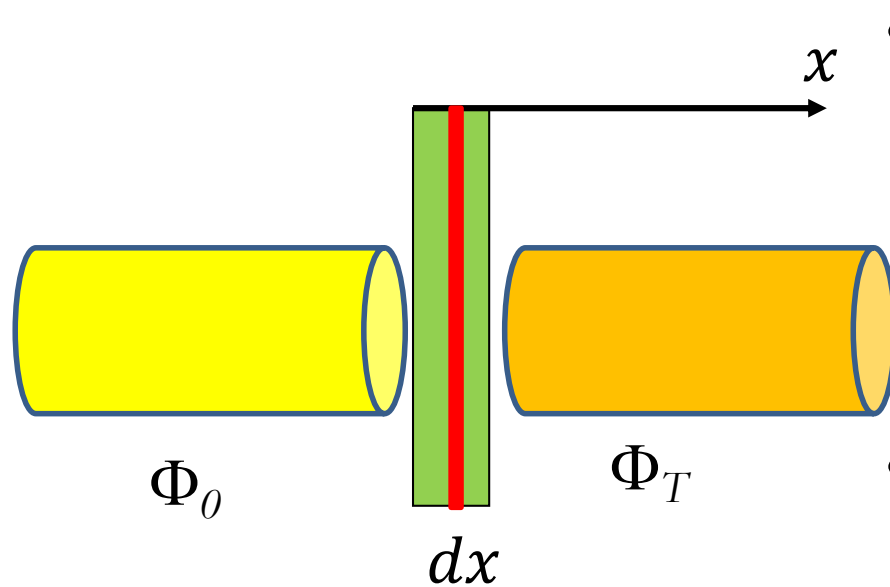
$$dN = -dI$$
$$dI = -I\,\sigma\rho\,dx$$

- This is the same relation which defines the linear attenuation coefficient, thus

$$\mu = \sigma\rho$$

Cross section & linear attenuation coefficient

- If the sample is composed of different atoms with densities ρ_i and cross sections σ_i then
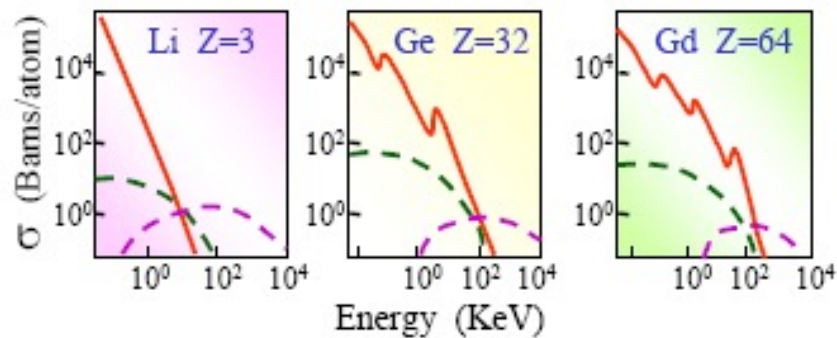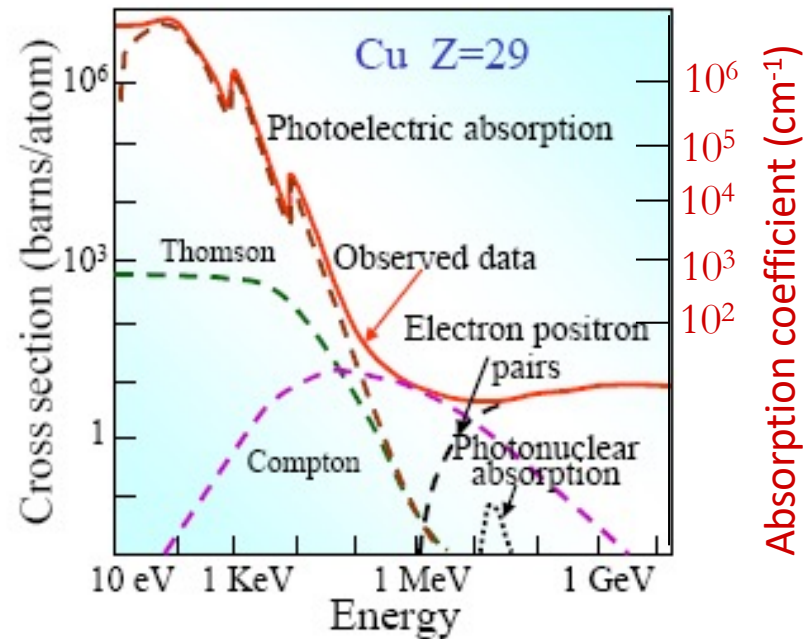
$$\mu = \sum_i \rho_i \sigma_i$$

- Cross sections are also expressed as mass attenuation coefficients, expressed as cm²/g, so that

$$\mu(cm^{-1}) = \rho(g/cm^3)\ \sigma(cm^2/g)$$

Cross section of various processes

NB order of magnitude
e.g. Cu @ 10 keV
$\mu^{-1} \sim 10^{-5}$ cm = 10 μm

Elastic scattering from 1 free electron (Thomson)

- Thomson scattering = coherent scattering
- The scattered electric field is (linear polarization case)

$$E(\vec{r}, t) = -E_0 r_0 \left(\frac{e^{i(kr - \omega t)}}{r} \right) \sin \theta$$

$$r_0 = \frac{e^2}{4\pi\varepsilon_0 m c^2} \cong 2.82 \times 10^{-15} \text{m}$$

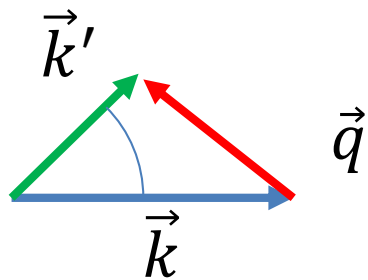"Thomson scattering length" or "classical electron radius"

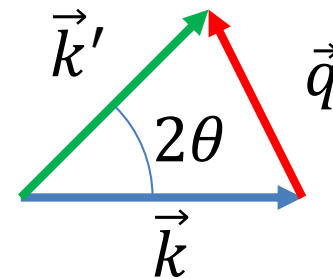Angle between the polarization vector and the scattered wave vector

The exchanged wave vector

- $\vec{q} = \vec{k}' - \vec{k}$

- For elastic scattering $|\vec{k}'| = |\vec{k}| = k$ and

$$q = \frac{4\pi}{\lambda} \sin \theta$$

General case

Elastic scattering

Elastic scattering from 1 free electron (Thomson)

- The differential cross section is

$$\frac{d\sigma}{d\Omega} = r_0^2 (\hat{\varepsilon} \cdot \hat{\varepsilon}')^2$$

Polarization vectors of the incident and scattered waves

Elastic scattering from 1 free electron (Thomson)

- The angle integrated (total) cross section is

$$\sigma = \frac{8\pi}{3} r_0^2$$

- NB: it is independent of energy

Elastic scattering from one atom

- For one atom

$$E(\vec{r}, t) = -E_0 r_0 \left(\frac{e^{i(kr - \omega t)}}{r} \right) f(Z, \theta) \sin \theta$$
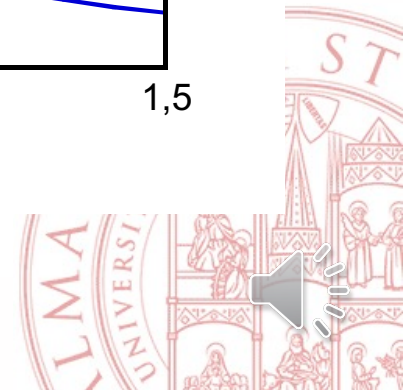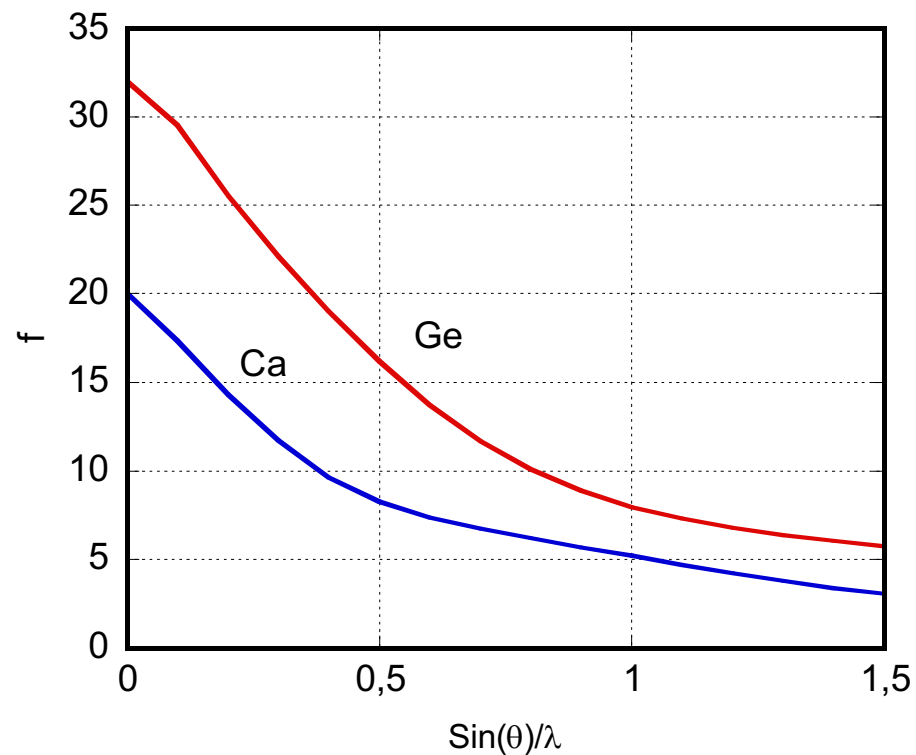
- $f(Z, \theta)$ is the «atomic form factor» or «scattering amplitude»; no physical dimensions

Elastic scattering from one atom

- The differential cross section $\dfrac{d\sigma}{d\Omega} = \dfrac{d\sigma_{electron}}{d\Omega}|f(Z,\theta)|^2$

- f depends quasi linearly on Z

- $f(\theta = 0) = Z$

Inelastic scattering

- The most common inelastic scattering mechanism for X-rays is the Compon effect (= "incoherent scattering")

$$\Delta\lambda = 2\pi\lambdabar_c(1 - \cos\theta),$$

$$\lambdabar_c = \frac{\hbar}{mc} \cong 3.86\times10^{-13}\text{m},$$

Reduced Compton wavelength

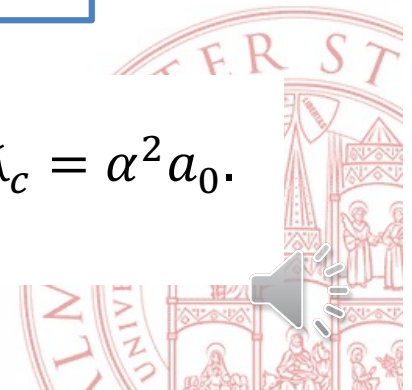$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{me^2} \cong 0.53\text{Å}$$

$$\alpha = \frac{e^2}{4\pi\varepsilon_0\hbar c} \cong \frac{1}{137}$$

Radius of the Bohr 1st orbit for H

Fine structure constant

$$\lambdabar_c = \left(\frac{e^2}{4\pi\varepsilon_0\hbar c}\right)\left(\frac{4\pi\varepsilon_0\hbar^2}{me^2}\right) = \alpha a_0$$

$$r_0 = \left(\frac{e^2}{4\pi\varepsilon_0\hbar c}\right)\left(\frac{\hbar}{mc}\right) = \alpha\lambdabar_c = \alpha^2 a_0.$$
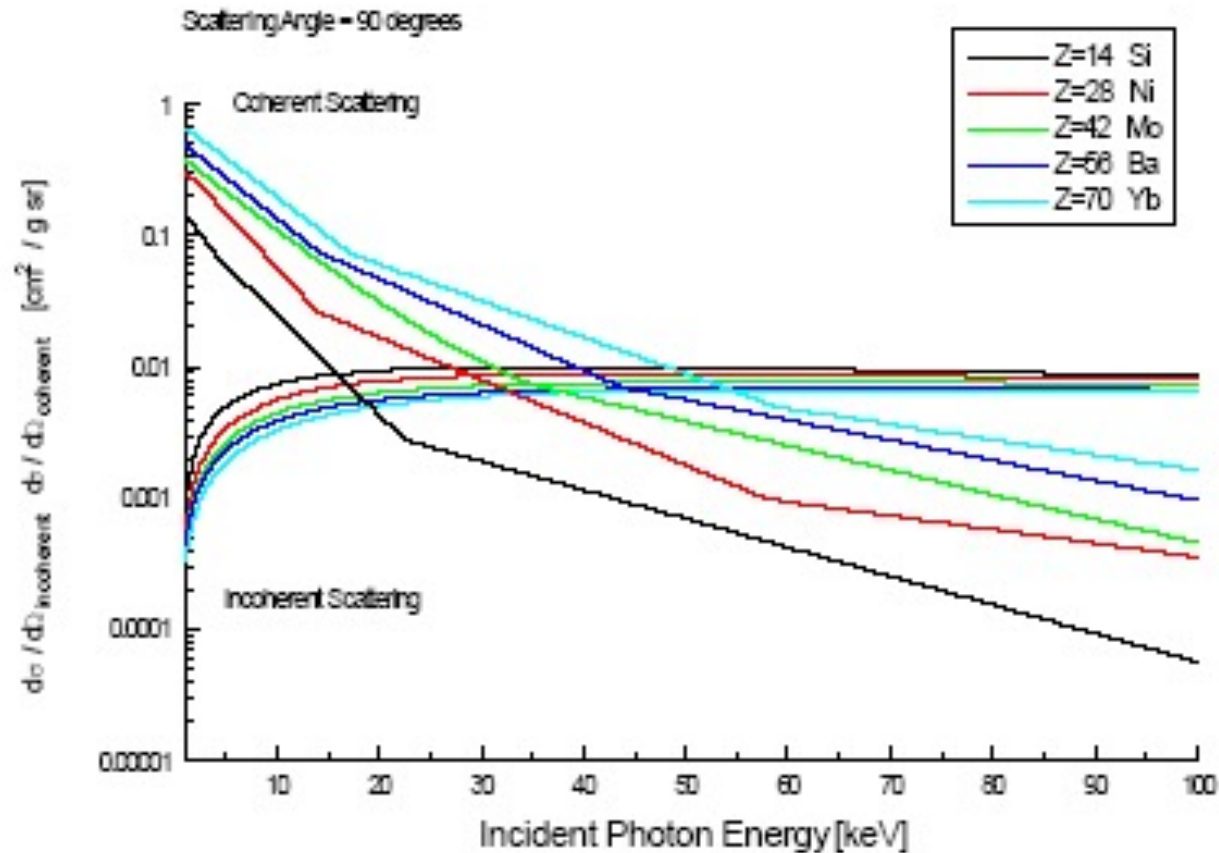
Compton cross section

- The Klein Nishina formula

$$\frac{d\sigma}{d\Omega} = r_0^2 \left(\frac{\omega'}{\omega}\right) \left| \hat{\varepsilon} \cdot \hat{\varepsilon}' + \frac{(\omega' - \omega)}{4\omega'\omega} \right|^2$$

Thomson and Compton scattering

Elastic and inelastic scattering differential cross section for different elements as a function of the incident photon energy for a fixed scattering angle equal to 90 degrees. (Calculated using the data from reference

Photoelectric absorption

- A photon is absorbed and gives its energy to an electron.

- The electron makes a transition to
  - A bound state (excitation) <u>or</u>
 - An unbound state (ionization): a photoelectron is created

E

0

2p

2s

$\hbar\omega$

1s
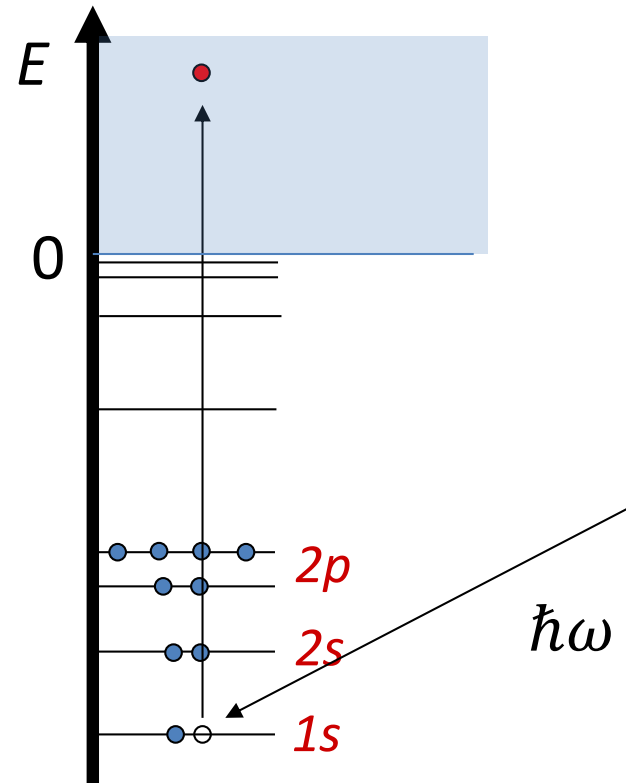
Energetics of photoelectric absorption in an atom (ionization)

Photoelectric absorption in solids

- In solids valence electrons form <u>bands</u>
  - Insulators and semiconductors: valence and conduction bands
  - metals: conduction band
- The «vacuum level» is the least energy an electron can have to leave the solid (with K.E. = 0)
  - Often taken as reference level
- At sufficiently high energies the photoelectron can be considered «free»: it has only kinetic energy
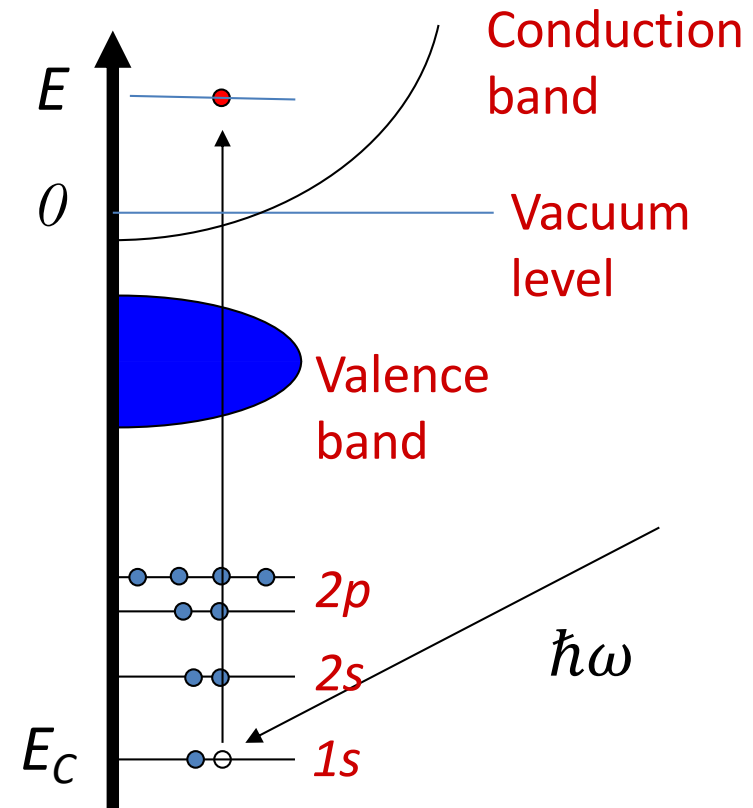
Conservation of energy

- In the one electron approximation for a transition from a core level:

Initial state energy
$$= \hbar\omega + E_C \ (E_C < 0)$$
Final state energy $= K$
$$K = \hbar\omega + E_C$$

$$E_C = -E_B \ \text{(binding genergy)}$$
$$K = \hbar\omega - E_B$$

E

0

Conduction band

Vacuum level

Valence band

2p

2s

$\hbar\omega$

E_C

1s
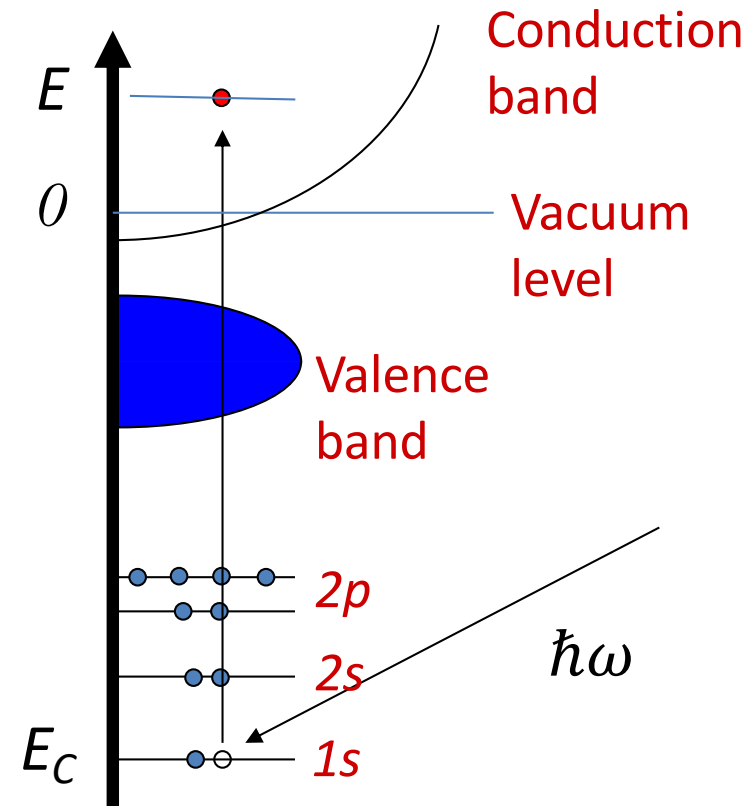
Absorption coefficient: energy dependence
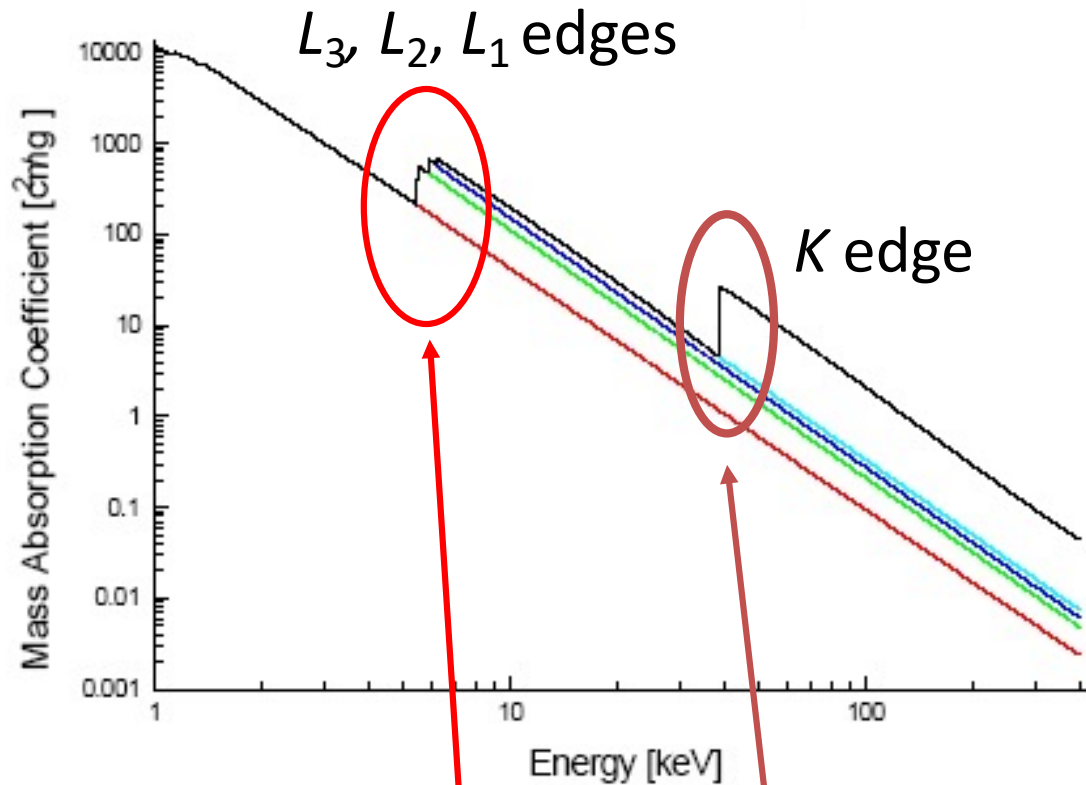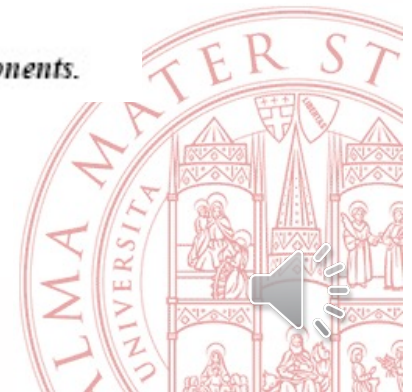

Mass absorption coefficient of Lanthanum (Z=57) versus energy of incident photons split in its components.

Z dependence of absorption edges
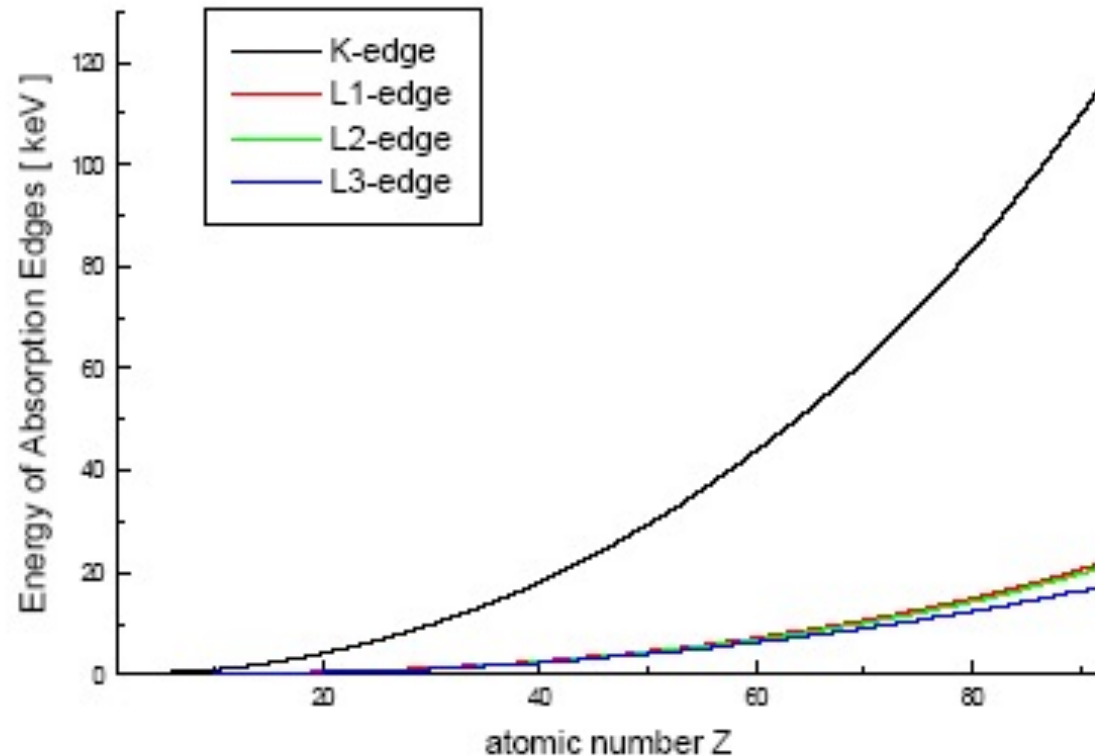
Energy of photoelectric absorption edges versus atomic number of the elements.

- The atomic number determines the energy of the absorption edge
- The observation of an edge at a given energy indicates the presence of the corresponding element
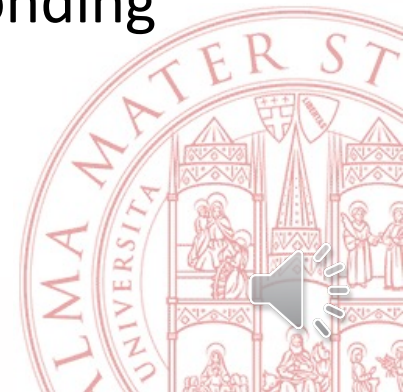
Photoelectric absorption: de-excitation
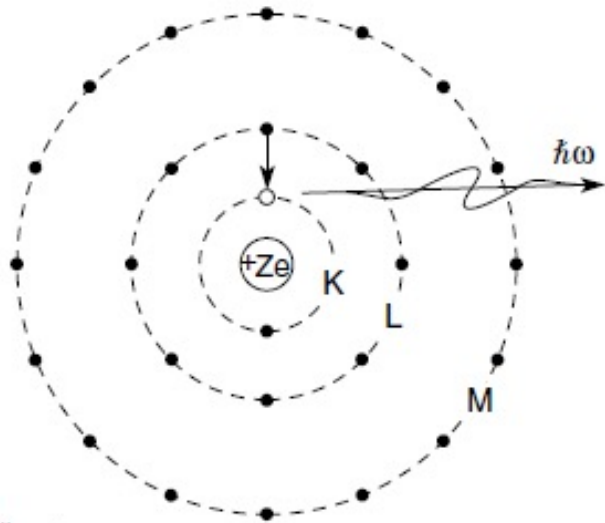
Emission of "characteristic" or
"fluorescence" X-rays,
also known as "emission lines"
$$\hbar\omega_f = E_L - E_K$$

Emission of
"Auger" electrons"
$$K_A = 2E_L - E_K$$

Probability for the two processes

Nomenclature for X-ray emission lines
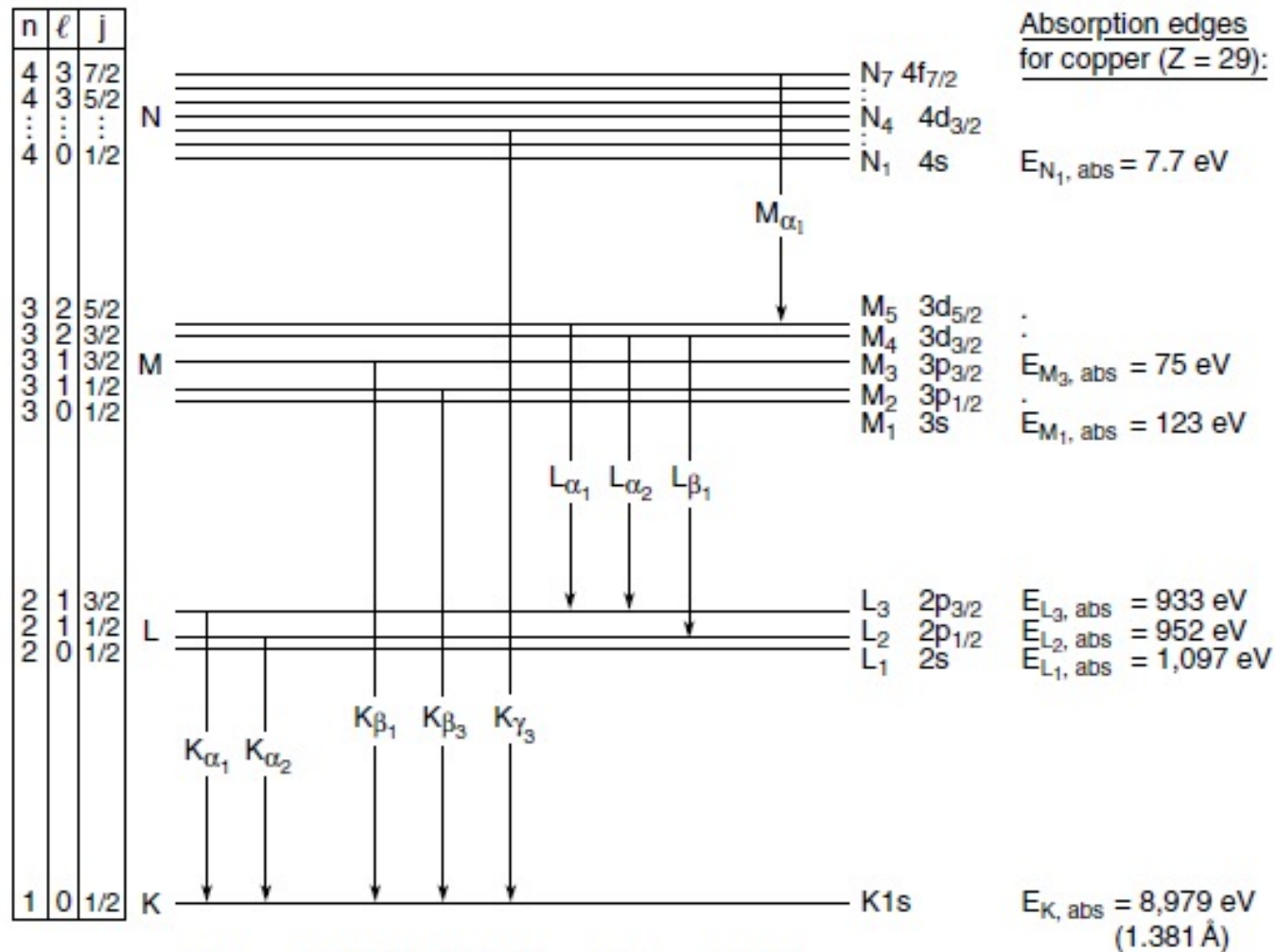
n	ℓ	j			
4	3	7/2		N_7	$4f_{7/2}$
4	3	5/2	N	N_4	$4d_{3/2}$
⁝	⁝	⁝			
4	0	1/2		N_1	$4s$

Absorption edges for copper (Z = 29):

$E_{N_1, abs} = 7.7$ eV

M_{α_1}

3	2	5/2		M_5	$3d_{5/2}$
3	2	3/2		M_4	$3d_{3/2}$
3	1	3/2	M	M_3	$3p_{3/2}$
3	1	1/2		M_2	$3p_{1/2}$
3	0	1/2		M_1	$3s$

$E_{M_3, abs} = 75$ eV

$E_{M_1, abs} = 123$ eV
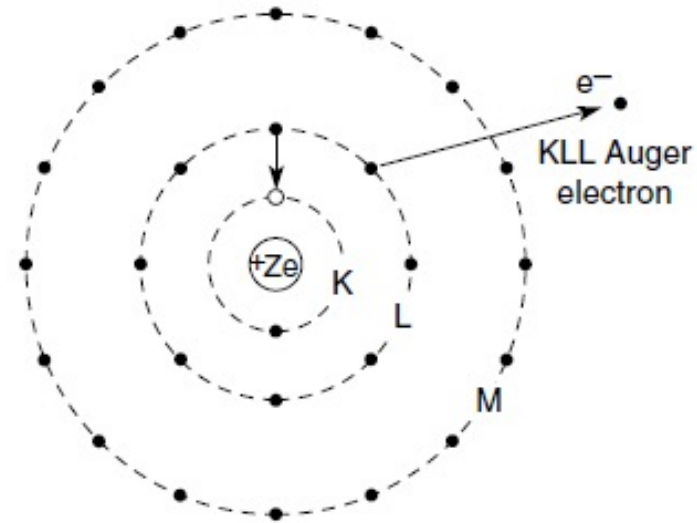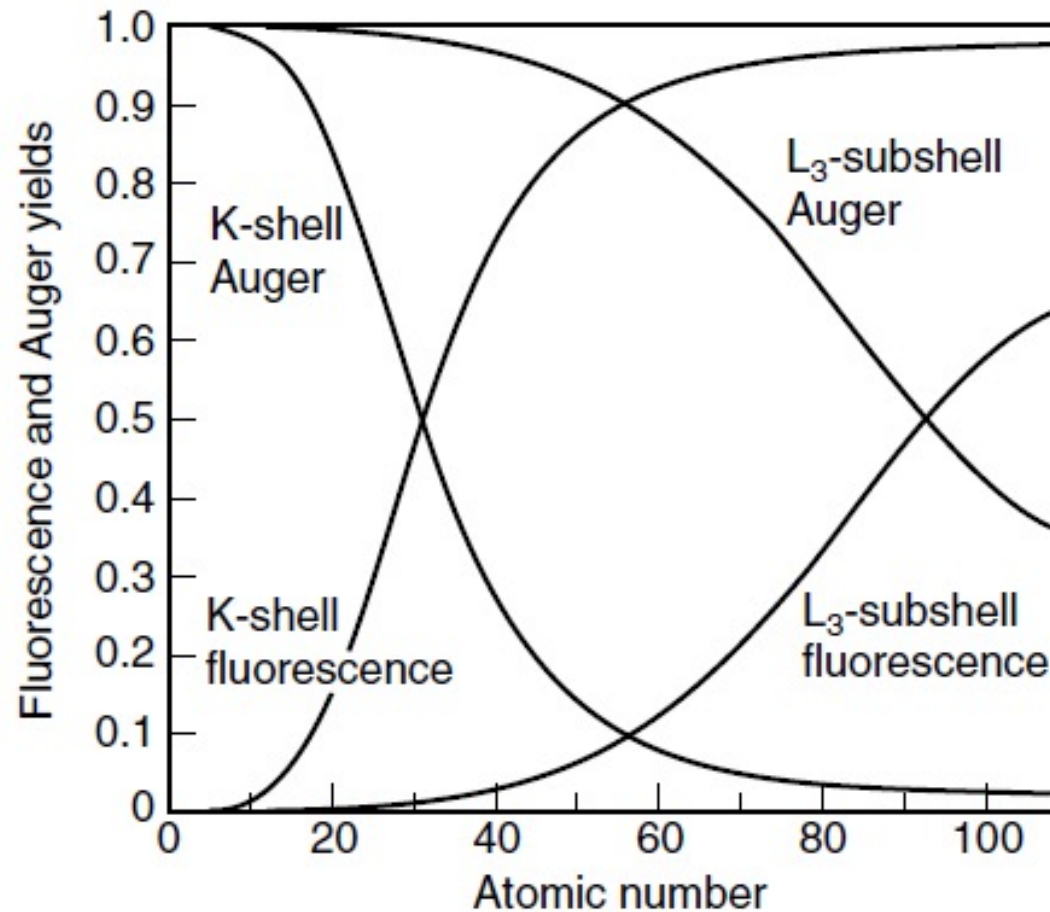
L_{α_1} L_{α_2} L_{β_1}

2	1	3/2		L_3	$2p_{3/2}$
2	1	1/2	L	L_2	$2p_{1/2}$
2	0	1/2		L_1	$2s$

$E_{L_3, abs} = 933$ eV
$E_{L_2, abs} = 952$ eV
$E_{L_1, abs} = 1,097$ eV

K_{β_1} K_{β_3} K_{γ_3}

K_{α_1} K_{α_2}

1	0	1/2	K	K1s

$E_{K, abs} = 8,979$ eV
(1.381 Å)

Cu K_{α_1} = 8,048 eV (1.541Å)   Cu L_{α_1} = 930 eV
Cu K_{α_2} = 8,028 eV (1.544Å)   Cu L_{α_2} = 930 eV
Cu K_{β_1} = 8,905 eV   Cu L_{β_1} = 950 eV

Energy of emission lines

TABLE B.2. Photon energies, in electron volts, of principal K and L shell emission [...]

Element	Kα_1	Kα_2	Kβ_1	Lα_1	Lα_2	Lβ_1
3 Li	54.3					
4 Be	108.5					
5 B	183.3					
6 C	277					
7 N	392.4					
8 O	524.9					
9 F	676.8					
10 Ne	848.6	848.6				
11 Na	1,040.98	1,040.98	1,071.1			
12 Mg	1,253.60	1,253.60	1,302.2			
13 Al	1,486.70	1,486.27	1,557.45			
14 Si	1,739.98	1,739.38	1,835.94			
15 P	2,013.7	2,012.7	2,139.1			
16 S	2,307.84	2,306.64	2,464.04			
17 Cl	2,622.39	2,620.78	2,815.6			
18 Ar	2,957.70	2,955.63	3,190.5			
19 K	3,313.8	3,311.1	3,589.6			
20 Ca	3,691.68	3,688.09	4,012.7	341.3	341.3	344.9
21 Sc	4,090.6	4,086.1	4,460.5	395.4	395.4	399.6
22 Ti	4,510.84	4,504.86	4,931.81	452.2	452.2	458.4
23 V	4,952.20	4,944.64	5,427.29	511.3	511.3	519.2
24 Cr	5,414.72	5,405.509	5,946.71	572.8	572.8	582.8
25 Mn	5,898.75	5,887.65	6,490.45	637.4	637.4	648.8
26 Fe	6,403.84	6,390.84	7,057.98	705.0	705.0	718.5
27 Co	6,930.32	6,915.30	7,649.43	776.2	776.2	791.4
28 Ni	7,478.15	7,460.89	8,264.66	851.5	851.5	868.8
29 Cu	8,047.78	8,027.83	8,905.29	929.7	929.7	949.8
30 Zn	8,638.86	8,615.78	9,572.0	1,011.7	1,011.7	1,034.7

- Energy depends on Z
- Measurement of the energy and intensity of x-ray emission lines is at the basis of many "analytical" techniques which measure the presence and concentration of elements in a sample
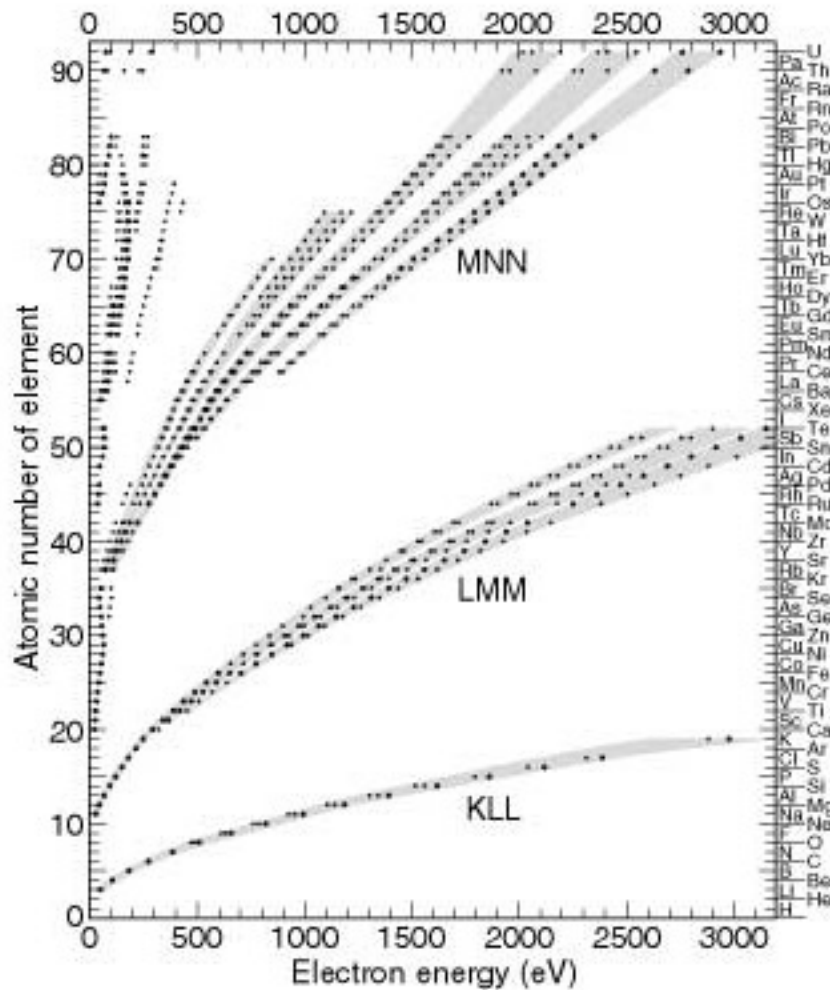
Auger electrons

- Nomenclature
  - (Hole)(1st e^{-})(2nd e^{-})
- The energy depends on Z
- Measurement of the energy and intensity of Auger electrons = "Auger Electron Spectroscopy", an analytic technique which measures the presence and concentration of elements on the surface of a sample

Relationship between two approaches

- Two approaches to describe the interaction between x-rays and matter
  - «Macroscopic»: by means of the dielectric function which describes the overall response
  - «Microscopic»: by means of interactions between photons and atoms
- What is the relation between these approaches?
- It is possible to derive a simple relation between the index of refraction and the atomic form factor

Relation between n and f

- For a sample composed of identical atoms with form factor f and density ρ

$$n(\omega) - 1 = -\frac{2\pi r_0 \rho f(\omega, q = 0)}{k^2}$$

- $n(\omega)$ has a real and immaginary part: also $f(\omega)$!

  – Real part: dispersion

  – Immaginary part: attenuation

«Anomalous" corrections to the form factor

- It is common to separate the dependence on $\vec{q}$ and ω: $f(\vec{q}, \omega) = f^0(\vec{q}) + f'(\omega) - if''(\omega)$
  - $f^0(\vec{q})$: atomic scattering far from resonance frequencies / absorption edges
  - $f'(\omega)$: correction to dispersive part, important near resonance frequencies
  - $f''(\omega)$: correction to attenuation part, important near resonance frequencies

The total cross section

- The total cross section determines the attenuation, $\sigma_T(\omega) = \dfrac{\mu(\omega)}{\rho} = \dfrac{2\omega n_2(\omega)}{c\rho}$

- Since $n_2(\omega) = \dfrac{2\pi r_0 \rho f''(\omega, q=0)}{k^2}$

$$\sigma_T(\omega) = \frac{4\pi r_0}{k} f''(\omega, q = 0)$$

one form of the «optical theorem», which links the total cross section to the imaginary part of the forward scattering amplitude