

Elettra Sincrotrone Trieste



Radiation-matter interaction



The lectures and Q&A sessions will take place in the training room.

23/10/2023	Monday	24/10/2023	Tuesday	25/10/2023	Wednesday	26/10/2023	Thursday	27/10/2023	Friday
8:30 - 8:45	Welcome L. Gregoratti - Elettra								
8:45 - 9:30	Introduction A. Migliori - IAEA	9:00 - 9:30	Q&A	9:00 - 10:00	XAS theory G. Agostini - Elettra	9:00 - 9:30	Q&A		
9:30 - 10:30	Students presentations	9:30 - 12:30	Hands on XRD and proposal writing (G1 XRD; G2 proposal) 11:00 - 11: 11:30 - 12:	10:00 - 11:00	XRF theory A. Migliori - IAEA	9:30 - 12:30	Hands on XAS and XRF beamlines (G1 XAS; G2 XRF)	9:00 - 13:00	Proposals presentations and discussion
10:30 - 11:00	Coffee break								
11:00 - 12:00	Radiation-matter interaction I.Carlomagno - Elettra			11:00 - 11:30	Coffee break				
				11:30 - 12:30	0 VRD applications				
		12.20 14.00			J. Flaisler - Elettia	12:30 - 13:00	Photo shooting	13:00 - 14:00	Lunch
12:00 - 13:30	Lunch	12:30 - 14:00	Lunch	12:30 - 13:30	Lunch	13:00 - 14:00	Lunch	14:00 - 14:15	Farewell
13:30 - 14:30	Synchrotron radiation G. Aquilanti - Elettra	14:00 - 17:00	Hands on XRD and proposal writing (G1 proposal; G2 XRD)	13:30 - 14:15		14:00 - 17:00	Hands on XAS and XRF beamlines (G1 XRF; G2 XAS)		
14:30 - 15:15	Beamlines: introduction G. Das - Elettra				XAS applications: material science G. Aquilanti - Elettra SR applications in bio- anthropology and heritage sciences				
15:15 - 15:30	Coffee break			14:15 - 15:00					
15:30 - 16:30	XRD Theory				Simone Lemmers - Elettra				
15.50 - 10.50	L. Gigli - Elettra			15:00 - 15:30	Coffee break				
16:30 - 17:15	How to write a good proposal I. Carlomagno - Elettra	17:00 - 17:30	Break and feedback of the day	15:30 - 16:15	XRF applications G. Das - Elettra	17:00 - 17:30	Break and feedback of the day		
17:15 - 17:45	Break and feedback of the day			16:15 - 17:00	Combined XRF and XAS applications S. Pollastri - UniMoRe				
				17:00 - 17:30	Break and feedback of the day				



Our subjects: light and matter



Take home message:

Interaction depends on λ !



Energy-frequency-wavelength



Energy of a photon $E = h\nu = hc/\lambda$ Planck's constant $h = 6.626 \times 10^{-34}$ J sFrequency of the radiation ν [Hz]Speed of light $c = 2.9979 \times 10^8$ m/sWavelength of light in vacuum λ [m]

In practical units for x-rays
$$\lambda[\text{Å}] = \frac{12.3984}{E[\text{keV}]}$$





Elettra Sincrotrone

Trieste



Interactions and their effects



Interactions:

- Scattering
- Absorption

Observed phenomena:

- 1. Transmission
- 2. Elastic scattering
- 3. Inelastic scattering
- 4. Fluorescence
- 5. Auger electrons
- 6. Photoelectrons



Matter-radiation interaction: scattering

Radiation-matter interaction – Ilaria Carlomagno

8



Scattering





Introduction – Visible light

Refraction

- The higher the refractive index, the slower the light travels
- Light path bends when crosses the boundary between two media
- Depends on wavelength!

Reflection

- Below the critical angle, light is completely reflected off a surface
- Conductive materials reflect light efficiently at any angle
- The reflectivity of Al is ~1 in the VIS and UV range
- Au reflects less well and has a yellow appearance, because of an absorption band in the blue







Introduction – Visible light 2

Visible light: 400 – 800 nm = few eV

- Small energy: enough to interact with free or valence electrons
- Inner ("core") electrons are tightly bound to nuclei: weak interaction, if any!
- Depends on...?

Refraction and reflection occur also in the X-rays and UV range





Introduction – X-rays



X-rays energies are similar to or larger than core electrons binding energies(Binding energy of electron in H atom: 13.6 eV)

 $E_B(1s) = 13.6 \cdot Z^2$

easy approximation ignoring any Coulomb interaction

Interaction strength or "cross section" is stronger for core electrons than for valence ones



Atomic level structural probes





- Structural properties
 - Macroscopic
 - Atomic level
- Electronic properties
- Vibrational properties









The scattering can be:

Elastic:

- no exchange of energy: $\Delta E = 0$ 0
- diffused photons have the same energy of the incoming ones 0
- "coherent" because the waves scattered by different parts of the system 0 interfere

Inelastic:

 \circ ΔE = energy of an excited state of the sample





- Classically, elastic scattering occurs when an electron is sinusoidally accelerated by the incoming electromagnetic field and reradiates light at the same frequency
- Emitted radiation: same frequency of the electromagnetic field (this is the scattered wave!)





- The strength of the re-emitted radiation depends on the component of the electric field seen from a given point
- No scattering occurs parallel to the electric field: no acceleration! $(\theta = \pi/2)$
- MAX scattering amplitude perpendicular to the electric field
- Scattering intensity ~ E² and to cos²θ

 (θ: angle between the plane perpendicular to the electric field and the direction of observation)



Electromagnetic *dipole* radiation



- Scattering length: ability of an electron to scatter an x-ray
- For an isolated electron **Thomson scattering length:** "classical radius" of a free electron
- The elastic scattering **amplitude** of an atom is proportional to the Thomson scattering length and Z (number of electrons in the atom)
- The elastic scattering intensity increases with Z²

$$\begin{cases} r_0 = \left(\frac{e^2}{4\pi\varepsilon_0 m_0 c^2}\right) = 2.82 \times 10^{-5} \text{ Å} \\ \text{Rest mass energy} \\ \text{of the electron} \end{cases}$$



The **Thomson scattering length** determines the scattering amplitude from a single electron

The scattering amplitude is proportional to:



(The factor -1 represents the 180° shift between incident and scattered waves)



One more step: the differential scattering cross section

Efficiency of the scattering process normalized to the flux of the incoming beam and size of the detector

$$\frac{d\sigma}{d\Omega} = \frac{I_{sc}}{\Phi_0 \Omega} \qquad \qquad \frac{d\sigma}{d\Omega} = r_0^2 |\hat{\boldsymbol{\varepsilon}} \cdot \hat{\boldsymbol{\varepsilon}}'|^2 \qquad \begin{array}{l} \text{Thomson differential} \\ \text{scattering cross section} \end{array}$$

 $(\varepsilon \cdot \varepsilon')^2$ has to be considered for the optimal choice of experimental geometry! SR is polarized horizontally, therefore...

- Scattering expt are done in the vertical plane, where $(\epsilon \cdot \epsilon')^2 = 1$
- Fluorescence expt, on the contrary, avoid scattering and stay in the horizontal plane, where $(\epsilon \cdot \epsilon')^2 = 0$



X-ray scattering: some considerations

"X-rays interact <u>mainly</u> with electrons in matter"

$$r_0 = \left(\frac{e^2}{4\pi\varepsilon_0 mc^2}\right)$$

Scattering amplitude ~ (mass of the particle)⁻¹ Scattering cross section ~ (scattering length)²

$m_{\rm nucl} \sim 10^6 m_{el}$

The nucleus can be completely ignored



- 1. From quantum mechanics: x-rays = photons
- 2. The electron is free at rest

In a collision, the **energy** of the photon can be **transferred** to the electron, and the scattered photon has a lower energy than that of the incident one





The photon energy loss increases with increasing scattering angle and incident photon energy

> For most applications using SR, the cross section for Compton scattering can be neglected







Inelastic scattering from a free electron: Compton scattering - 3



Energy conservation

$$hv_0 + m_0c^2$$

Rest mass of the electron

Momentum conservation x direction $\frac{hv_o}{c}$ y direction0

Radiation-matter interaction – Ilaria Carlomagno



Scattering from a cloud of free electrons - 1

Assumption:

the electrons in an atom can move freely and are unaffected by being in bound states



Electron distribution $\rho(\mathbf{r}) =$ electron density

Scattered radiation: superposition of contributions from different volume elements



Scattering from a cloud of free electrons

The scattering takes place **in all directions** with intensities depending on the electron density

At a **given angle** the scattered waves differ in amplitude and phases

The **resulting wave** at a given angle is obtained by taking into account the amplitudes and the relative phases





- Each scattered wave from an infinitesimal volume element has an **amplitude** $\propto \rho(\mathbf{r})$





Scattering from a cloud of free electrons - 3



- k = wave vector of the incident beamk' = wave vector of the scattered beam
- $\mathbf{k} \cdot \mathbf{r}$ phase difference of the **incident wave** in A and B

phase difference of the **scattered** wave in A and B

$$\Delta \phi(\mathbf{r}) = \mathbf{k} \cdot \mathbf{r} - \mathbf{k}' \cdot \mathbf{r} = (\mathbf{k} - \mathbf{k}') \cdot \mathbf{r} = \mathbf{Q} \cdot \mathbf{r}$$



 $|\mathbf{k}| = |\mathbf{k'}| = 2\pi/\lambda$ (elastic scattering)

Q = **k** – **k'** scattering vector [Å⁻¹] describes scattering

$$|\mathbf{Q}| = \frac{4\pi}{\lambda} \sin \theta$$

ħQ momentum transfer to the scattered photon



It describes the total scattering amplitude as a function of **Q**

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

When $Q \rightarrow 0$ all the different volume elements scatter in phase so that $f^{0}(Q = 0) = Z$ As Q increases the different volume elements scatter out of phase and consequently $f^{0} \rightarrow 0$ Typically, electron density is approximated to a sphere, and hence f^{0} depends only on |Q|

$$f^{0}(\sin\theta/\lambda) = \sum_{i=1}^{4} a_{i} \exp\left(-b_{i} \sin^{2}\theta/\lambda^{2}\right) + c$$



Atomic scattering factor/Atomic form factor









Time for a break!



...but the electrons are not free!

Quantum mechanics: atomic electrons are bound and have discrete energy levels Correction terms (energy dependent!) must be added to scattering factor As a general rule the atomic form factor is reduced of a factor f'



Energy



Correction terms for the atomic scattering factor - 2



When Ei = Eb (close to an absorption edge) x-rays are partially absorbed and **f**' has a **resonant** behavior.

After a delay, some **radiation is re-emitted**, which **interferes** with the **elastically scattered part**, thereby **altering the phase and the amplitude**

This is allowed by including a term **if**" that is imaginary and is related to absorption



f'' is related to the photoabsorption cross section σ_a at that photon energy: $f'' = \frac{\sigma_a}{2r_0\lambda}$



f' and f'' are functions of energy: their behavior is correlated to the bound electrons



Correction terms for the atomic scattering factor



- f' and f'' assume extremal values when hv = absorption edges
- The real part *f*-*f* has a deep at the absorption edges and then converges to Z
- **f**^{''} falls away as E⁻² with discontinuity at the absorption edges



Refractive index - 1

Dimensionless number describing how an EM wave propagates through a medium

$$n = \frac{\mathcal{C}}{\mathcal{V}}$$
 Speed of light in vacuum
 \mathcal{V} Speed of light in the medium

n determines the refraction, the interface reflectivity, and the critical angle for total reflection

 \boldsymbol{n} is a factor by which the speed and λ are reduced with respect to vacuum

n varies with λ : due to this, white light splits into its constituent colors in prisms



Refractive index - 2

Light propagation in absorbing materials can be described using a complex-valued refractive index:

 $n = n_R + i n_I$

The **real part** accounts for **refraction**, the **imaginary part** handles the **attenuation**

For x-rays, *n* is related to the **atomic scattering factors** of the individual atoms in a material:





Real part of the refraction index

$$n = 1 - \frac{r_0}{2\pi} \lambda^2 \sum_{i} N_i f_i(0)$$
 Complex atomic scattering factor in the forward direction of the *i*th atom δ is the real part of $f_i(0)$
$$n = 1 - \delta + i\beta$$

Far from an absorption edge f' can be ignored: $\sum_i N_i f_{1,i}(0) = \rho$

$$\implies \delta = \frac{2\pi\rho r_0}{k^2} \quad \text{Proportional to (photon energy)}^2$$

Assuming
$$\rho = 1 \text{ el/Å}^3$$
, $\delta \sim 5 \times 10^{-6}$: $\Box > n_R = 1 - \delta \le 1$

Radiation-matter interaction – Ilaria Carlomagno



Snell's law - 1

If $n_R < 1$, then it exists a minimum incident angle α_c angle such that:



- for $\alpha > \alpha_c$ refraction into the material
- for $\alpha < \alpha_c$ total external reflection



- Surfaces reflect x-rays but only at small angles ≈ mrads
- Parabolic mirrors can focus x-rays at $\alpha < \alpha_c$
- Low incident angles = large footprint and large mirrors





For $\alpha < \alpha_c$ x-rays are «totally» reflected...

...but reflection itself requires a sort of interaction!

The penetration depth at $\alpha < \alpha_c$ (few nm) is 3 orders of magnitude smaller than at $\alpha > \alpha_c$

X-rays are a *surface-sensitive probe* down to the atomic level in grazing-incidence



Penetration depth and reflectivity





Matter-radiation interaction: absorption

Radiation-matter interaction – Ilaria Carlomagno



Absorption





X-ray absorption: general idea



It is **element-specific** and a function of the x-ray energy It increases with the atomic number of the element ($\propto Z^4$) It decreases with increasing photon energy ($\propto E^{-3}$)

It is an indication of the electron density in the material and the electron binding energy

- Chemical substances having different geometric ('allotropic') forms (hence different densities) have different absorption
- Chemically-different compounds having the similar electronic and mass densities will have similar absorption properties (except close to absorption edges)







It measures the ability of a sample to attenuate the photon beam

The photon excites the absorber

When the excited state is above the vacuum level, one or more photoelectron can be emitted

Secondary photons are re-emitted (fluorescence), or electrons

Quantitatively absorption is described by the absorption coefficient that can be measured

- **Directly** by measuring the attenuation of the beam as a function of the photon energy
- Indirectly by measuring:
 - $_{\circ}$ Photoelectrons
 - Fluorescence photons from the decay process
 - Auger electrons from the decay process



Photoelectric absorption

Upon photon absorption, an electron is expelled from the atom, leaving it ionized





The absorption coefficient





Emission lines nomenclature



Characteristic energy of the K α line (Moseley law)

X-ray frequency $\nu = K(Z - 1)^2$ Atomic number \downarrow For K α lines, K = $(2.47 \cdot 10^{15} \text{ Hz})$



Measuring the absorption -1

Quantitatively, the absorption is given by the linear absorption coefficient μ μdz attenuation of the beam through an infinitesimal thickness dz at a depth z





Measuring the absorption - 2

The intensity I(z) through the sample fulfills the condition

 $-dI = I(z)\mu dz$

Which leads to the differential equation

$$\frac{dI}{I(z)} = -\mu dz$$



If $I(z = 0) = I_0$, (I_0 : incident beam intensity) then

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



Measuring the absorption - 3

$$I(z) = I_0 e^{-\mu z} \Rightarrow ln \frac{I_0}{I} = \mu z$$

Experimentally, μ can be obtained from the ratio of the beam intensities before / after the sample





Atomic absorption cross section σ_a



 $\sigma_a[\text{cm}^2]$...or... $\sigma_a[barn]$

 $1 barn = 10^{-28} \text{ m}^2$

$$\sigma_a \left[\frac{\mathrm{cm}^2}{\mathrm{g}} \right] = \frac{N_A}{A} \, \sigma_a \, [\mathrm{cm}^2] = \frac{\mu}{\rho_m}$$



• Different atoms, each with a number density $\rho_{at,j}$ and absorption cross section $\sigma_{a,j}$

• Total probability for absorption in a layer dz is the sum over $\rho_{at,j} \sigma_{a,j} dz$ the probability of absorption for an atom for type j:

$$\mu = \sum_{j} \rho_{at,j} \, \sigma_{a,j}$$



Absorption/scattering-atomic scattering factor



The photoelectric absorption arises from a physical process that is different from the scattering of a photon

However, absorption and scattering are related



Absorption coefficient and n - 1

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

Complex atomic scattering factor in the forward direction of the *i*th atom

$$f_i(0) = f_{i1} + i f_{i2}$$
 , $n = 1 - \delta + i \beta$

$$n = 1 - \frac{r_0}{2\pi} \lambda^2 \sum_i N_i (f_{i1} + if_{i2})$$
$$n = 1 - \frac{r_0}{2\pi} \lambda^2 \sum_i N_i f_{i1} - \frac{r_0}{2\pi} \lambda^2 \sum_i N_i i f_{i2} \longrightarrow i\beta$$

$$\beta = \frac{r_0 \lambda^2 \rho}{2\pi} f_2 = \frac{2\pi r_0 \rho}{k^2} f_2$$

since
$$f_2 \propto \frac{1}{E^2} \Longrightarrow \beta \propto \frac{1}{E^4}$$



Absorption coefficient and n - 2

For a wave travelling in vacuum $E(z,t) = E_0 exp[i(k_0 z - \omega t)]$

In a medium $E(z,t) = E_0 exp[i\mathbf{n}k_0z - \omega t]$

Since
$$n = 1 - \delta + i\beta$$
:
 $E(z,t) = E_0 exp(-\beta k_0 z) exp[i((1 - \delta)k_0 z - \omega t)]$

measures the damping in a medium



Absorption coefficient and n - 3

In practice we measure the intensity which is $\propto |E|^2$

$$|E(z,t)|^{2} = E_{0}^{2} exp(-2\beta k_{0}z) exp\left[2i\left((1-\delta)k_{0}z-\omega t\right)\right]$$

The intensity drops by an amount 1/e over a depth $1/2\beta k_0$

In terms of the absorption coefficient:
$$\frac{I}{I_0} = exp(-\mu z)$$
, then:

$$\mu = 2\beta k_0$$

Therefore:

$$f_{2} = \frac{k^{2}}{2\pi r_{0}\rho}\beta = \frac{k^{2}}{2\pi r_{0}\rho}\frac{\mu}{2k} = \sigma_{a}\frac{k}{4\pi r_{0}} = \sigma_{a}\frac{2\pi}{\lambda}\frac{1}{4\pi r_{0}} = \frac{\sigma_{a}}{2r_{0}\lambda}$$

f'' related to the photoabsorption cross section σ_a at that photon energy



Secondary effects





X-ray fluorescence - 1

Any material emit fluorescence if bombarded it with x-rays or highenergy electrons.

If electrons are used, the energy spectrum of the emitted light has two parts:

- A broad background is produced as electrons collide with the atoms due to the strong deceleration (Bremsstrahlung). It has a maximum cut-off energy corresponding to the highest kinetic energy of the electrons impinging on the target
- The sharp fluorescence lines, which are characteristic for each element
- In the case of excitation by x-rays, the Bremsstrahlung is missing...







These characteristic x-ray lines result from the transition of an outer-shell electron relaxing to the hole left behind by the ejection of the photoelectron from the atom

This occurs on a timescale of the order of 10 to 100 fs

The energy difference between the two involved levels is well defined \rightarrow lines are very sharp

From Heisenberg's uncertainty principle $\Delta E \Delta t \sim \hbar$, the natural linewidth is $\sim 0.01 \text{ eV}$, (but depends on the element and on the transition)



Auger Emission - 1

It is a three-electron process:

- 1. a core electron (**E**_c) is emitted upon absorption
- 2. an outer electron $(E_n < E_c)$ fills the hole of the photoelectron
- 3. the excess energy ($\Delta E = E_c E_n$) is transferred to the Auger electron

Auger emission may occur for those electrons whose binding energy is $< \Delta E$





3 letters: 3 electronic levels involved in Auger emission (using Barkla notation of *K*, *L*, *M*,...)

For a KLL Auger electron:

- K is the core-level from which the photoelectron originates (with energy E_c)
- L is the level from which the electron that fills the core-hole originates (energy E_N)
- L is the original level of the Auger electron (energy E_A)





Fluorescence or Auger?

- The probability of Auger emission increases with decreasing energy difference between the excited atom and the atom after Auger emission
- LMM events are more likely than KLL events
- Lower Z atoms have higher Auger yields
- Higher Z elements have larger positive charges at the nucleus: electrons are more tightly bound and the probability of Auger emission is lower

