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Physical and Chemical Analyses of Materials

Interactions beam-matter: matter excitation

Introduction

⇨ In this chapter we will discuss on the mechanistic aspects of the interactions of photons and electrons with the matter.

Interactions of photons

General considerations

⇨ Photons scattering occurs by elastic and inelastic interactions with the electrons of the atoms constituting the material. The ratio inelastic/elastic interactions decreases when the atomic number increases.

Elastic scattering

⇨ Elastic scattering occurs with the whole electronic cloud of the target atoms, so called Rayleigh scattering. The cross-section of this scattering is much lower than that of the inelastic ones.

⇨ The energy $\mathbf{E_0}$, so the wavelength λ_0 and the magnitude of the wave vector $\left\|\overrightarrow{\mathbf{k_0}}\right\|$ of the incoming photons are conserved.

Inelastic scattering

⇨ Inelastic scattering takes place with individual electrons.

⇨ For photons of low energy, the beam interacts with electrons involved in chemical bonds generating electronic transitions (UV-vis) or electronic vibration (IR, Raman).

⇨ For photons of high energy *i.e.* X-Ray photons, the interactions occur with core electrons, the ones closest to the nucleus.

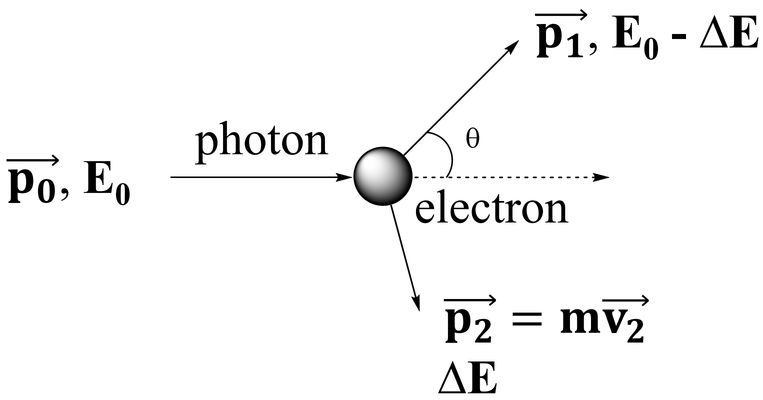
⇨ For photons of very high energy *i.e.* γ photons, the interactions occur with the nucleus components.

⇨ In the following we will consider only the interactions of X-ray photons with the matter. These interactions are described by two mechanisms: the Compton effect and the excitation/ ionisation of the chemical elements of the material.

Compton effect

⇨ In this inelastic interaction, a photon gives a fraction of its energy to a target electron through a collision. The cross-section for the Compton effect increases with the photon energy (see slide 7).

⇨ Here is the scheme used to describe the Compton effect:



$$\Delta\lambda = \lambda - \lambda_0 = \frac{h}{mc}(1 - \cos\theta)$$

↳ The energy left by the photon is transformed into a kinetic energy given to the target electron. The target electron oscillates around its position.

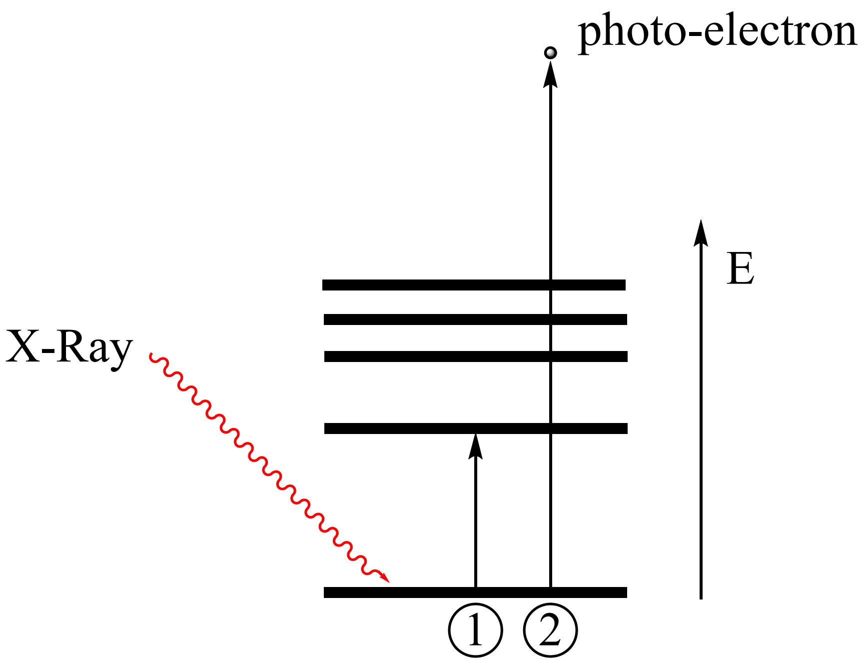
↳ The photon diffuses with an energy lower than its initial energy so with a higher wavelength.

↳ This interaction gives rise to a modification of the energy and the magnitude of the wave vector of the incoming beam. The impulsion $\vec{P}$ is conserved during the interaction.

↳ The energy lost by the photon is: $\Delta E = \frac{hc}{\Delta\lambda} = \frac{mc^2}{1 - \cos\theta}$

Excitation/ionisation

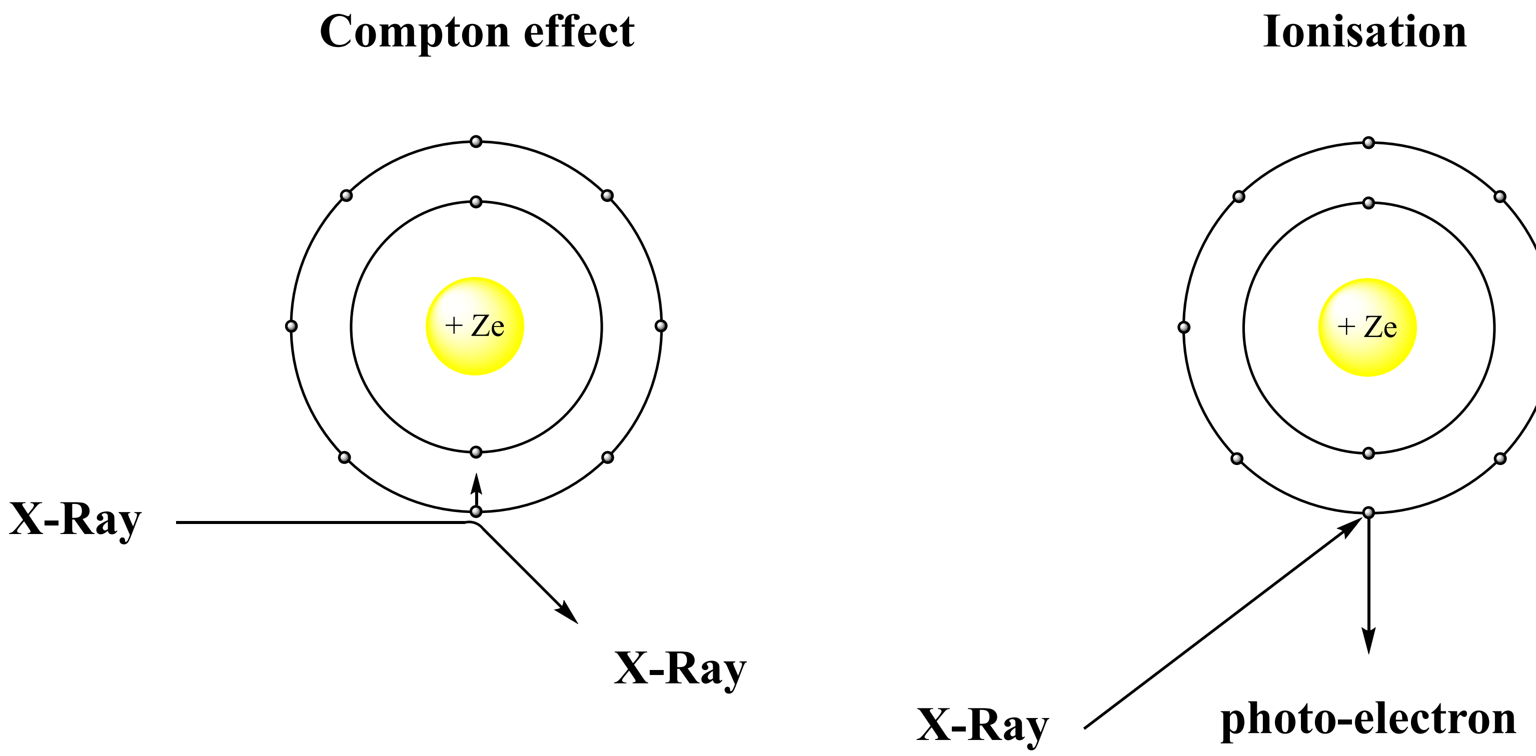
⇨ This interaction gives rise, depending on the energy of the incoming X-Ray photon, to either the excitation (1) or to the ejection (2) of a core electron of the target chemical element which results in its ionisation. For X-Rays, the cross section of these events related to a target element with Z protons is proportional to $\mathbf{Z^4/(h\nu)^3}$.



- The energy of the incoming photon is totally transferred to the target.
- (1): The energy of the incoming photon is converted into a potential energy given to the atom.
- (2): The energy is used to ionise the atom and its excess is converted into a kinetic energy given to the photo-electron (photo-electric effect).
- There is no scattered photon.
- The energy loss is: $\mathbf{\Delta E = 0 - E_0 = -E_0}$

Inelastic scattering of photons: classic approach

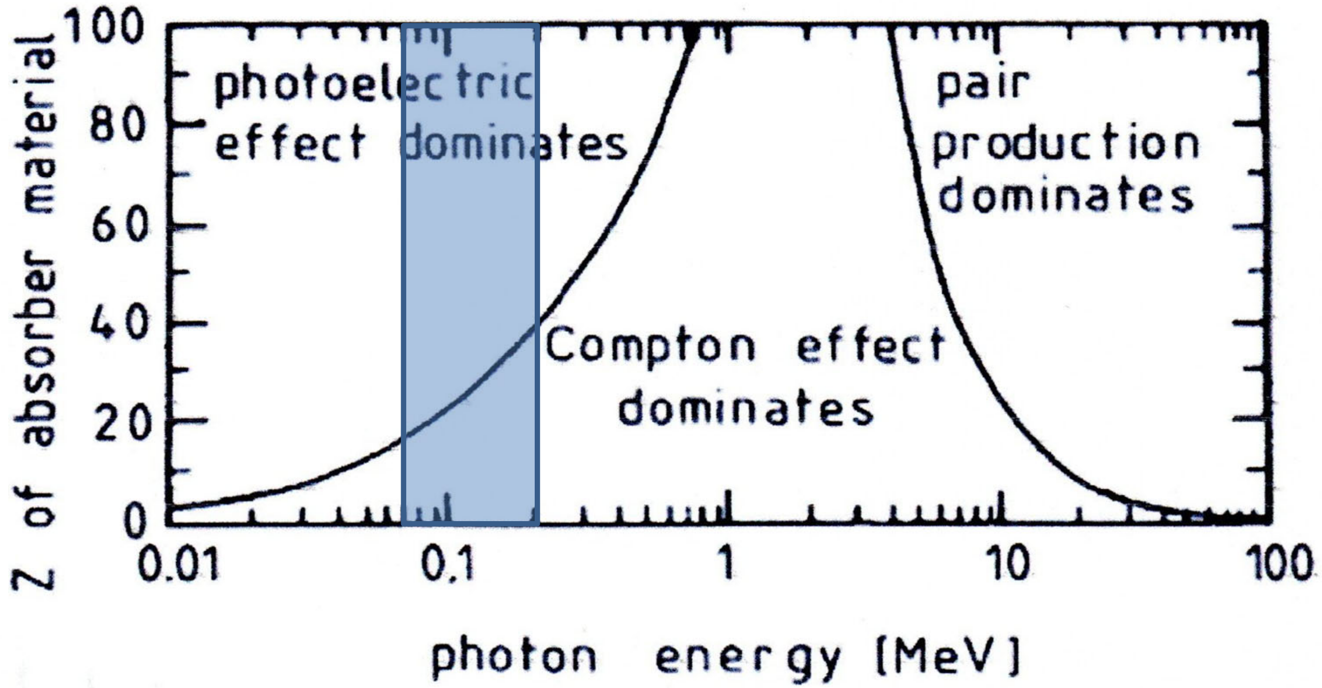
⇨ Using a classic approach of the atomic structure, one can represent the scattering events as follows:



↳ Through Compton effect, in most cases, the target electron recoils, but ionisation could also occur (depending on the energy of the incoming electron).

Inelastic scattering of photons: ionisation vs Compton effect

⇨ Below are depicted the cross-sections related to the photoelectric (ionisation) and the Compton effects as a function of the incoming photon energy and the chemical nature of the target element (absorber material):



⇨ The frame represents our working domain in terms of photon energy.

Interactions of electrons

General considerations

⇨ The interactions of electrons with the matter is more intense than the one involving photons.

⇨ In contrast with photons, the energy of electrons is not quantified.

⇨ Electrons could leave their energy to the matter randomly in subsequent interactions.

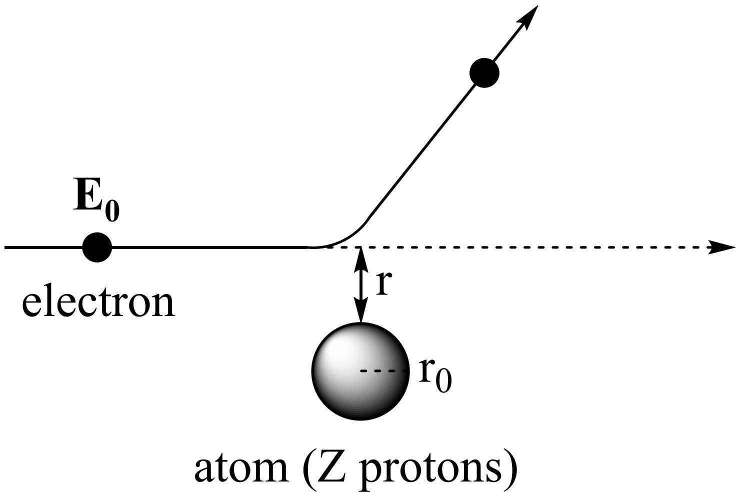
⇨ Compared to photons, electrons show an important increase of their cross-section of interaction.

⇨ Electrons exhibit a lower free mean path than photons, so a lower penetration of the beam in the material is observed.

⇨ As for photons, electrons undergo elastic and inelastic scattering.

⇨ The type of scattering depends on the interaction distance between an electron and a target atom. The classic radius of an electron is 2.818×10^{-15} m.

⇨ To describe these interactions with an atom of radius $\mathbf{r_0}$, one has to consider the following interaction scheme:



↳ Elastic interactions occur for $\mathbf{r} >> \mathbf{r_0}$.

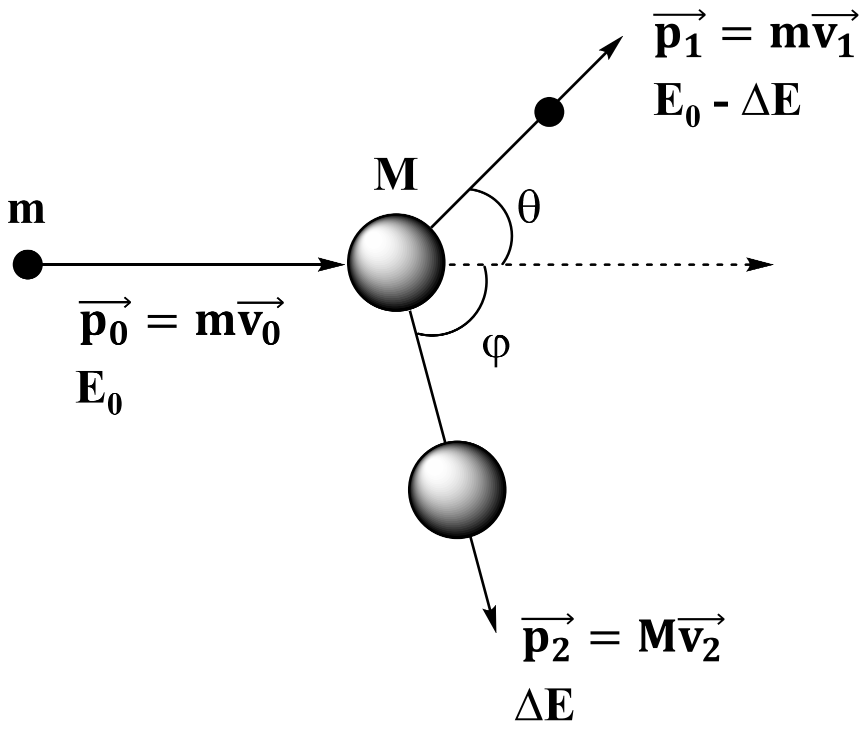
↳ Inelastic interactions occur for $\mathbf{r} \approx \mathbf{r_0}$.

Elastic scattering

Elastic scattering: mechanism

⇨ Elastic scattering occurs when an incoming electron moves at a distance greater than the target atom radius. The cross-section of the elastic scattering is proportional to $\mathbf{Z^2/E_0^2}$.

⇨ Whatever the energy of the electrons of the incoming beam, the elastic interactions could be described by the general following scheme:



⇘ We should then consider a system with two masses **m** and **M** interacting through an elastic collision with the conservation of the impulsion $\vec{\mathbf{P}}$.

⇘ The energy communicated to the object of mass **M** is:

$$\Delta E = 4E_0 \frac{m}{m+M} \sin^2\left(\theta/2\right)$$

⇘ As **M** >> **m**, the relation becomes:

$$\Delta E = 4E_0 \frac{m}{M} \sin^2\left(\theta/2\right)$$

↳ For an electron-nucleus interaction, if $\mathbf{E_0} \leq 100$ keV (non-relativistic):

$$\Delta E = 4E_0 \frac{m}{M} \sin^2\left(\theta/2\right)$$

↳ For an electron-nucleus interaction, if $\mathbf{E_0} > 100$ keV (relativistic):

$$\Delta E = \frac{2E_0\left(E_0 + 2mc^2\right)}{Mc^2} \sin^2\left(\theta/2\right)$$

Elastic scattering: matter reaction

⇨ Elastic scattering of electrons can produce many matter changes, depending on the amount of energy transfered to the matter.

⇨ Electrons back scattering can also be observed. This case corresponds to θ = 180°, almost no energy is transfered to the matter:

$$\Delta E = 4E_0 \frac{m}{M} \sin^2\left(\theta/2\right) \Rightarrow \frac{\Delta E}{E_0} = \frac{4m}{M} \approx 0$$

⇨ Thermal effects are observed for an energy loss of 10^{-2} to 10^{-1} eV, leading to the oscillation of the target atoms around their equilibrium position: single oscillation (debye effect) or collective oscillations (emission of phonons in the case of crystals).

↳ Theses oscillations leads to heat transfers that causes side effets especially for high energy electron beams used in electronic miscroscopy and in X-rays production (see slide 12).

⇨ Chemical effects are observed for an energy loss of 3 to 5 eV, leading to the breaking of weak chemical bonds.

↳ Theses effects are due to reduction processes.

⇨ Atomic displacements occur when the energy comunicated to the atom is greater than the displacement threshold.

↳ These phenomena can take place with electrons of energy around 15 to 30 eV.

↳ The target atom can leave its potential well leading to permanent damages of the material. This phenomenon can be observed in electron microscopy.

⇨ The energy loss for all these events is assessed by the linear energy transfert (**LET**) to the matter which will be discussed further.

Inelastic scattering

⇨ The interactions of the incoming electron can take place either with an electron of the target atom or with the its nucleus. They occur when $\mathbf{r} \approx \mathbf{r_0}$.

⇨ The proper description of these cross-sections requires a quantum approach, but the cross-section of the inelastic scattering can be approximated to be proportional to $\mathbf{Z/E_0^2}$.

⇨ The energy loss for all these events is assessed by also by the **LET** (discussed further).

Inelastic scattering: interaction electron-electron

⇨ The interaction electron-electron gives rise to several mechanisms, depending on the energy of the electron beam:

↳ Excitation of valence or conduction electrons of the material. The excitation of the conduction electrons lead to collective oscillations, that is plasmons.

↳ Ionisation of valence or conduction levels.

↳ Excitation/ionisation of core electrons.

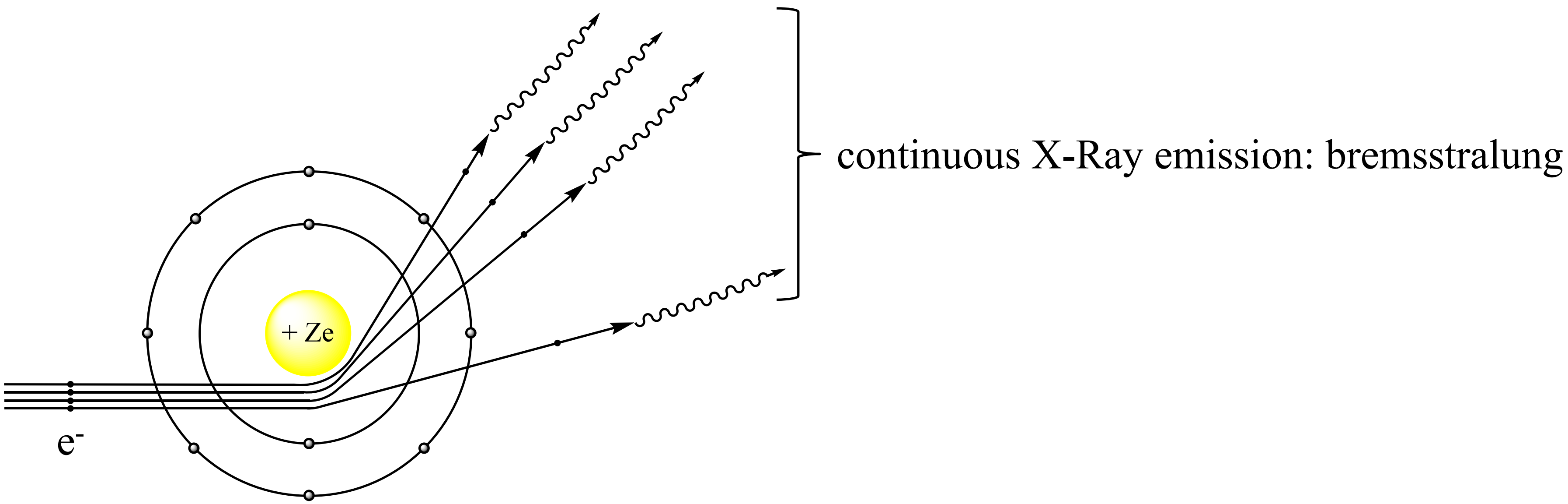
↳ In constrat with X-Rays induced ionisation, the ejected electron is now named secondary electron instead of photo-electron (see slide 5).

Inelastic scattering: interaction electron-nucleus

⇨ The interaction electron-nucleus gives rise to an electron braking with a trajectory deviation.

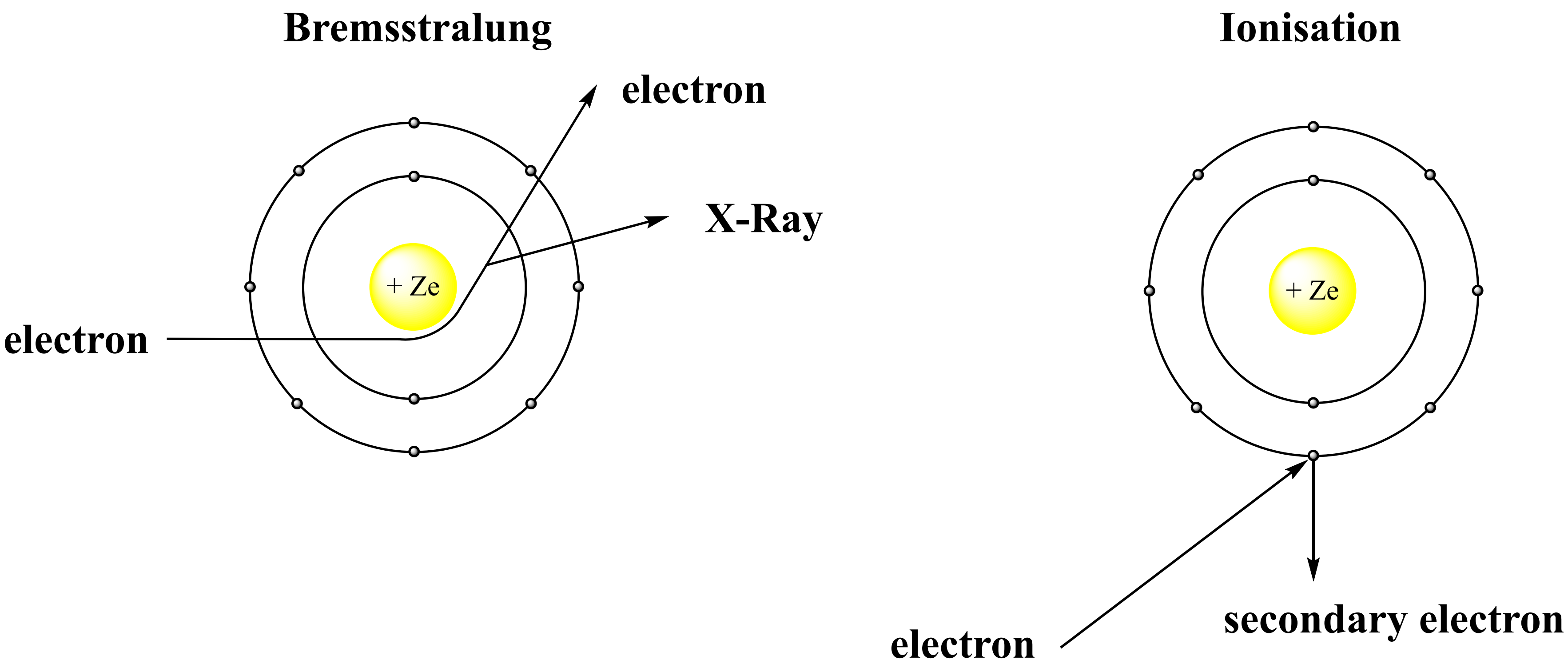
↳ The electron trajectory deviation depends on the distance between the incoming electron and the target nucleus. The closer trajectory to the nucleus, the greater electron braking and so, the higher energy loss. The energy loss is also qualified by the **LET**.

↳ The energy lost by an electron when braking is transformed into an X-Ray emission.



Inelastic scattering of electrons: classic approach

⇨ Using a classic approach of the atomic structure, one can represent the scattering events as follows:



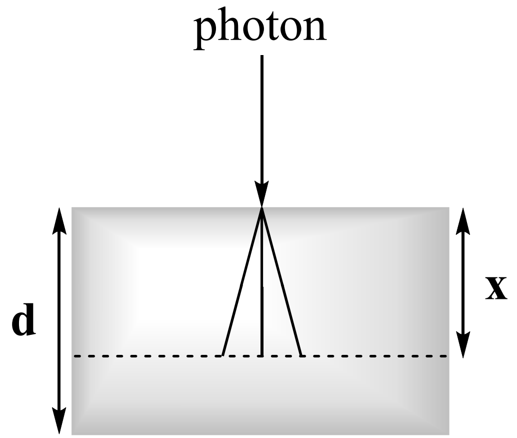
↳ In the ionisation scheme, one must consider that the primary electron, after a first collision, can have enough energy to ensure other ionisation/excitation processes.

Beam absorption

Photons

⇨ The absorption of the beam by the matter is qualified by $\mathbf{I_0}$**'**, the intensity measured along the wave vector $\overrightarrow{\mathbf{k_0}}$ after having crossed the material (thickness **d**).

➥ The intensity of the beam after a penetration **x** in the matter follows the general equation:



$$\frac{\mathbf{I_x}}{\mathbf{I_0}} = \mathbf{e}^{-\mu\rho x}$$

➥ In this equation, **μ** ($m^2 \cdot kg^{-1}$) stands for the massic absorption coefficient. The beam has a penetration depth of **x** (m) into a material of volumetric mass **ρ** ($kg \cdot m^{-3}$).

↳ One has to notice that the absorption depends on the wavelength of the incoming beam.

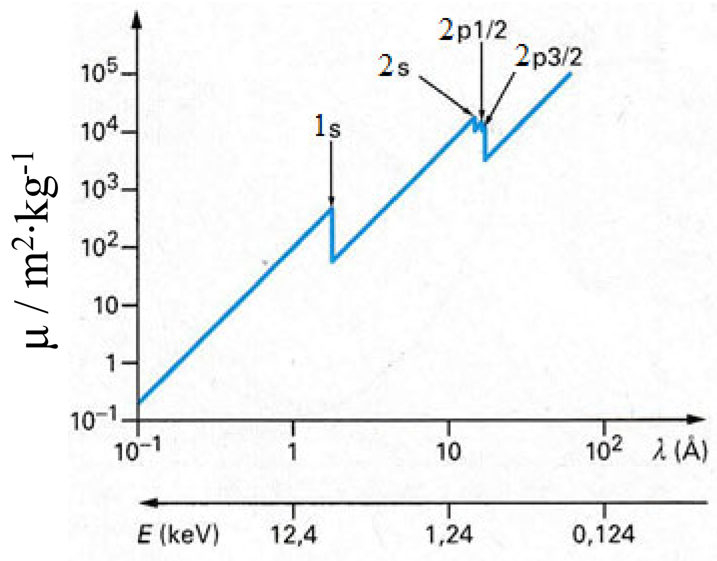
↳ For a given wavenlength corresponding to an excitation /ionisation process, $\mathbf{I_x/I_0 \rightarrow 0}$, which is not the case for other incoming beam wavelengths.

↳ As a conclusion, **μ** is not unique for a given material but also depends on the wavelength of the incoming beam.

↳ **μ** decomposes as: $\mu = \mu_{Rayleigh} + \mu_{Compton} + \mu_{excitation/ionisation}$. $\mu_{excitation/ionisation}$ is always bigger than $\mu_{Compton}$ except for light chemical elements.

↳ As already mentionned **μ** depends on **λ** but also on the atomic number **Z** of the target element as:

$$\mu = kZ^{\alpha}\lambda^{\beta}$$



↳ In this equation, **k** ($kg^{-1}\cdot m^{-(0,2-1)}$), **α** and **β** are some constants. $\mathbf{2.5 < \alpha < 3.5}$, $\mathbf{2.2 < \beta < 3}$.

↳ **k** varies as a function of the wavelength domain.

↳ For a material constituted by various chemical elements $\mathbf{E_i}$, $\boldsymbol{\mu}$ depends on each chemical element ($\boldsymbol{\mu_i}$ ($m^5 \cdot kg^{-2}$)) and its massic concentration $\mathbf{C_{m,\,i}}$ ($kg \cdot m^{-3}$) as:

$$\mu = \sum_i \mu_i C_{m,\,i}$$

⇨ The measurement of the outcoming beam intensity $\mathbf{I_0}$**’** after having crossed the material of thickness **d** allows the determination of $\boldsymbol{\mu}$ and so the mean free path **l** of the beam particles: $\mathbf{l = (\mu\rho)^{-1}}$.

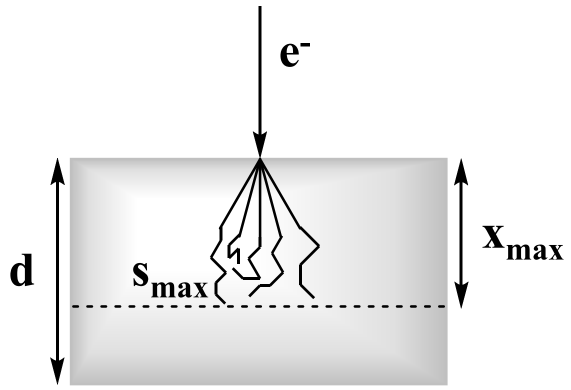
Electrons

⇨ For electrons, the absorption of the beam is qualified by the determination of its intensity at the maximum penetration distance $\mathbf{x_{max}}$.

↳ In the case of $\mathbf{x_{max} < d}$, there is no outcoming beam.

↳ If $\mathbf{x_{max} > d}$, as for photons, the outcoming beam intensity will be $\mathbf{I_0}$**’**.

⇨ Each electron has its own path **s**. The electron path $\mathbf{s}_{max}$ in the material is greater than the maximum penetration distance $\mathbf{x}_{max}$ of the beam.



↳ The mean electron path $\bar{s}$ is: $\bar{s} = l = \left(\sigma_t\left(\vec{k}_1\right)N_{V,\,target}\right)^{-1}$

⇨ The intensity decrease is given by:

$$\frac{I_{x_{max}}}{I_0} = \exp\left[-\left(\frac{x_{max}}{C\left(E_0\right)^n}\right)^p\right]$$

↳ In this equation: $\mathbf{C = 3.33\times10^{-2}/\rho_s}$, $\mathbf{n = 2.44(Z/A)^{0.5}}$, $\mathbf{p = 1.51nlog(Z)}$.

↳ This equation is valid for an incoming beam energy from 50 to 250 keV.

↳ $\boldsymbol{\rho_s}$ ($g\cdot cm^{-2}$) is the surface density, **Z** and **A** (g) are the atomic number, and the atomic mass of the target element, $\mathbf{X}_{max}$ (μm) and $\mathbf{E}_0$ (keV) are the maximum penetration length and the energy of the electron incoming beam.

Linear energy transfer to the matter

General considerations

⇨ The linear energy transfer, **LET**, is the energy transfered by a particle to the matter per distance unit.

⇨ The greater **LET**, the lower free mean path **l** of a given particle: larger ionisation processes will occur.

⇨ The **LET** ($keV \cdot \mu m^{-1}$) is given by: $\mathbf{LET} = -\frac{\mathbf{dE}}{\mathbf{dx}}$

⇨ By evaluating the **LET**, one can determine the maximum penetration of a specific beam of given energy in a target material.

Photons

⇨ For photons, inelastic scattering gives rise to an energy loss which follows a similar behaviour than the intensity.

⇨ After a penetration distance of **x**, the energy attenuation of a monochromatic photon is:

$$\frac{E_x}{E_0} = e^{-\mu' x}$$

↳ **μ'** (cm^{-1}) is the coefficient of the global linear attenuation which depends on the energy of the incoming photons $\mathbf{E_0}$ and on the nature of the material.

⇨ Considering **μ'** as a constante, the **LET** is then: $\mathbf{LET = \mu' E_0 e^{-\mu' x}}$

Electrons

⇨ For electrons, the **LET** which takes into account both elastic and inelastic scattering events can be approached by:

$$\mathbf{LET = k \frac{e^2 N_{v,target} Z}{v_0^{\,2}}}$$

↳ In this expression, **k** is a constant, **e** is the elemental charge (1.602×10^{-19} C), $\mathbf{N_{V,\ target}}$ is the number of target particles (number·m^{-3}), **Z** is the atomic number of the target atom and $\mathbf{v_0}$ is the speed of the incoming electron (m·s^{-1}).

⇨ The **LET** resulting from ionisation and/or excitation events is:

$$-\frac{dE}{dx}=\frac{0,3071}{A}\times\frac{Z}{\beta^2}\times\left[\frac{1}{2}\ln\left(\frac{(\gamma-1)m^2\beta^2\gamma^2}{2I^2}\right)-\frac{1}{2\gamma^2}\left[1-(2\gamma-1)\ln(2)\right]+\frac{1}{16}\left(\frac{\gamma-1}{\gamma}\right)^2\right]$$

↳ In this expression, **A** is the atomic mass (g) of the target atom, **Z** is the atomic number of the target atom, **β** and **γ** are the Lorentz factors of the electron, **m** is the masse of the electron (511 keV/C^2), **I** is the mean excitation/ionisation energy (eV) of the target atom.

⇨ The **LET** resulting from the bremsstralung is:

$$-\frac{dE}{dx}=4\alpha N_A\frac{Z^2}{A}r_e{}^2E_0\ln\left(\frac{183}{Z^{1/3}}\right)$$

↳ In this expression, **α** is the constant of the hyperfine structure (1/137), $\mathbf{N_A}$ (6.022×10^{23} mol^{-1}) is the Avagadro number, **Z** is the atomic number of the target atom and **A** is its mass (g), $\mathbf{r_e}$ is the classic radius of the electron (2.818×10^{-15} m) and $\mathbf{E_0}$ is the energy of the incident electrons.

⇨ For a material composed by several elements **i**, the total **LET** depends on the massic fraction $\mathbf{f_i = m_i / m}$ of each element constituting the material of mass **m**:

$$\mathbf{LET = -\sum_i f_i \frac{dE_i}{dx}}$$

↳ In this expression, $\mathbf{dE_i / dx}$ represents the **LET** of the electrons interacting with an element **i**.