Introduction to matter – radiation interaction

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Content

- Macroscopic
  - Dielectric response of matter
    - Index of refraction, dielectric function
    - Attenuation and dispersion
  - Model dielectric functions
- Microscopic
  - Phenomenology, from IR to x-rays
  - Cross section and attenuation coefficient
  - Scattering processes and the atomic form factor
  - Photoelectric absorption
    - absorption edges, de-excitation processes
- Relation between the atomic form factor and index of refraction
- Interaction between radiation and hydrogen – like atoms, semi-classical
  - Photoelectric absorption cross - section
  - Scattering cross - section

References

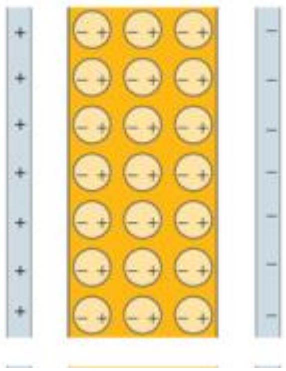
- This presentation
- J.D. Jackson, *Classical Electrodynamics*, Wiley, 3rd Edition, 7.1, 7.2, 7.5 (parts)
- J. Als – Nielsen and D. McMorrow, *Introduction to Modern X-ray Physics*, Wiley, New York, 2001, Chap. 1
- D. Attwood and A. Sakdinawat, *X-rays and extreme ultraviolet radiation*, 2nd edition, Cambridge University Press (2017)

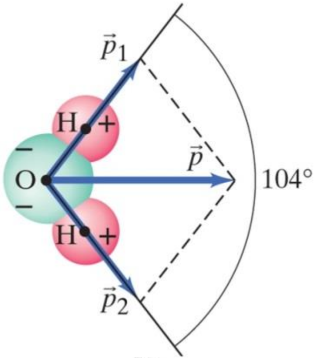
Dielectric response

- General problem: how does condensed matter respond to the application of an external pertubation?
- The EM wave is the external pertubation
- First approach:
  macroscopic / collective
- Second approach:
  microscopic /atomic / particle

Elementary phenomenology

- An electric field applied to a dielectric (no free charges) <u>polarization</u>
  - By distortion
  - By orientation





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Dielectric response

- The applied field will in general have a space and time dependence $\vec{E}(\vec{r}, t)$ which will affect the response

Polarization and susceptibility

- Assume the response of matter to the applied field is linear
  - OK for not too high fields
  - not OK for high power visible, EUV and X-ray lasers
- Apply linear response theory
- The electric dipole moment per unit volume is the polarization vector $\vec{P}$
- Within the linear approximation introduce the electric susceptibility χ

$$\vec{P} = \varepsilon_0 \chi \vec{E}$$

Polarization and susceptibility

- Susceptibility is in general a tensor quantity; for simplicity here consider it a scalar.
- We will study the scalar relations in the frequency domain

$$P(\omega) = \varepsilon_0 \chi(\omega) E(\omega)$$

- The dielectric response of matter determines $\chi(\omega)$

Dielectric displacement

- The dielectric displacement vector is defined as
$$\vec{D} = \varepsilon_0 \vec{E} + \vec{P}$$
- The direct proportionality between $\vec{D}$ and $\vec{E}$ is written as
$$\vec{D} = \varepsilon_0 \varepsilon\, \vec{E}$$
in which ε is the «dielectric constant», better called permittivity or dielectric function
- Clearly
$$\varepsilon = 1 + \chi$$

Dielectric displacement

- We will study dynamics (time dependent properties)
- Susceptibility and dielectric function are «linear response functions»
    - Independent of the external field
    - Describe system properties

The dielectric function

- $D(\omega) = \varepsilon_0 \varepsilon(\omega) E(\omega)$
  - $\varepsilon(\omega)$ has a real and imaginary part: $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$
- The ω dependence of ε is determined by
  - The spectral range
  - The corresponding type of excitations possible
  - The specific properties of the system

Spectral range	System	Excitation processes
Micro - waves	Molecules, free or in solution	Molecular rotations
Infra - red	Molecules, free or in solution	Molecular vibrations
Infra - red	Solids	Phonons
Visibile – UV	Atoms, molecules, solids	Valence electron transitions
X - rays	Atoms, molecules, solids	Core level electron transitions

Dispersion and attenuation

- The dielectric function determines <u>dispersion</u> and <u>attenuation</u> of an EM wave propagating in a polarizable medium
  - a not too rarefied gas, a liquid, a solid or any other state of aggregation (liquid crystal, plasma …)
- In vacuum the dispersion relation for EM waves is

$$\omega = ck$$

c is the speed of light in vacuo.

Dispersion and attenuation

- In the medium the dispersion relation is modified by the presence of the index of refraction $n(\omega)$:

$$\omega = \frac{c}{n(\omega)} k$$

- The index of refraction is

$$n(\omega) = \sqrt{\varepsilon(\omega)\mu(\omega)}$$

- Neglecting magnetic effects, $\mu(\omega) = 1$

$$n(\omega) = \sqrt{\varepsilon(\omega)}$$

- $n(\omega)$ and $\varepsilon(\omega)$ are macroscopic quantities which describe the interaction between the wave and the medium

Dispersion and attenuation

- Consider a plane wave propagating along x

$$E = E_0 e^{i(kx-\omega t)}; \;\; k(\omega) = \frac{n(\omega)\,\omega}{c}$$

- $n(\omega)$ has a real and an imaginary part:

$$n(\omega) = n_1(\omega) + i n_2(\omega)$$

- Therefore, also the wave number has a real and imaginary part

$$k(\omega) = \frac{[n_1(\omega) + i n_2(\omega)]\,\omega}{c} = k_1(\omega) + i k_2(\omega)$$

$$k_1(\omega) = \frac{n_1(\omega)\,\omega}{c}, \qquad k_2(\omega) = \frac{n_2(\omega)\,\omega}{c}$$

Dispersion and attenuation

- $k(\omega) = \frac{[n_1(\omega)+in_2(\omega)]\,\omega}{c} = k_1(\omega) + ik_2(\omega)$

$$k_1(\omega) = \frac{n_1(\omega)\,\omega}{c}, k_2(\omega) = \frac{n_2(\omega)\,\omega}{c}$$

- The effect on the space propagation is

$$e^{ikx} = \underbrace{e^{ik_1(\omega)\,x}}_{\boxed{\text{Propagation term}}} \; \underbrace{e^{-k_2(\omega)\,x}}_{\boxed{\text{Attenuation term}}}$$

- The space – time dependence of the wave is thus

$$E = E_0 e^{i[k_1(\omega)x-\omega t]} e^{-k_2(\omega)\,x}$$

Dispersion and attenuation

- $E = E_0 e^{i[k_1(\omega)x - \omega t]} e^{-k_2(\omega)\,x}$
- $k_1(\omega) = \frac{\omega n_1(\omega)}{c}$ is the modified wave vector
  - the phase velocity of the wave is $v = \frac{c}{n_1(\omega)}$
- $k_2(\omega) = \frac{\omega n_2(\omega)}{c}$ determines the attenuation of the wave as it traverses the medium
- $n_1(\omega)$: dispersion (modifies the speed of propagation)
  - If the wave crosses the interface between two media it will change direction (refraction)
- $n_2(\omega)$: attenuation

The linear attenuation coefficient

- $k_2(\omega) = \frac{\omega n_2(\omega)}{c}$: attenuation of the amplitude
- Since $I \propto |E|^2$ the attenuation coefficient of the intensity is

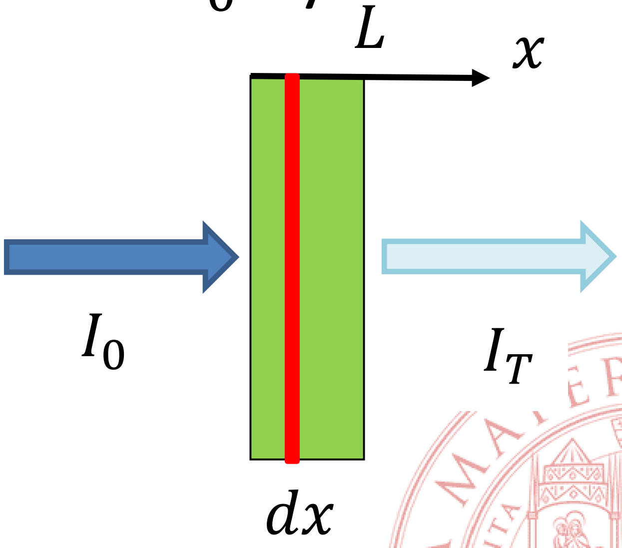
$$\mu = \frac{2\omega n_2(\omega)}{c}$$

- If the total thickness traversed is L the trasmitted intensity I_T is related to the incident one I_0 by

$$I_T = I_0 e^{-\mu L}$$

- For an infinitesimal thickness

$$\frac{dI}{I} = -\mu\, dx$$



Relation between $\varepsilon\,(\omega)$ e $n(\omega)$

- $n_1(\omega) + i n_2(\omega) = \sqrt{\varepsilon_1(\omega) + i\varepsilon_2(\omega)}$
- Therefore:
  - $\varepsilon_1 = {n_1}^2 - {n_2}^2 \,, \varepsilon_2 = 2 n_1 n_2$
  - $n_1 = \frac{\sqrt{\varepsilon_1 + |\varepsilon|}}{\sqrt{2}}, n_2 = \frac{\sqrt{-\varepsilon_1 + |\varepsilon|}}{\sqrt{2}}$

$\boldsymbol{\varepsilon(\omega)}$ and $\boldsymbol{n(\omega)}$ – weak interaction

- With $\varepsilon = 1 + \varepsilon' + i\varepsilon_2$ if ε' and $\varepsilon_2 \ll 1$: weak interaction limit (X-ray range)
- In this limit

$$n = \sqrt{1 + \varepsilon' + i\varepsilon_2} \cong 1 + \tfrac{1}{2}\varepsilon' + i\tfrac{1}{2}\varepsilon_2$$

- By convention, in the weak interaction limit the index of refraction is written as

$$n(\omega) = 1 - \delta(\omega) + i\beta(\omega)$$

$$\delta = -\tfrac{1}{2}\varepsilon', \qquad \beta = \tfrac{1}{2}\varepsilon_2$$

δ and $\beta \ll 1$

Typical values of δ and β (17.5 keV)

- δ: : 10^{-6} (plexiglas) $\rightarrow$ 10^{-5} (Au)
- β: 6×10^{-10} (plexiglas) $\rightarrow$ 1.2×10^{-6} (Au)
- $n_1 \lesssim 1$
  - Refraction is very weak
  - Difficult (but not impossible) to construct «x-ray lens»
  - Total external reflection is possible at very small grazing angles

Model dielectric functions

- Study two simple models for $\varepsilon(\omega)$ to illustrate general features of the dielectric response of matter
  - Static ($\omega = 0$) distortion polarization
  - Damped harmonic oscillator

Static distortion polarization

- A static electric field applied to a classical molecule consisting of point charges: nuclei and electrons
- *N* charges q_j with mass m_j, elastically bound to their equilibrium position by a restoring force

$$-m_j\omega_j{}^2 r_j$$

in which r_j is the displacement of the *j*–th charge in the direction of the electric field

  - *j* = 1, … *N*
  - ω_j is the resonance frequency of the *j*–th charge

Static distortion polarization

- The force acting on each charge is $q_j E$
- At equilibrium the displacement of each charge is

$$r_j{}^e = \frac{q_j}{m_j \omega_j{}^2} E$$

- The induced dipole moment is $p_j = \frac{q_j{}^2}{m_j \omega_j{}^2} E$
- The total induced dipole moment is

$$\sum_{j=1}^{N} \frac{q_j{}^2}{m_j \omega_j{}^2} E$$

Static distortion polarization

- If the (number) density of molecules is ρ the static permittivity is

$$\varepsilon(\omega = 0) = 1 + \frac{\rho}{\varepsilon_0}\sum_{j=1}^{N} \frac{{q_j}^2}{m_j{\omega_j}^2}$$

  - Always > 1
  - Reasonable behaviour as a function of masses, density and resonance frequency
    - increases with ρ
    - decreases with m_j and ω_j

Damped harmonic oscillator: approximations

- In describing the effect of an EM on a collection of charges which simulate the dielectric response of matter we make the following important approximations

1) Electric dipole approximation
   - λ » displacement of charges (neglect spatial variation of field): validity depends on spectral range
2) Neglect motion of nuclei, consider only the contribution of electrons
   - Justified in view of the great difference in mass
3) Neglect effect of force $q\left(\vec{v} \times \vec{B}\right)$ due to magnetic field
   - Justified since it is weaker than qE
4) Neglect «radiation damping» due to emission of radiation
   - An accelerated charge will always emit radiation: it will thus lose energy
   - This effect is often considered as due to a «self – force».

Damped harmonic oscillator

- First consider a single electron
  - equilibrium position in the origin, displacement r at time t
  - charge $-e$ and mass m
  - elastically bound to its equilibrium position by a restoring force

$$-m{\omega_0}^2 r$$

    - ω_0 is the resonant frequency (frequency of unforced oscillations)

  - subject to a dissipative viscous force

$$-m\gamma\frac{dr}{dt}$$

Damped harmonic oscillator

- The external electric field is written as

$$E_0e^{-i\omega t}$$

- The classical equation of motion is

$$-eE_0e^{-i\omega t} - m{\omega_0}^2r - m\gamma\frac{dr}{dt} = m\frac{d^2r}{dt^2}$$

Damped harmonic oscillator

- We seek a solution of the type $r(t) = R(\omega)e^{-i\omega t}$
- We easily find

$$R(\omega) = \frac{e}{m(\omega^2 - \omega_0{}^2 + i\gamma\omega)} E_0$$

- The induced dipole moment is

$$p(\omega)e^{-i\omega t} = \frac{e^2}{m(\omega_0{}^2 - \omega^2 - i\gamma\omega)} E_0 e^{-i\omega t}$$

An atom as an ensemble of oscillators

- Model an atom as composed of *Z* electrons arranged in *M* shells with equal characteristic ω_j, γ_j
- Each shell contains f_j electrons, with

$$\sum_{j=1}^{M} f_j = Z$$

An atom as an ensemble of oscillators

- Following the single electron result, the atomic dipole moment induced by the external field is

$$p(\omega) = \frac{e^2}{m} \sum_{j=1}^{M} \frac{f_j}{\left({\omega_j}^2 - \omega^2 - i\gamma_j \omega\right)} E_0$$

- f_j is known as the «oscillator strength»: it determines the contribution of the *j*–th shell to the dipole moment

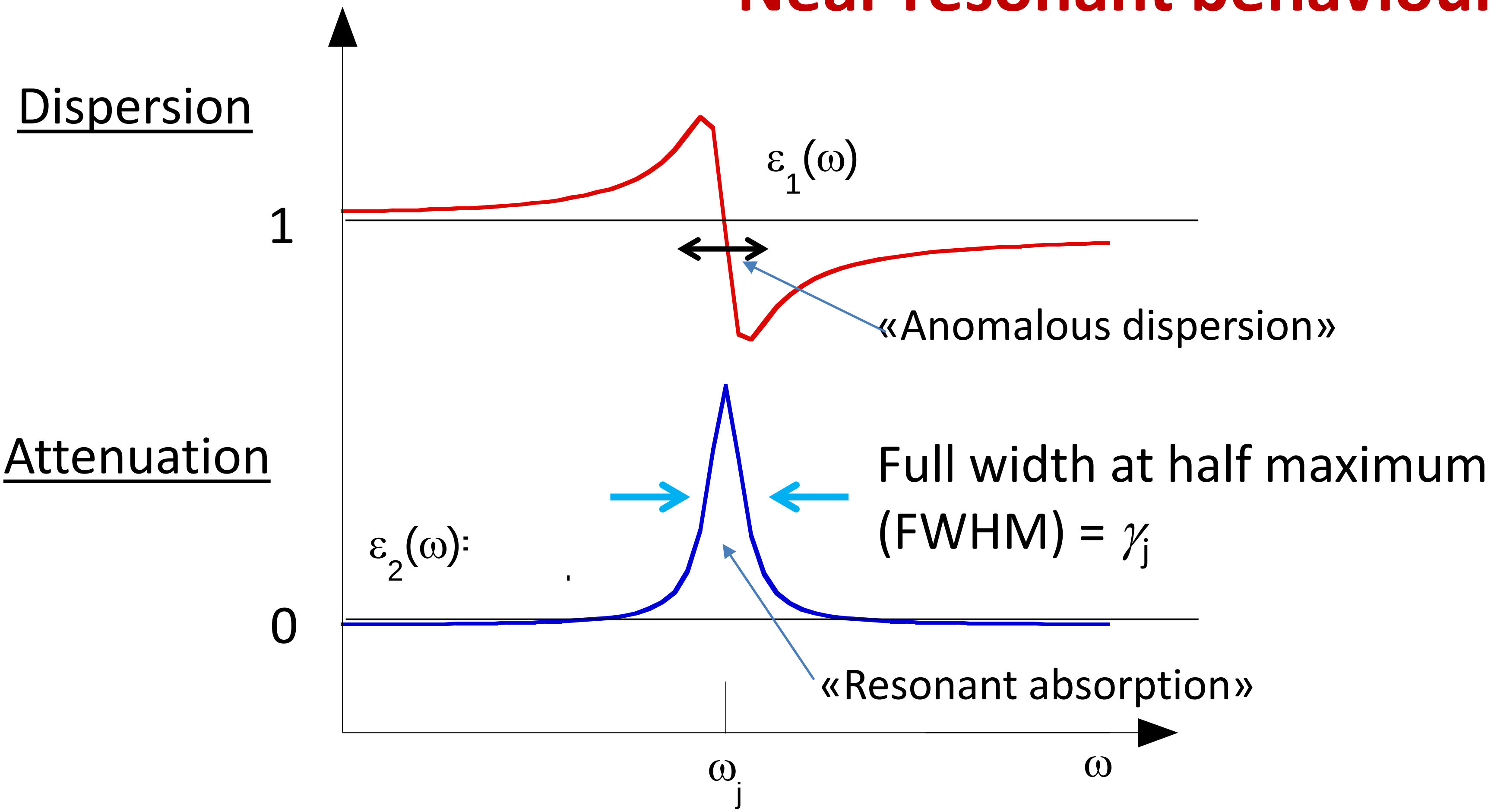
A medium as an ensemble of polarizable atoms

- If the (number) density of identical atoms is ρ , we find

$$\varepsilon(\omega) = 1 + \frac{\rho e^2}{\varepsilon_0 m} \sum_{j=1}^{M} \frac{f_j}{\left(\omega_j{}^2 - \omega^2 - i\gamma_j\omega\right)}$$

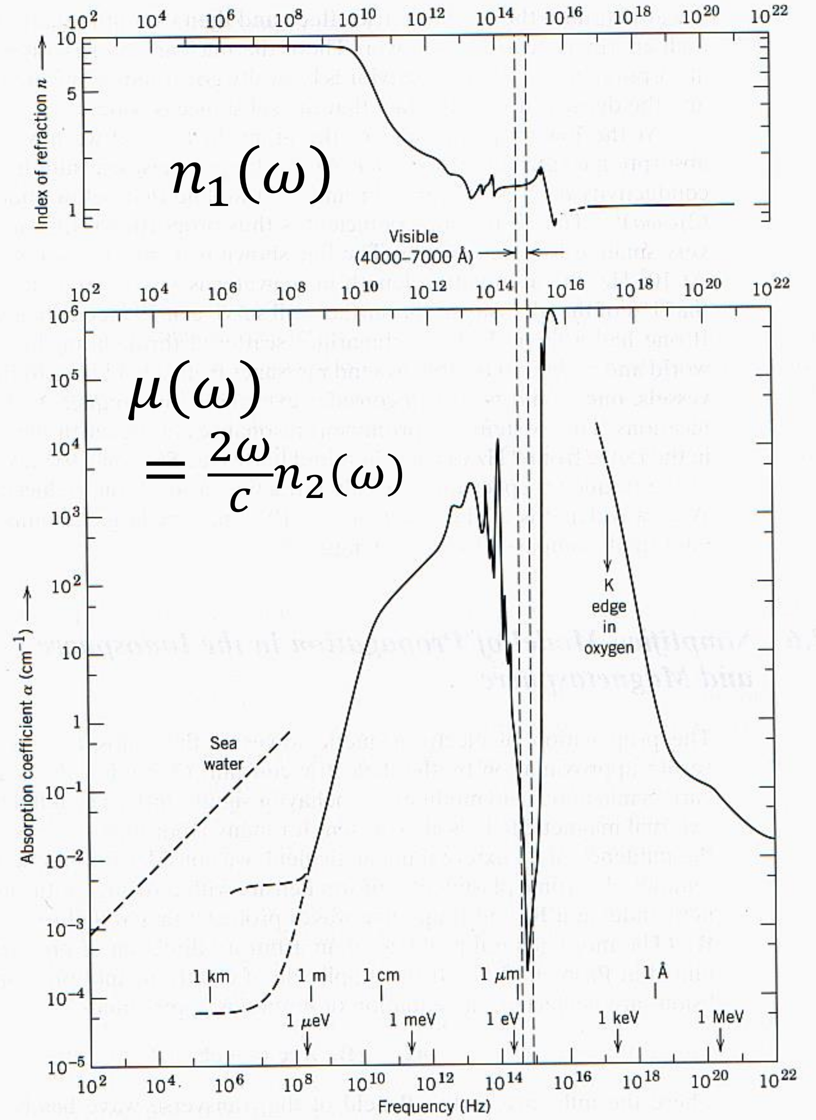
- $\varepsilon_1(\omega) = 1 + \frac{\rho e^2}{\varepsilon_0 m} \sum_{j=1}^{M} \frac{f_j\left(\omega_j{}^2 - \omega^2\right)}{\left[\left(\omega_j{}^2 - \omega^2\right)^2 + \left(\gamma_j\omega\right)^2\right]}$
- $\varepsilon_2(\omega) = \frac{\rho e^2}{\varepsilon_0 m} \sum_{j=1}^{M} \frac{f_j\gamma_j\omega}{\left[\left(\omega_j{}^2 - \omega^2\right)^2 + \left(\gamma_j\omega\right)^2\right]}$
- Kramers – Heisenberg or electric dipole dielectric function

Near resonant behaviour



- A simple model which reproduces well the response of polarizable media in many frequency ranges

The dielectric response of liquid water as a function of frequency



$n_1(\omega)$

$$\mu(\omega) = \frac{2\omega}{c} n_2(\omega)$$

Figure 7.9 The index of refraction (top) and absorption coefficient (bottom) for liquid water as a function of linear frequency. Also shown as abscissas are an energy scale (arrows) and a wavelength scale (vertical lines). The visible region of the frequency spectrum is indicated by the vertical dashed lines. The absorption coefficient for seawater is indicated by the dashed diagonal line at the left. Note that the scales are logarithmic in both directions.

Jackson, Classical Electrodynamics
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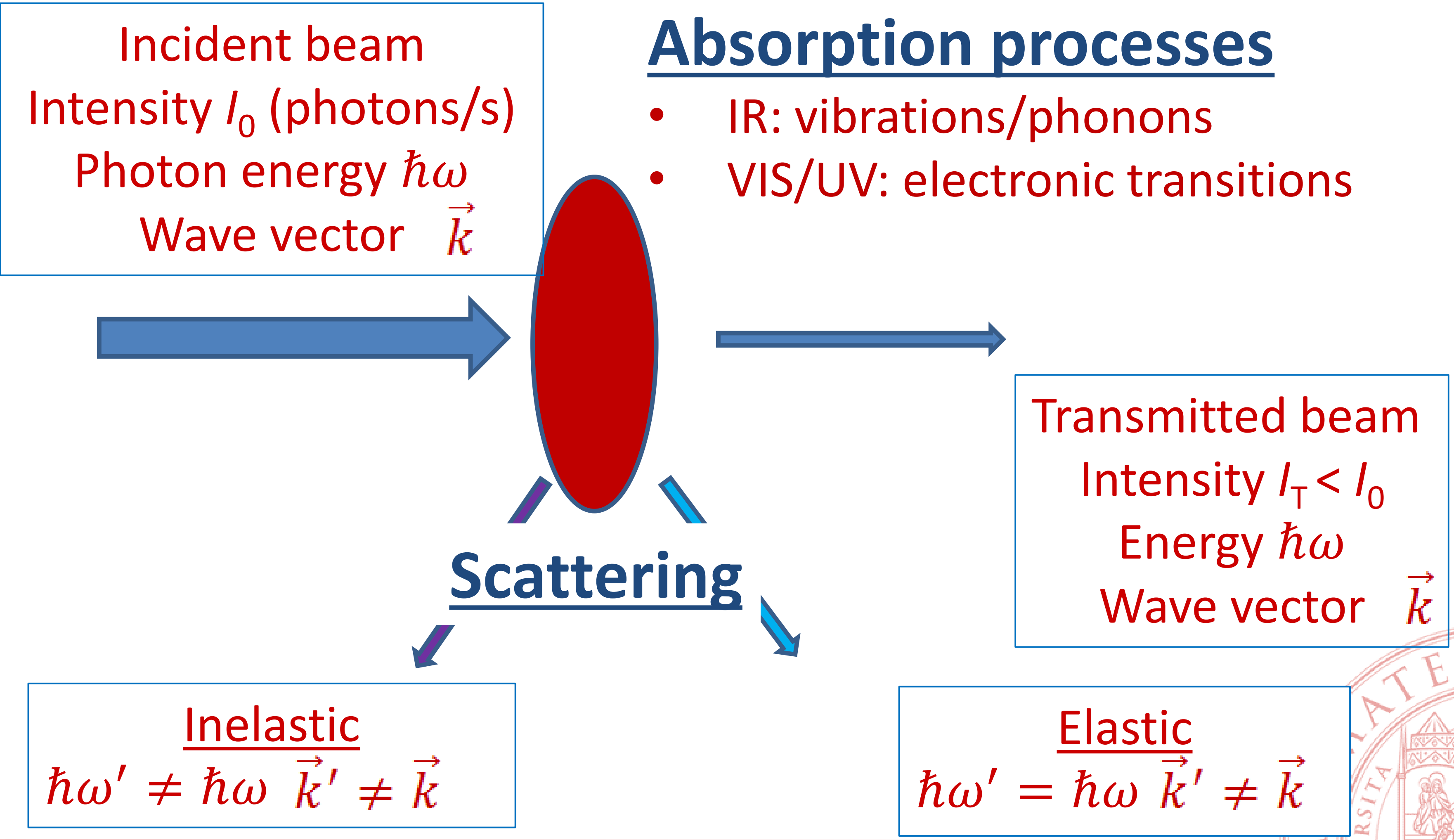
Interaction: atomic approach (IR to vis/UV)



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

Absorption processes

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

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

Scattering

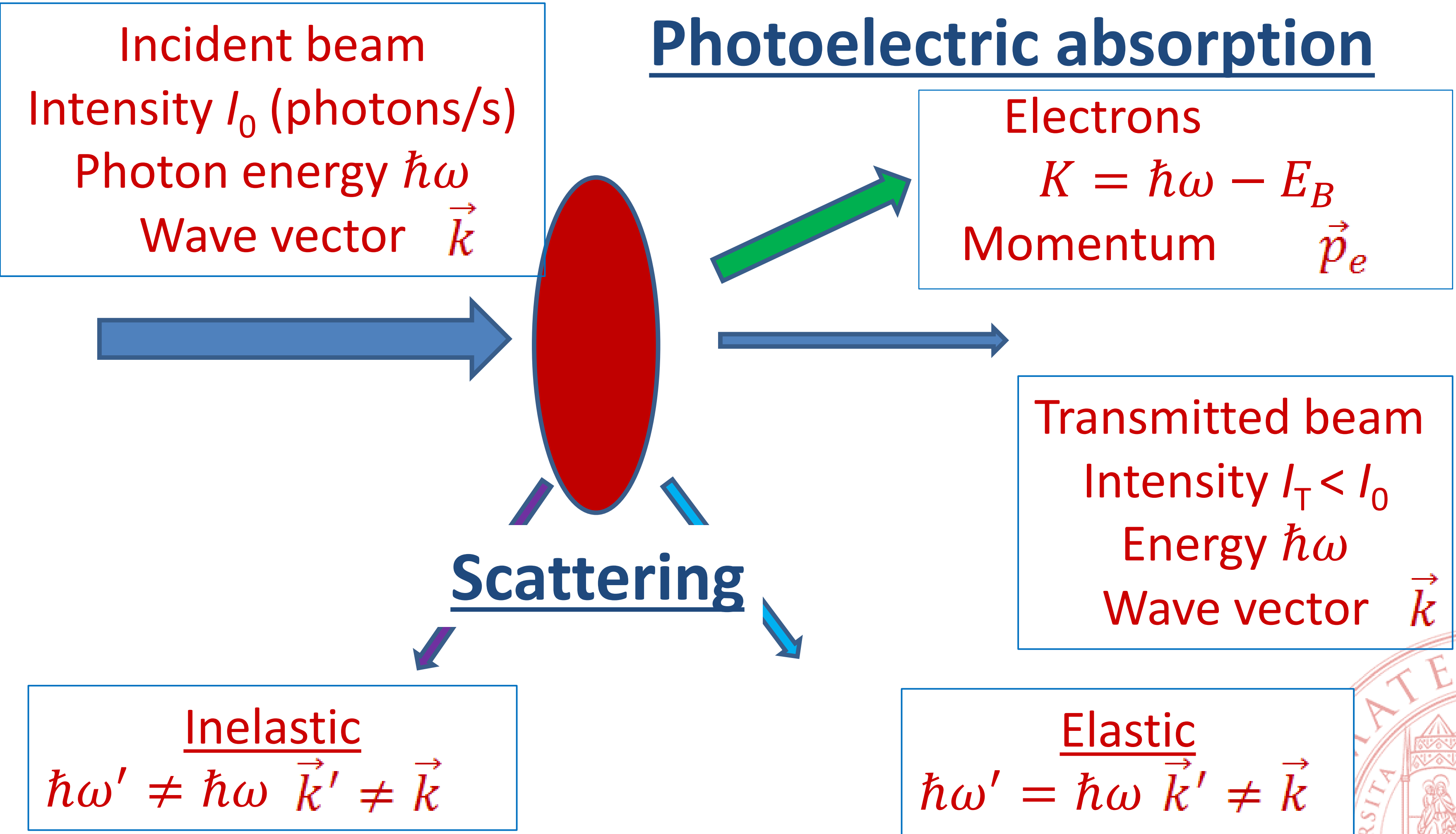
Inelastic

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

Elastic

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

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 $\vec{p}_e$

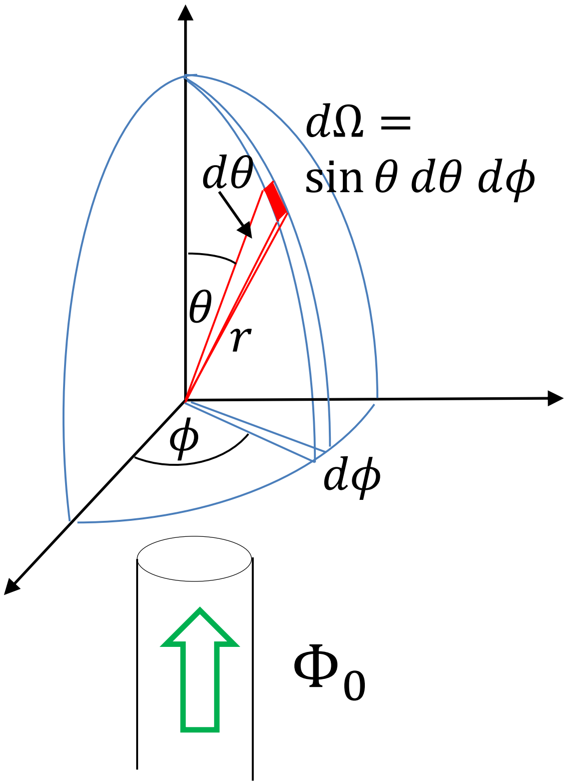
Transmitted beam
Intensity $I_T < I_0$
Energy $\hbar\omega$
Wave vector $\vec{k}$

Scattering

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

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

Cross section



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 $d\Omega$

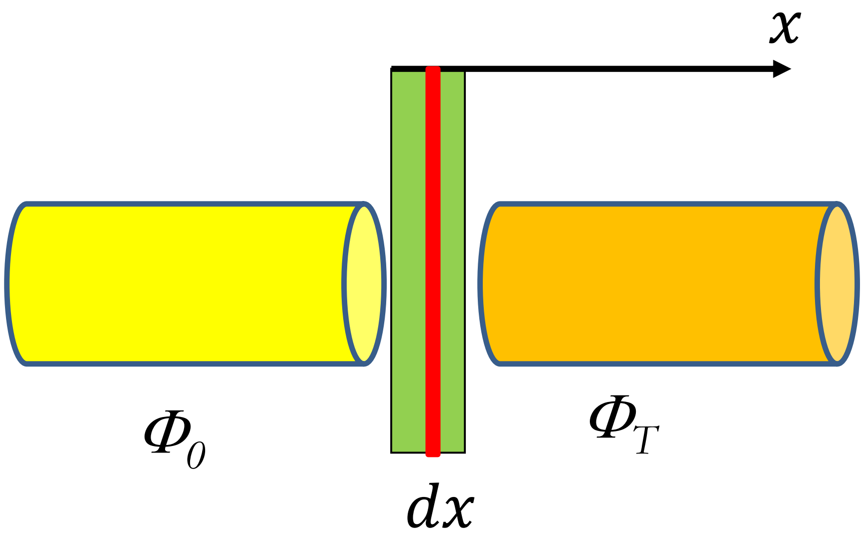
$$dN = \Phi_0 d\sigma = \Phi_0 \left(\frac{d\sigma}{d\Omega}\right) d\Omega$$

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

$[\sigma]$ = 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

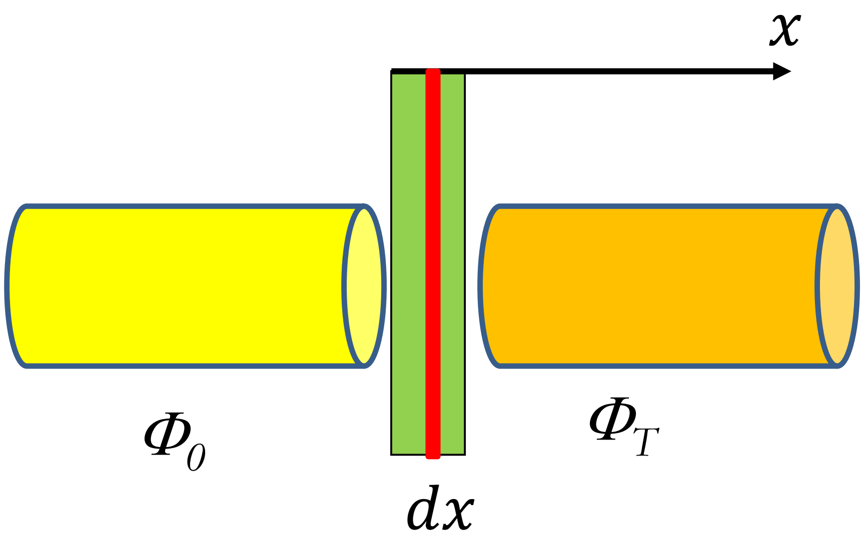


A homogeneous sample composed by identical atoms with density ρ (atoms/cm^3)

- 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

$$\begin{aligned} dN &= \Phi\,\sigma\,dn \\ &= \Phi\,\sigma\,\rho A\,dx \\ &= I\,\sigma\rho\,dx \end{aligned}$$

Cross section & linear attenuation coefficient



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

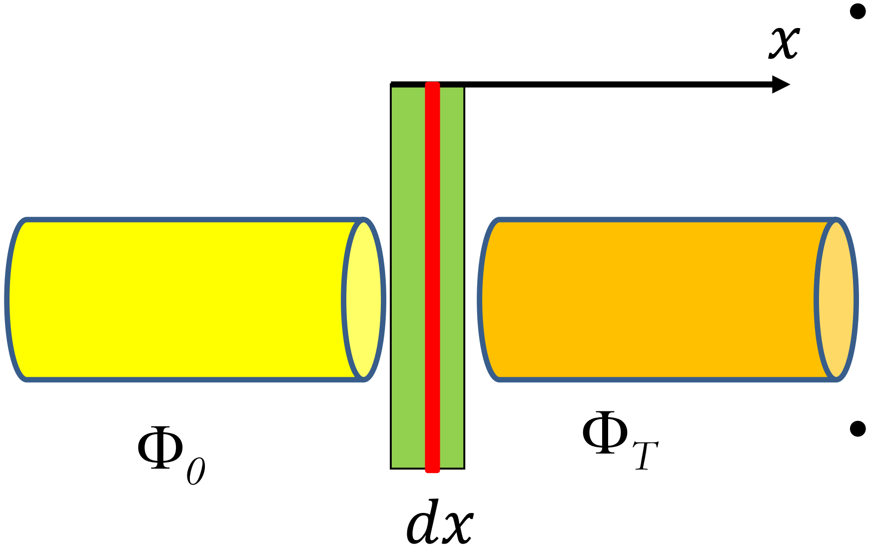
$$dN = -dI$$

$$dI = -I\,\sigma\rho\,dx$$

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

$$\boxed{\mu = \sigma\rho}$$

Cross section & linear attenuation coefficient



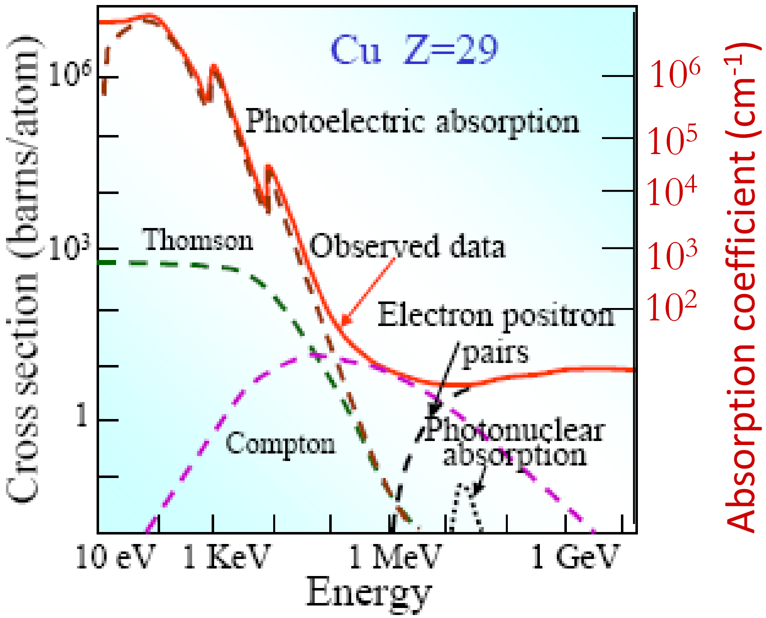
- If the sample is composed of different atoms with densities ρ_i and cross sections σ_i then

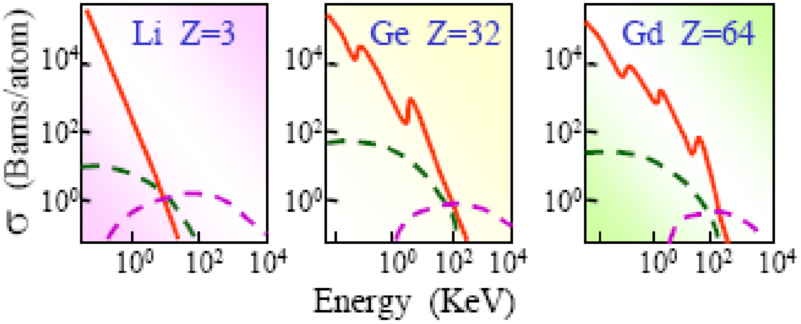
$$\mu = \sum_i \rho_i \sigma_i$$

- Cross sections are also expressed as mass attenuation coefficients, expressed as cm^2/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

$$\mu^{-1} \sim 10^{-5}\, cm \;=\; 10\ \mu m$$

Elastic scattering from 1 free electron (Thomson)

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

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

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

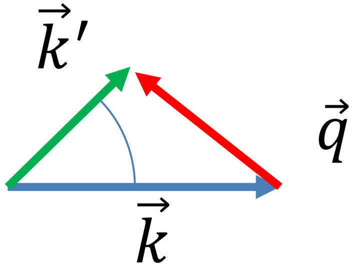
“Thomson scattering length”
or “classical electron radius”

Angle between the polarization
vector and the
scattered wave vector

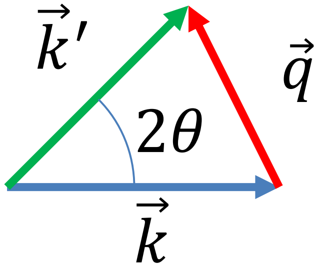
The exchanged wave vector

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

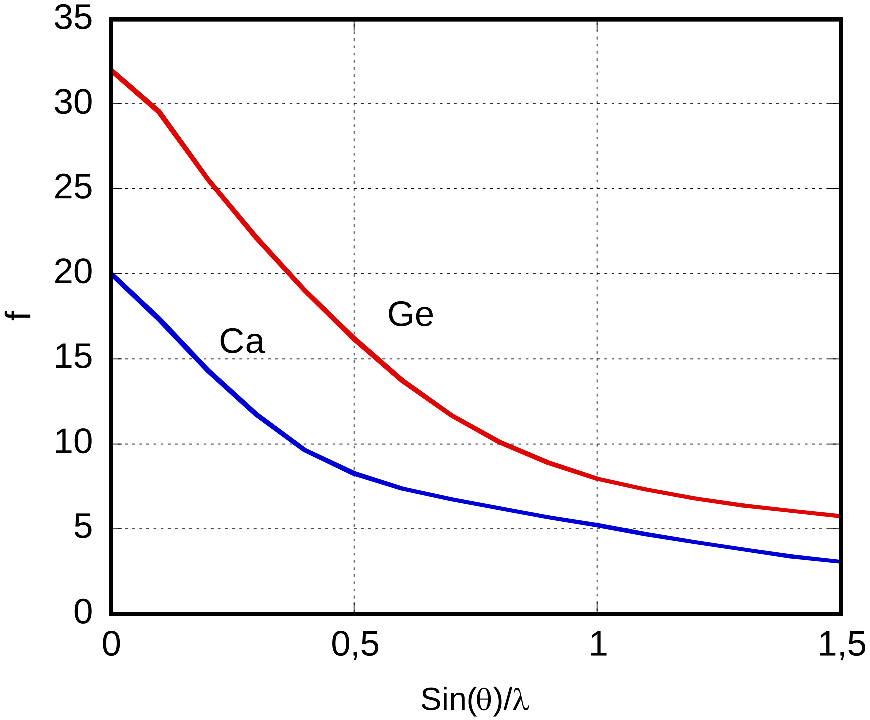
$$E(\vec{r},t) = -E_0 r_0 \left(\frac{e^{i(kr-\omega t)}}{r}\right) f(Z,\theta)\sin\theta$$

- $f(Z,\theta)$ is the «atomic form factor» or «scattering amplitude»; no physical dimensions

Elastic scattering from one atom

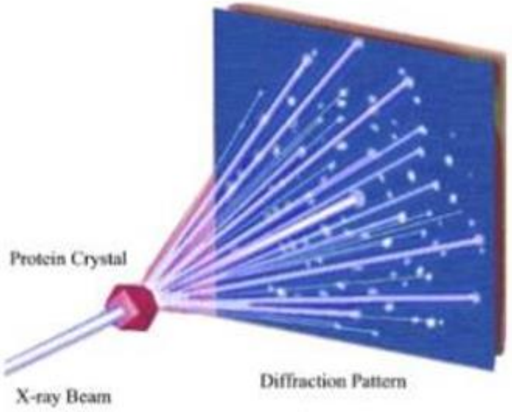
- The differential cross section $\frac{d\sigma}{d\Omega} = \frac{d\sigma_{electron}}{d\Omega} |f(Z,\theta)|^2$

- *f* depends quasi linearly on *Z*
- $f\,(\theta = 0) = Z$



X-ray diffraction

- Elastic X-ray scattering is at the base of X-ray scattering (XRD), a class of methods which are the premiere experimental methods to determine the atomic structure of condensed matter
    - Measure the intensity of x-ray beams scattered by a sample as a function of their deviation



Diffraction Process

Inelastic scattering

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

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

$$\lambdabar_c = \frac{\hbar}{mc} \cong 3.86\times 10^{-13}\,\mathrm{m},$$

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

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

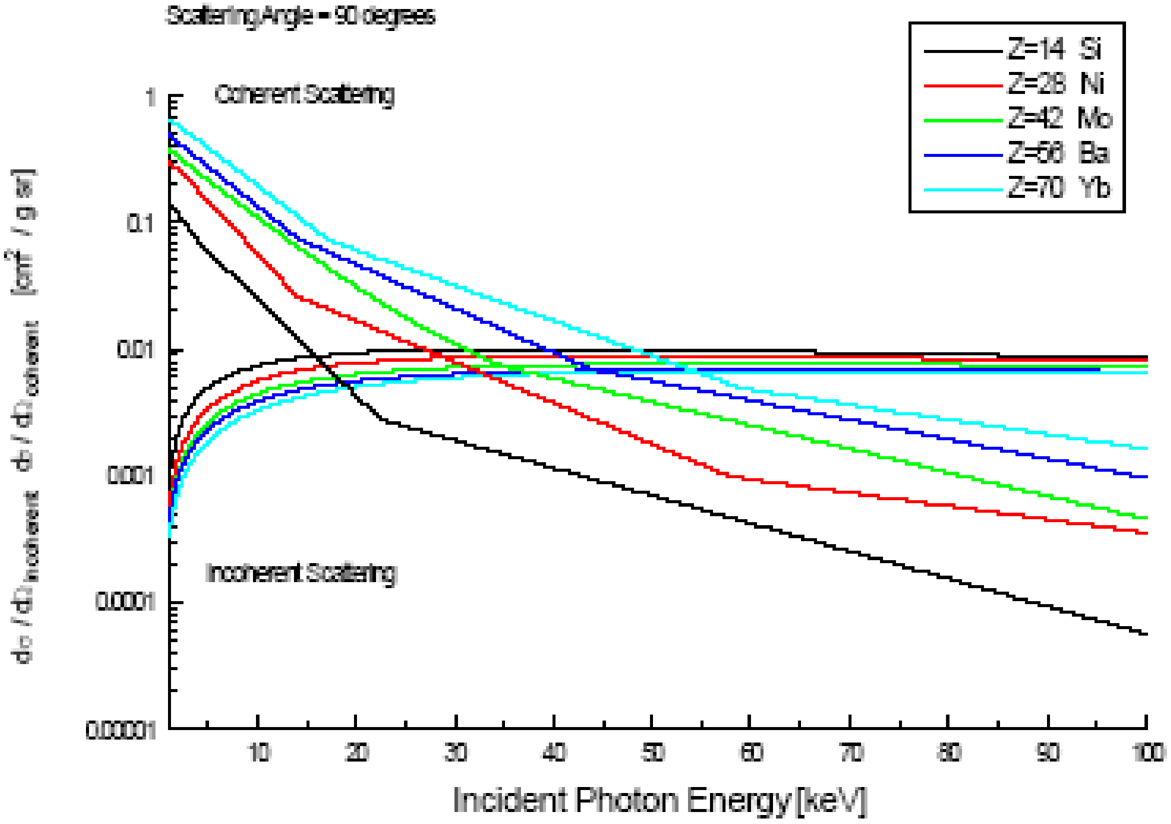
$$r_0 = \left(\frac{e^2}{4\pi\varepsilon_0\hbar c}\right)\left(\frac{\hbar}{mc}\right) = \alpha\lambdabar_c = \alpha^2 a_0.$$

Compton cross section

- The Klein Nishina formula

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

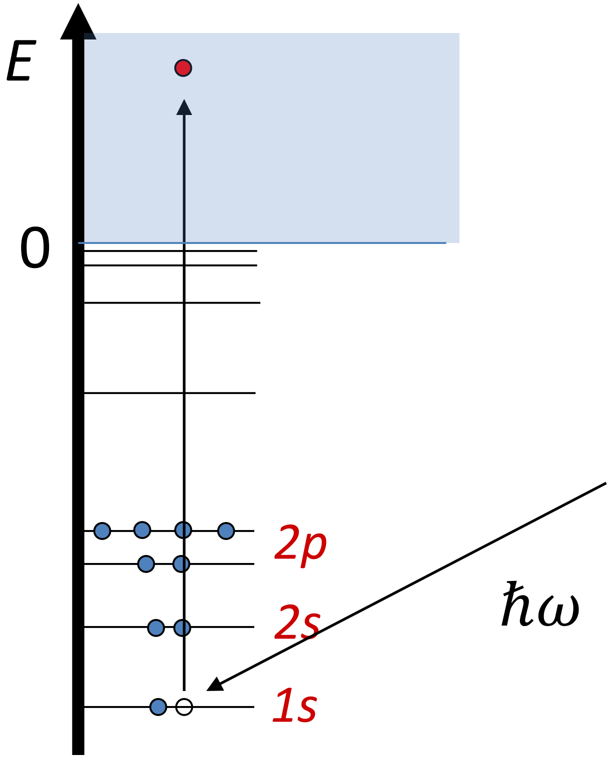
Thomson and Compton scattering



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

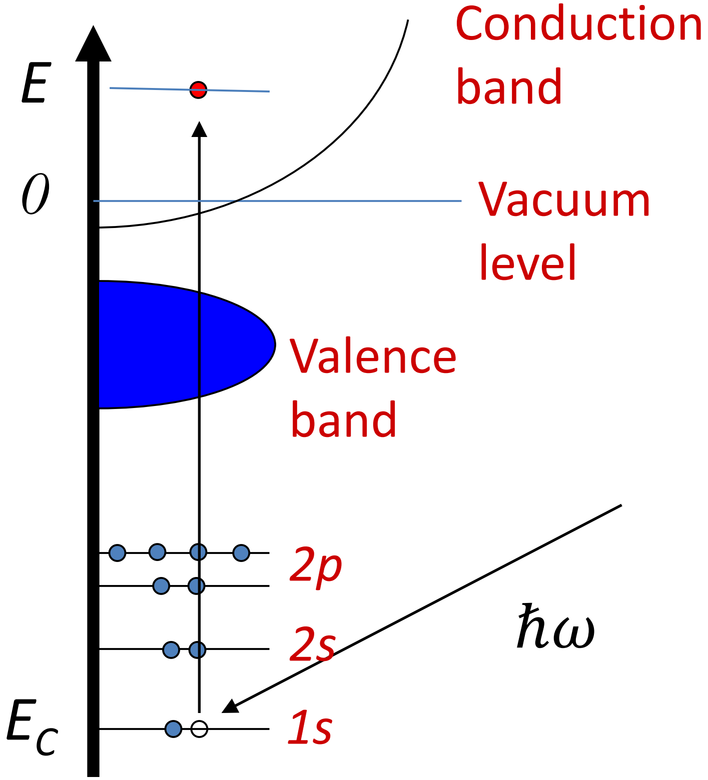
- A photon is absorbed and gives its energy to an electron.
- The electron makes a transition to
  - A bound state (excitation) <u>or</u>
  - An unbound state (ionization): a photoelectron is created



Energetics of photoelectric absorption in an atom (ionization)

Photoelectric absorption in solids

- In solids valence electrons form bands
  - 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:

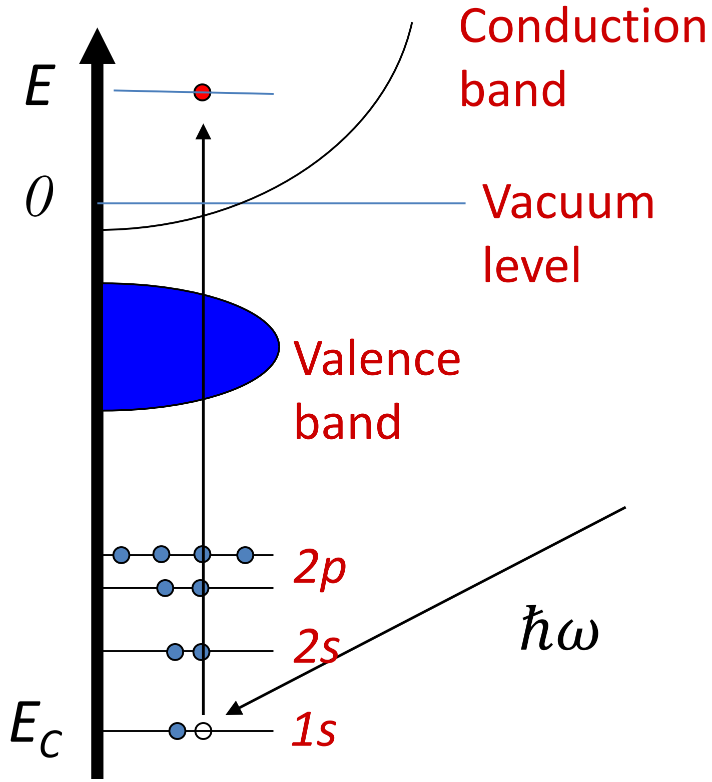
$$\text{Initial state energy} = \hbar\omega + E_C \ (E_C < 0)$$

$$\text{Final state energy} = K$$

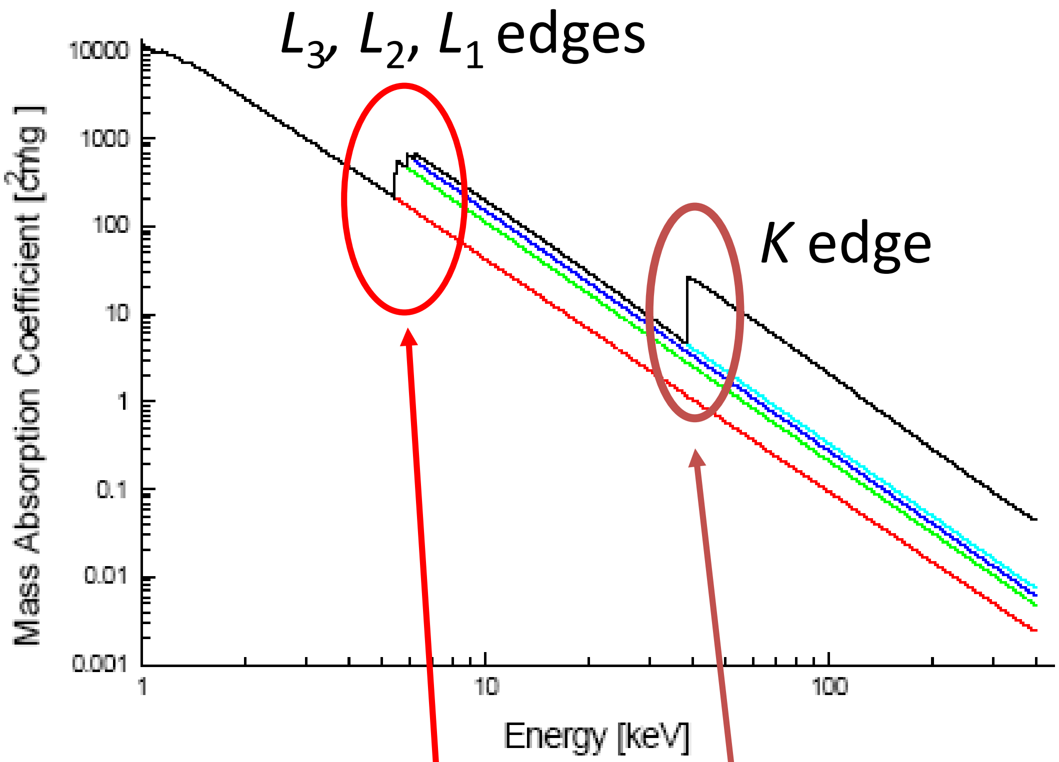
$$K = \hbar\omega + E_C$$

$$E_C = -E_B \ \text{(binding energy)}$$

$$K = \hbar\omega - E_B$$



Absorption coefficient: energy dependence



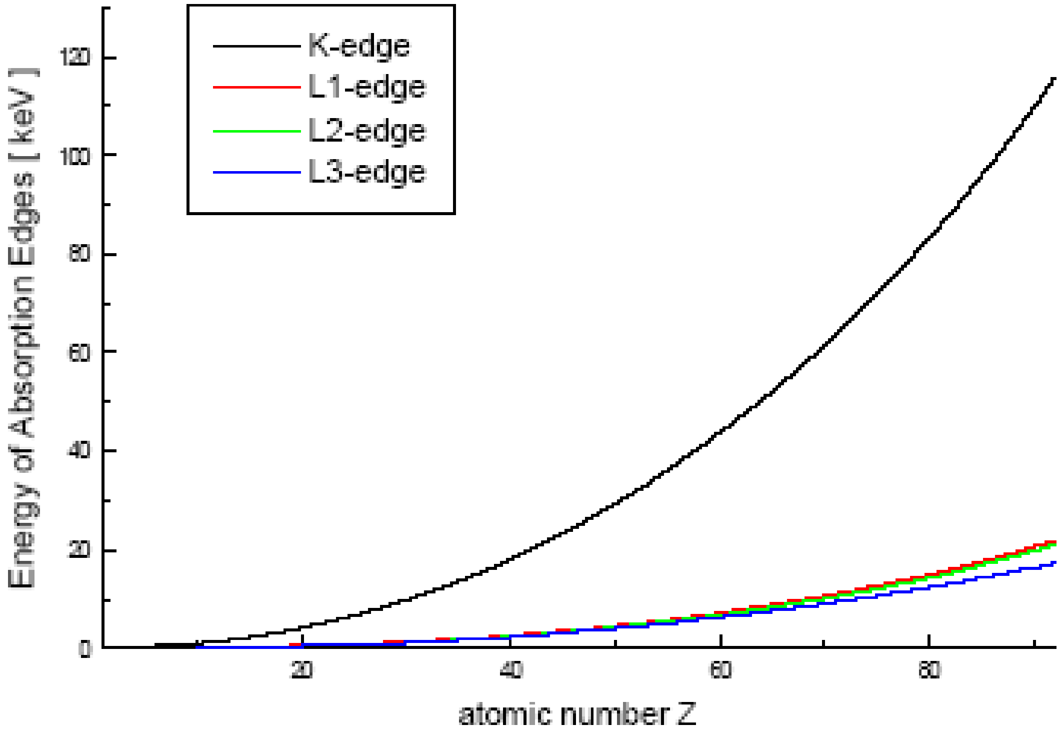
L_3, L_2, L_1 edges

K edge

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

Absorption edges

Z dependence of absorption edges

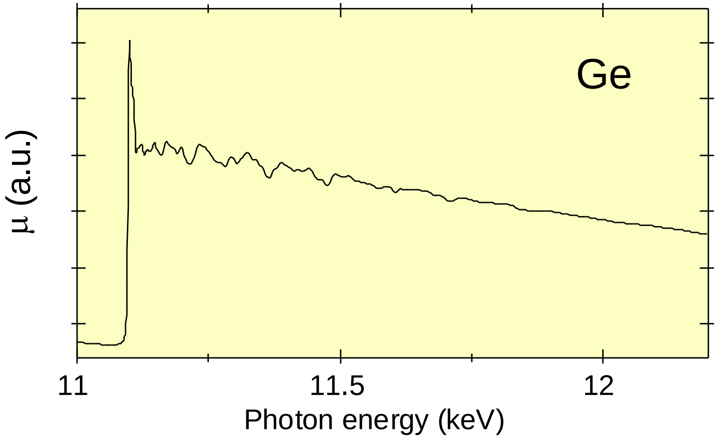


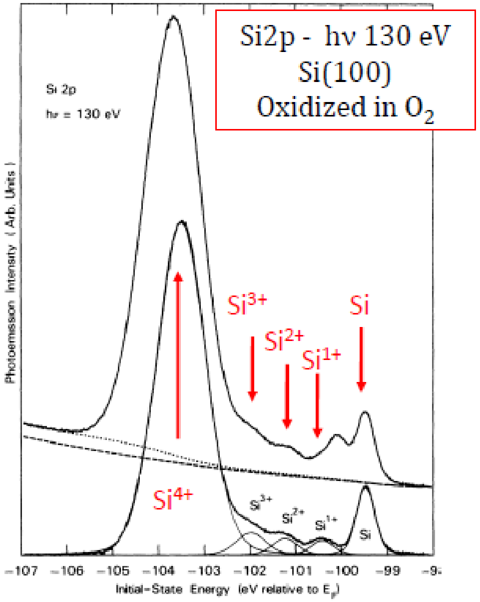
Energy of photoelectric absorption edges versus atomic number of the elements.

- 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

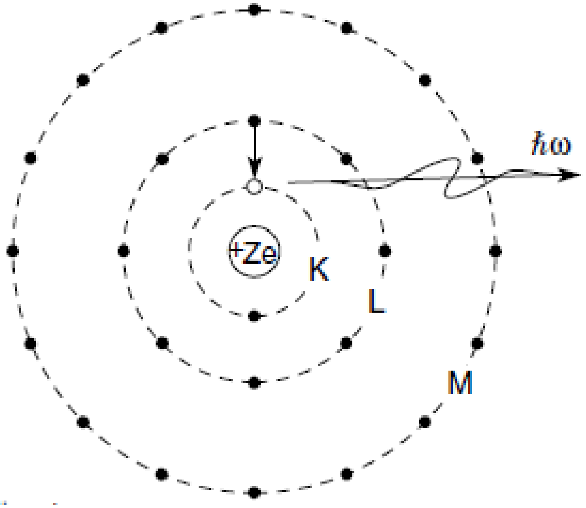
Photoemission and X-ray absorption spectroscopy

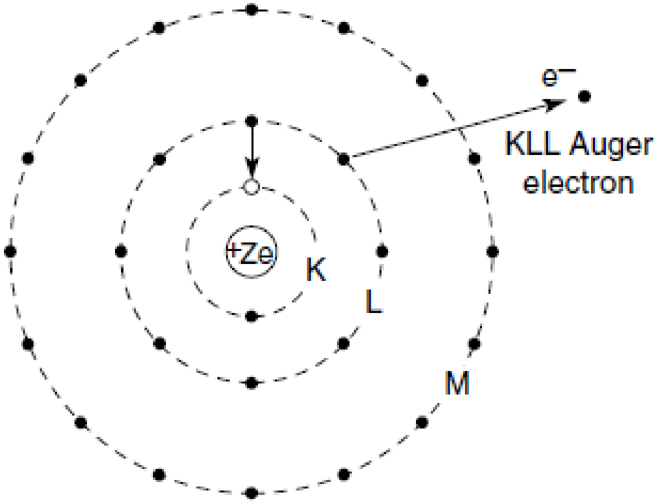
- Photoelectric absorption is at the base of
  - Photoemission spectroscopy (PES, UPS, XPS), the premiere experimental method to determine electronic structure
    - measure the spectrum of electrons emitted from a sample
  - X-ray absorption spectroscopy (XAS, XAFS), the premiere experimental method to determine local atomic and electronic structure with chemical sensitivity
    - measure the photon energy dependence of the fine structure of the attenuation coefficient





Photoelectric absorption: de-excitation

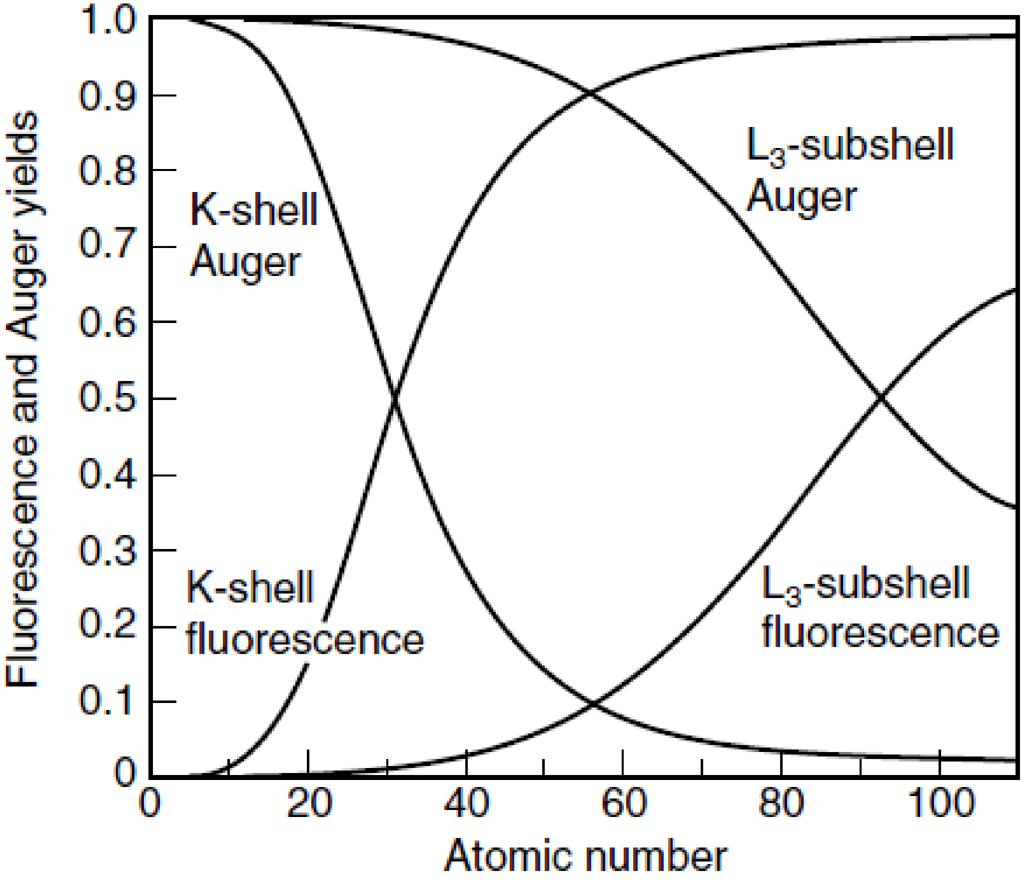




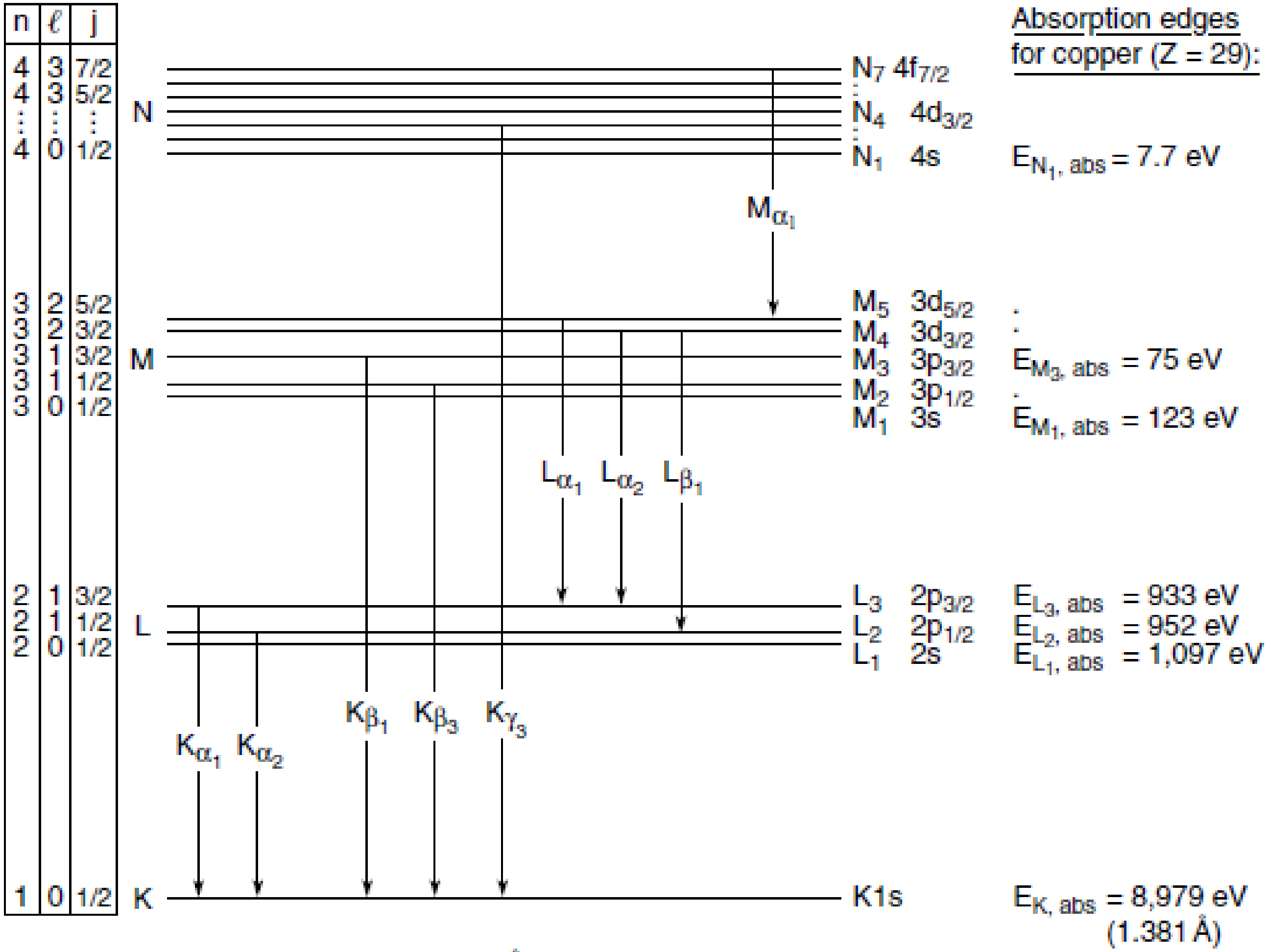
Emission of "characteristic" or "fluorescence" X-rays,
also known as "emission lines"
$\hbar\omega_f = E_L - E_K$

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

Probability for the two processes



Nomenclature for X-ray emission lines



Absorption edges for copper (Z = 29):

$E_{N_1,\text{ abs}} = 7.7$ eV

$E_{M_3,\text{ abs}} = 75$ eV

$E_{M_1,\text{ abs}} = 123$ eV

$E_{L_3,\text{ abs}} = 933$ eV

$E_{L_2,\text{ abs}} = 952$ eV

$E_{L_1,\text{ abs}} = 1{,}097$ eV

$E_{K,\text{ abs}} = 8{,}979$ eV (1.381 Å)

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

Cu L_{α_1} = 930 eV
Cu L_{α_2} = 930 eV
Cu L_{β_1} = 950 eV

Energy of emission lines

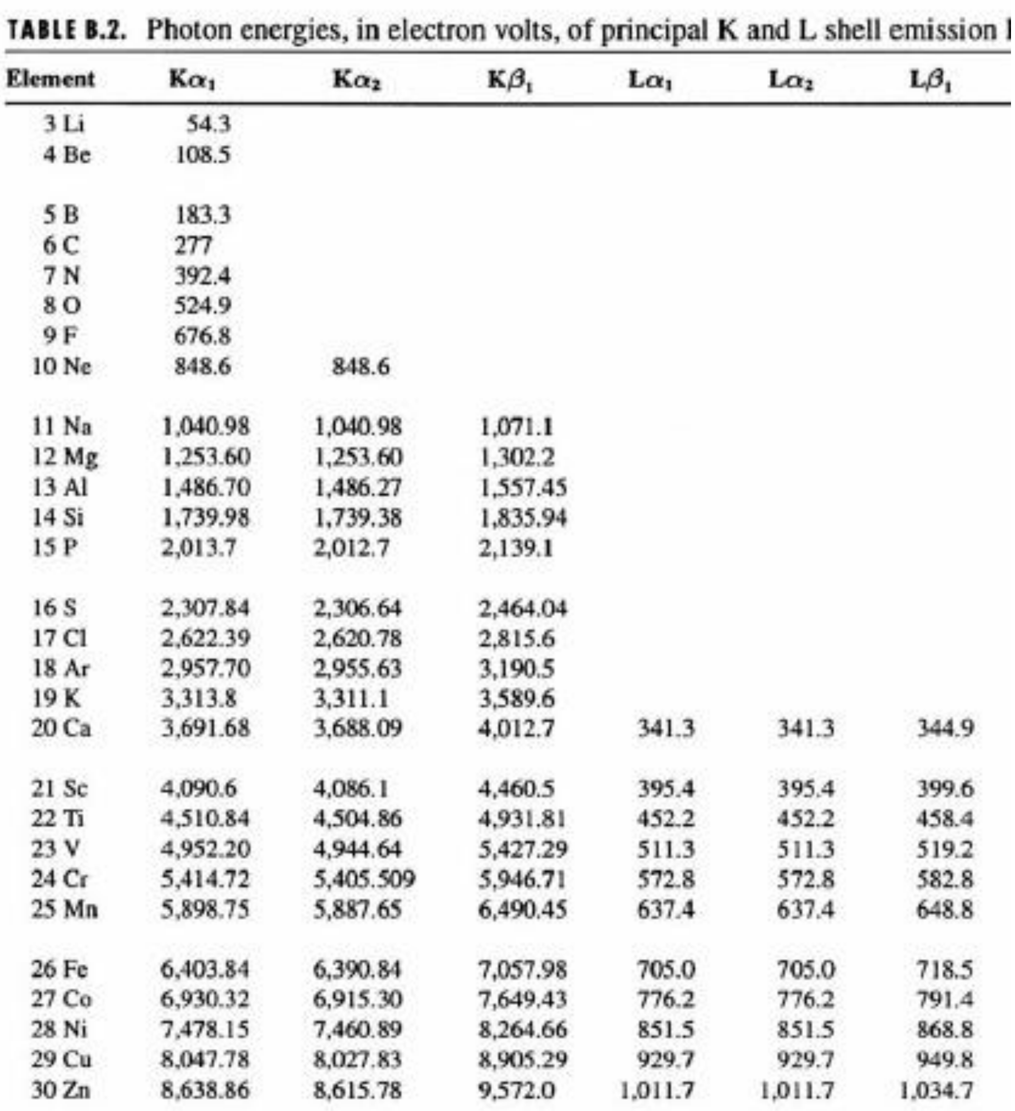
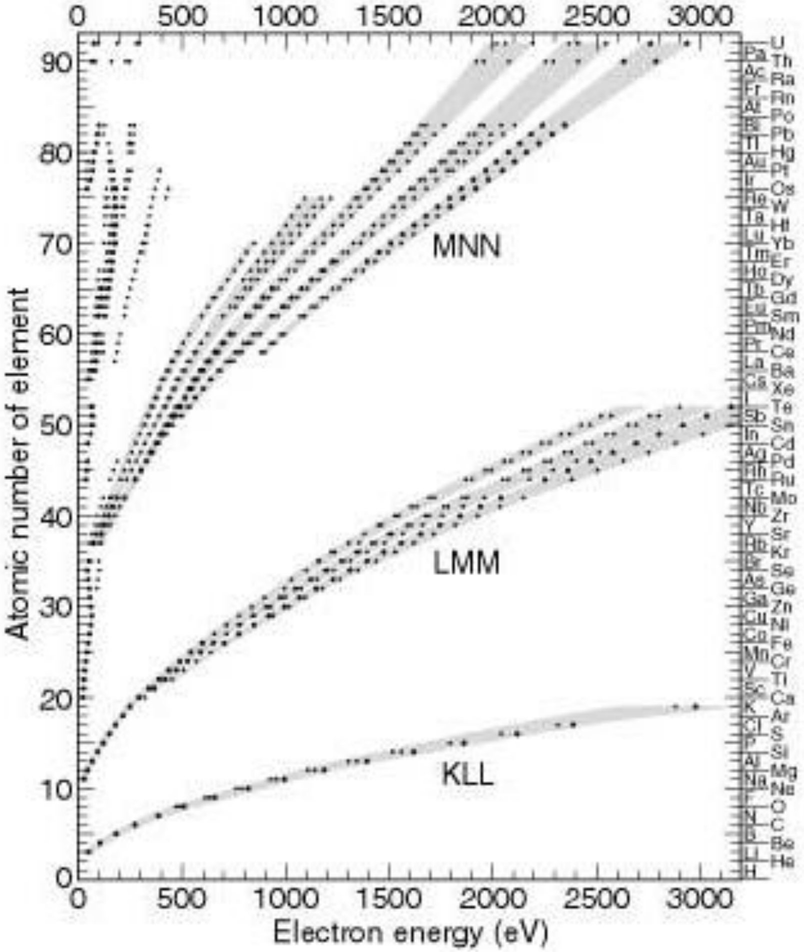


TABLE B.2. Photon energies, in electron volts, of principal K and L shell emission

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

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

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

Interaction between EM radiation and hydrogen-like atoms: semiclassical theory

References

- B.H. Bransden & C.J. Joachain, “Physics of atoms and molecules”, 2nd edition, Pearson Education – Prentice Hall (2003)
  Chapter 4 (except 4.4), in parts

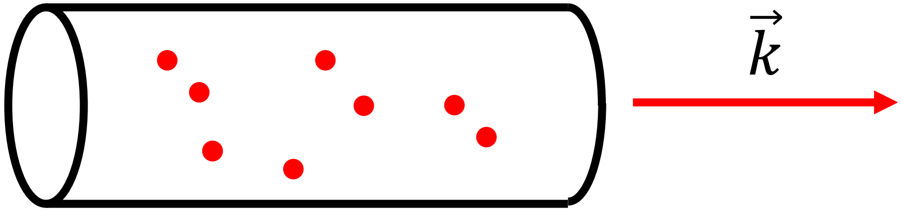
Introduction

- Semi-classical theory of the interaction between radiation and hydrogen – like atoms.
- Semi-classical since
  - Radiation is treated as wave
  - Atom is treated with quantum mechanics
- This approach is adequate since it can describe scattering and stimulated absorption and emission
  - It cannot describe spontaneous emission
- Full quantum treatment requires quantization of EM field: more formal
- All phenomena occurring in hydrogen – like atoms are present in many electron ones

A monochromatic photon beam

- Even within the semi-classical approach we will find that absorption and emission of energy between the beam and atoms occurs in quanta of magnitude $\hbar\omega$, that is photons
- Even scattering will be describe in terms of photons.
- Therefore: extend definitions of intensity and flux in particle – like terms.

Monochromatic radiation beam: definitions



$N =$
(Number of photons which cross a surface perpendicular to $\vec{k}$)/ (unit time)

I : Intensity = (Energy crossing the surface) / (unit time)

Φ : Photon flux =
(Number of photons crossing the surface) / (unit time × area)

F: Energy flux= (Energy crossing the surface) / (unit time × area)

$$I = N\hbar\omega \qquad F = \frac{N}{A}\hbar\omega \qquad F = \Phi\ \hbar\omega$$

Interaction between a wave and an atom

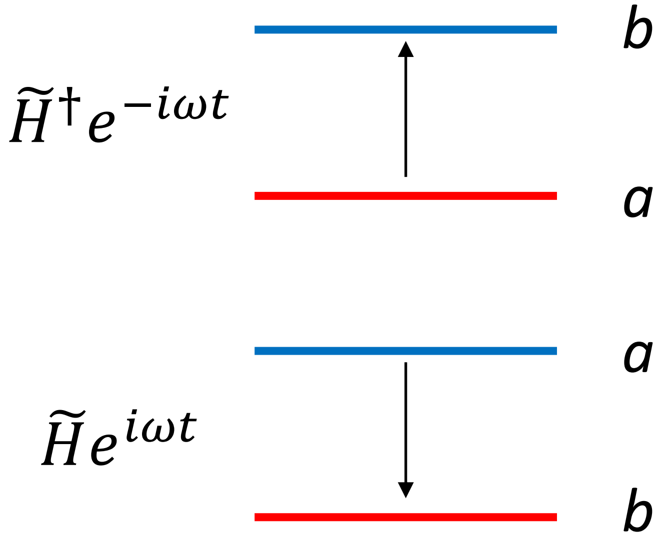
- The interaction is treated with time dependent pertubation theory
- The unperturbed atom's Hamiltonian is H_o
- The pertubation is an EM wave and the time dependent interaction Hamiltonian is $H'(t)$
- The EM wave has a harmonic dependence on time, thus it is expressed by an Hermitian operator of the type

$$H'(t) = \widetilde{H} e^{i\omega t} + \widetilde{H}^{\dagger} e^{-i\omega t}$$

in which $\widetilde{H}$ is an operator which does not depend on time

Time dependent perturbation theory

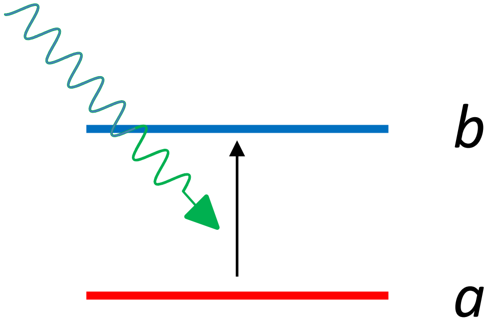
- The unpertubed atom has eigenstates labelled «a» and «b» with energies ${E_a}^0$ and ${E_b}^0$
  - Often called the «initial» and «final» states
- It can be demonstrated that the transition probability is maximized for two «resonant» conditions deriving from different terms in $H'(t)$



$$\boxed{\hbar\omega = {E_b}^0 - {E_a}^0}$$

$$\boxed{\hbar\omega = {E_a}^0 - {E_b}^0}$$

Time dependent perturbation theory

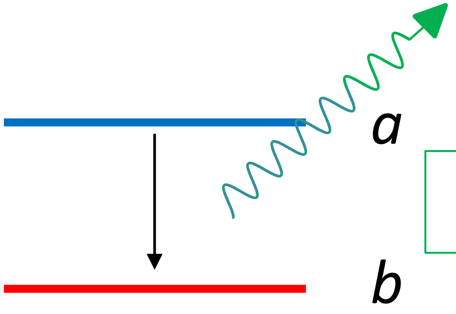


$$\tilde{H}^{\dagger} e^{-i\omega t}$$

$$\boxed{\hbar\omega = E_b{}^0 - E_a{}^0}$$

<u>Stimulated absorption</u>

- A photon of energy $\hbar\omega$ is absorbed by the atom
- The atom makes a transition from *a* to *b*



$$\tilde{H} e^{i\omega t}$$

$$\boxed{\hbar\omega = E_a{}^0 - E_b{}^0}$$

<u>Stimulated emission</u>

- A photon of energy $\hbar\omega$ is emitted from the atom
- The atom makes a transition from *a* to *b*

Fermi’s golden rule: transition to discrete states

- For the case of absorption it can be demonstrated that, to first order in the pertubation, the transition probability per unit time for transitions between discrete levels *a* and *b* is

$$W_{ba} = \frac{2\pi}{\hbar} \left|\widetilde{H}^{\dagger}{}_{ba}\right|^{2} \delta\left(E_{b}{}^{0} - E_{a}{}^{0} - \hbar\omega\right)$$

- $\widetilde{H}^{\dagger}{}_{ba} = \langle b|\widetilde{H}^{\dagger}|a\rangle$ is the <u>matrix element</u> of the perturbation
- The Dirac δ function is an expression of the <u>conservation of energy</u>
  - Apparently unphysical: the probability is always 0 except at resonance in which case it diverges. This will be resolved by introducing the concept of <u>lifetime</u> of the eigenstates

Fermi's golden rule: transition to continuum states

- For absorption with final states *b* in the continuum it can be shown that

$$W_{ba} = \frac{2\pi}{\hbar} \left| \widetilde{H}^{\dagger}{}_{ba} \right|^2 \rho\left({E_b}^0\right)$$

with the condition that ${E_b}^0 = {E_a}^0 + \hbar\omega$

- $\rho(E)$ is the density of states, such that the number of states between E and $E + dE$ is

$$dN = \rho(E)\, dE$$

The classical EM field

- The EM field is described in terms of the vector and scalar potentials $\vec{A}(\vec{r},t)$ and $\phi(\vec{r},t)$

;

$$\vec{E}(\vec{r},t) = -\vec{\nabla}\varphi(\vec{r},t) - \frac{\partial\vec{A}(\vec{r},t)}{\partial t}$$

Electric field

$$\vec{B}(\vec{r},t) = \vec{\nabla} \times \vec{A}(\vec{r},t).$$

Magnetic induction field

A plane monochromatic EM wave

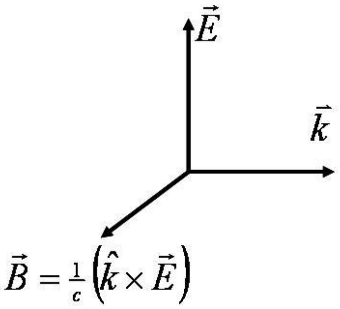
$$\vec{A}(\vec{r},t) = \hat{\varepsilon}\left[A(\omega)e^{i(\omega t-\vec{k}\cdot\vec{r})} + A^{*}(\omega)e^{-i(\omega t-\vec{k}\cdot\vec{r})}\right]$$

$$\vec{E}(\vec{r},t) = -\frac{\partial\vec{A}(\vec{r},t)}{\partial t} = i\omega\hat{\varepsilon}\left[-A(\omega)e^{i(\omega t-\vec{k}\cdot\vec{r})} + A^{*}(\omega)e^{-i(\omega t-\vec{k}\cdot\vec{r})}\right]$$

$$\vec{B}(\vec{r},t) = \frac{1}{c}\left(\hat{k}\times\vec{E}\right)$$

$$= i\left(\vec{k}\times\hat{\varepsilon}\right)\ \left[-A(\omega)e^{i(\omega t-\vec{k}\cdot\vec{r})} + A^{*}(\omega)e^{-i(\omega t-\vec{k}\cdot\vec{r})}\right]$$

- The polarization is defined by $\hat{\varepsilon}$.
  It can be linear or circular
- $A(\omega)$ determines the amplitude and intensity of the wave
  - Actually it is real, but we keep the complex notation for consistency



Interaction Hamiltonian

- The unpertubed Hamiltonian for a H – like atom with nucleus of charge *Z* is

$$H_0 = \frac{\left(-i\hbar\vec{\nabla}\right)^2}{2m} - \frac{Ze^2}{(4\pi\varepsilon_0)r}$$

- It can be proved that the total Hamiltonian, including the interaction term is

$$H = -\frac{\hbar^2\vec{\nabla}^2}{2m} - \frac{Ze^2}{(4\pi\varepsilon_0)r} - i\hbar\frac{e}{m}\vec{A}\cdot\vec{\nabla} + \frac{e^2}{2m}\vec{A}^2$$

Interaction Hamiltonian

$$H = -\frac{\hbar^2\vec{\nabla}^2}{2m} - \frac{Ze^2}{(4\pi\varepsilon_0)r} \boxed{- i\hbar\frac{e}{m}\vec{A}\cdot\vec{\nabla}} + \boxed{\frac{e^2}{2m}\vec{A}^2}$$

- Two pertubation terms: one linear and the other quadratic in $\vec{A}$
- Consider now the linear term

$$H' = -i\hbar\frac{e}{m}\vec{A}\cdot\vec{\nabla}$$

- Since $\vec{A}(\vec{r},t) = \hat{\varepsilon}\left[A(\omega)e^{i(\omega t-\vec{k}\cdot\vec{r})} + A(\omega)e^{-i(\omega t-\vec{k}\cdot\vec{r})}\right]$

  it is precisely of the form

$$H'(t) = \widetilde{H}e^{i\omega t} + \widetilde{H}^{\dagger}e^{-i\omega t}$$

  considered in time dependent pertubation theory

  - $\widetilde{H} = \hat{\varepsilon}A(\omega)e^{-i\vec{k}\cdot\vec{r}}$, $\widetilde{H}^{\dagger} = \hat{\varepsilon}A(\omega)e^{i\vec{k}\cdot\vec{r}}$

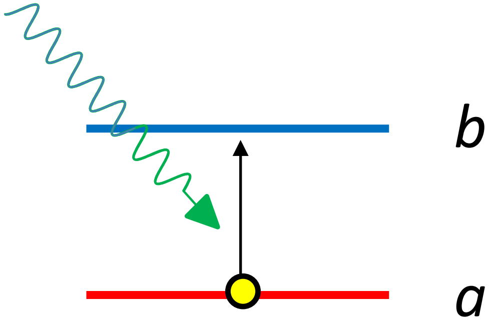
Interaction Hamiltonian

,

$$H' = -i\hbar\frac{e}{m}\vec{A}\cdot\vec{\nabla}$$

$$H'(t) = \widetilde{H}e^{i\omega t} + \widetilde{H}^{\dagger}e^{-i\omega t}$$

- This term describes stimulated absorption and emission processes. Let’s concentrate on absorption, also aptly called <u>photoelectric absorption</u> since in the atom an electron makes a transition induced by the absorption of a photon.
- Absorption is due to $\widetilde{H}^{\dagger}e^{-i\omega t}$, emission to $\widetilde{H}e^{i\omega t}$



Cross section for photoelectric absorption

- Use Fermi’s golden rule. Consider transitions between discrete bound states *a* and *b*.

$$W_{ba} = \frac{2\pi}{\hbar} \left|\widetilde{H}^{\dagger}{}_{ba}\right|^2 \delta\left(E_b{}^0 - E_a{}^0 - \hbar\omega\right)$$

$$\widetilde{H}^{\dagger} = -i\left(\frac{\hbar e}{m}\right)\hat{\varepsilon}A(\omega)e^{i\vec{k}\cdot\vec{r}} \cdot \vec{\nabla}$$

$$W_{ba} = \frac{2\pi}{\hbar}\left(\frac{\hbar^2 e^2}{m^2}\right)A^2(\omega)\left|\langle\psi_b|e^{i\vec{k}\cdot\vec{r}}\hat{\varepsilon}\cdot\vec{\nabla}|\psi_a\rangle\right|^2 \delta\left(E_b^{(0)} - E_a^{(0)} - \hbar\omega\right)$$

Dipole approximation

- Consider the matrix element

$$M_{ba} = \langle \psi_b | e^{i\vec{k}\cdot\vec{r}} \hat{\varepsilon} \cdot \vec{\nabla} | \psi_a \rangle$$

- An important approximation can be performed in most spectral ranges. Re-write the matrix element as an integral in real space:

$$M_{ba} = \int_V d^3r \;\; \psi_b{}^*(\vec{r})\; e^{i\vec{k}\cdot\vec{r}}\; \hat{\varepsilon} \cdot \vec{\nabla}\, \psi_a(\vec{r})$$

Dipole approximation

- $M_{ba} = \int_V \; d^3r \;\; {\psi_b}^*(\vec{r})\, e^{i\vec{k}\cdot\vec{r}}\, \hat{\varepsilon} \cdot \vec{\nabla}\, \psi_a(\vec{r})$
- The spatial extent of the wavefunctions is at most of the order of the typical atomic size $d_a \sim 1$ Å: this determines the maximum effective value of r in the integral
- The modulus of the wavevector is $k = \frac{2\pi}{\lambda}$
- Therefore if the wavelength is such that

$$\frac{2\pi d_a}{\lambda} \ll 1$$

we can make the approximation that

$$\boxed{e^{i\vec{k}\cdot\vec{r}} = 1}$$

Dipole approximation

- For valence initial states the dipole approximation $e^{i\vec{k}\cdot\vec{r}} = 1$ is valid up to the UV.
- For core level initial states of not too light atoms the dipole approximation continues to be valid.

The cross section in the dipole approx.

$$\boxed{\sigma = 4\pi^2 \; \hbar\omega \; \alpha \; |\langle\psi_b|\hat{\varepsilon}\cdot\vec{r}|\psi_a\rangle|^2 \delta\left(E_b^{(0)} - E_a^{(0)} - \hbar\omega\right)}$$

- Clearly, dimensions = L^2
- The order of magnitude is determined by the dipole matrix element, an effective “area” roughly of the order of ${a_0}^2$, depending on the overlap of initial and final wavefunctions
- The Dirac δ function is an expression of the conservation of energy
- The apparent unphysical divergence will be solved introducing the concept of lifetime of states

Selection rules

;

- Using the properties of the spherical harmonics it can be shown that the selection rule on ℓ is

$$\boxed{\Delta\ell = \pm 1}$$

- The selection rule on m depends on the state of polarization of the radiation
  - For linealy polarized radiation $\Delta m = 0$
  - For circularly polarized radiation $\Delta m = \pm 1$

Selection rules

$$\Delta \ell = \pm 1$$

Conservation of angular momentum
(modulus)

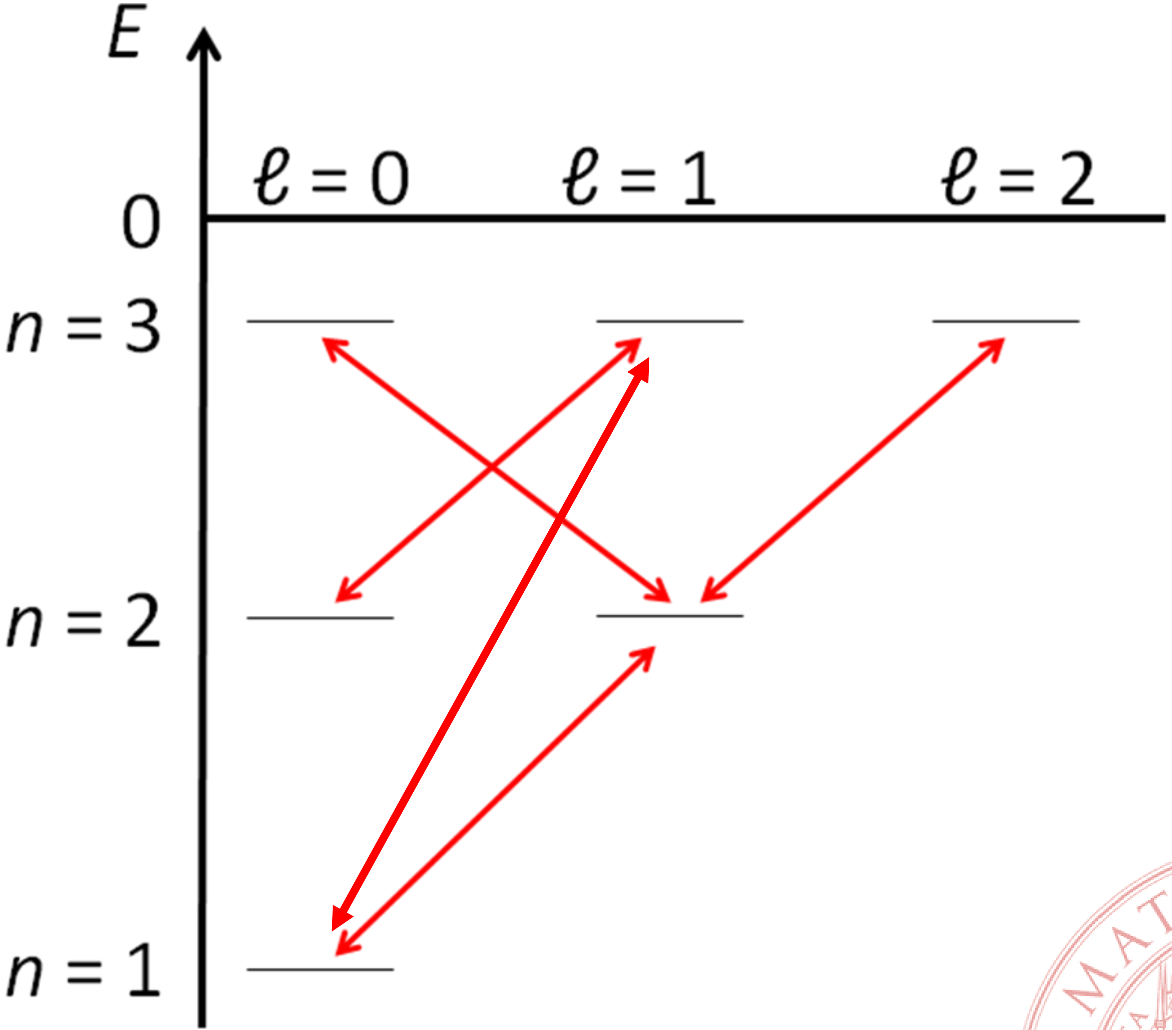
$$\Delta m = \pm 1$$

Conservation of angular momentum
(quantization axis component)

Selection rules

$$\Delta\ell = \pm 1$$

$$\begin{aligned} \Delta m_\ell &= 0, \quad \text{lin} \\ &= \pm 1, \quad \text{circ} \end{aligned}$$



Lifetime and lineshape

- We have implicitly assumed that all atomic eigenstates have infinite lifetime. Apart from the fundamental state (1*s*) this is not true.
- All states have a finite lifetime due to
  - Spontaneous emission, also present for isolated atoms
  - Collisions between atoms, which induce electron transitions, present in gases at non negligible pressure
- If N_0 atoms are in a given state at $t = 0$, their number decays exponentially as

$$N(t) = N_0 e^{-\frac{t}{\tau}}$$

- For the H atom, the lifetimes τ of electronic states are

Level	2p	3s	3p	3d	4s	4p	4d	4f
Lifetime (ns)	1.6	160	5.4	15.6	230	12.4	36.5	73

Lifetime and lineshape

- A finite lifetime implies a <u>spectral broadening</u>
  - ➢ Transitions do not occur at a single photon energy

$$\hbar\omega_{ba} = E_b{}^0 - E_a{}^0$$

  - ➢ Transitions occur in a <u>band</u> centered around $\hbar\omega_{ba}$ with a broadening Γ which can be estimated from the Heisenberg uncertainty principle
- From the energy – time Heisenberg uncertainty principle, interpret τ as uncertainty in time, thus

$$\Gamma \geq \frac{\hbar}{\tau}$$

Lifetime and lineshape

- It can be proved that this spectral broadening results in a Lorentzian lineshape as a function of energy
- For a transition between states with lifetimes τ_a and τ_b the Lorentzian half width at half maximum (HWHM) is

$$\Gamma = \hbar\left(\frac{1}{\tau_a} + \frac{1}{\tau_b}\right)$$

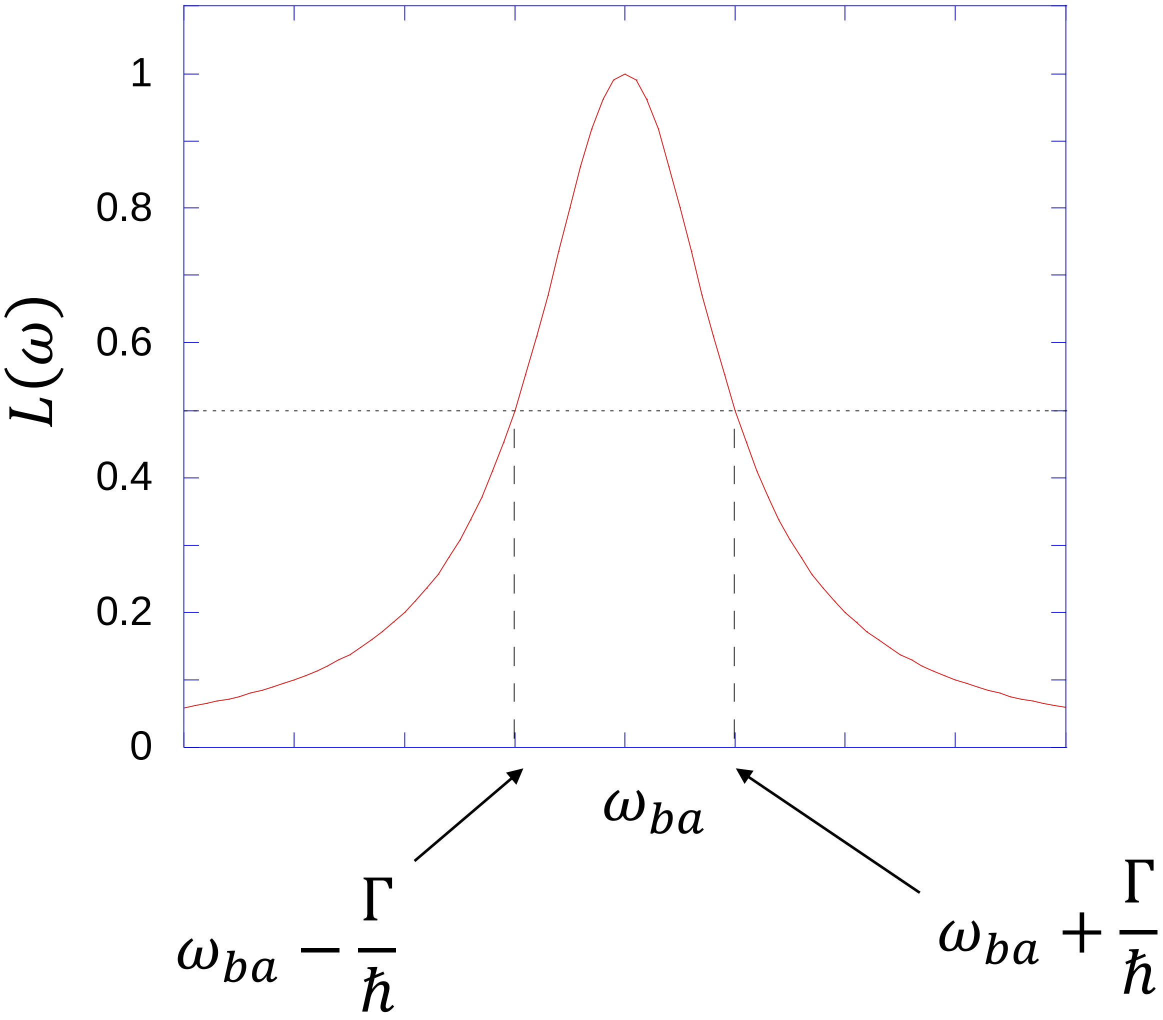
- The energy dependence of the cross section, the lineshape, is proportional to

$$L(\omega) = \frac{\Gamma^2}{\hbar^2(\omega_{ba} - \omega)^2 + \Gamma^2}$$

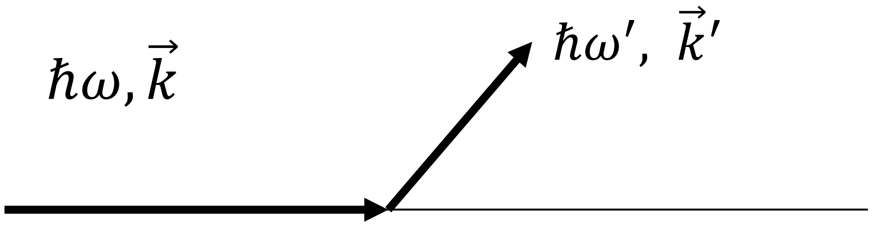
- This spectral broadening resolves the apparently unphysical result that the cross section is proportional to a δ function.

Lifetime and lineshape

$$L(\omega) = \frac{\Gamma^2}{\hbar^2(\omega_{ba} - \omega)^2 + \Gamma^2}$$



Scattering of radiation



- From the particle point of view scattering is a 2 photon process: a photon is absorbed (destroyed) and another is emitted (created).
- The scattered photon in general has a different energy and different wave vector (modulus and/or direction)

- $\omega' = \omega$: elastic scattering
  - In general: Raleigh
  - For a free electron: Thomson

- $\omega' \neq \omega$: inelastic scattering
  - In general: Raman
  - For a free electron: Compton ($\omega' < \omega$)

Scattering cross section

- Recall that the interaction Hamiltonian is

$$H' = \frac{e}{m}\vec{A}\cdot\vec{p} + \frac{e^2}{2m}\vec{A}^2$$

with

$$\vec{A}(\vec{r},t) = \hat{\varepsilon}\left[A(\omega)e^{i(\omega t-\vec{k}\cdot\vec{r})} + A(\omega)e^{-i(\omega t-\vec{k}\cdot\vec{r})}\right]$$

- Absorption is due to $A(\omega)e^{-i(\omega t-\vec{k}\cdot\vec{r})}$
- Emission is due to $A(\omega)e^{i(\omega t-\vec{k}\cdot\vec{r})}$

Scattering cross section

- Scattering is a 2 photon process which is due to
  - The quadratic term $\frac{e^2}{2m}\vec{A}^2$, in first order pertubation theory (Fermi's golden rule)
  - The linear term $\frac{e}{m}\vec{A} \cdot \vec{p}$, treated as a second order pertubation
- Qualitatively, it can be justified by interpreting each $\vec{A}$ term as involving 1 photon (either absorbed or emitted).

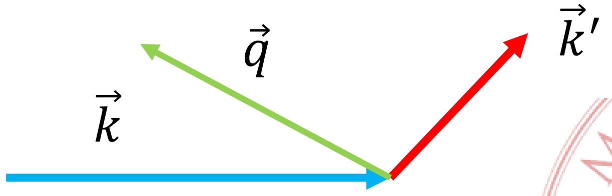
X-ray scattering cross section

- Term which describes scattering of X-rays (high energy limit) is $\frac{e^2}{2m}\vec{A}^2$ using 1st order pertubation theory.

- Define

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

the exchanged wavevector.



Fermi’s GD for continuum final states

- Fermi’s GD for final states in the continuum is

$$W_{ba} = \frac{2\pi}{\hbar} \left|\widetilde{H}^{\dagger}{}_{ba}\right|^2 \rho\left({E_b}^0\right)$$

$$E_b{}^0 = E_a{}^0 + \hbar\omega$$

- The density of states $\rho(E)$ is the number of states of energy between E and $E + dE$:

$$dN = \rho(E)\, dE$$

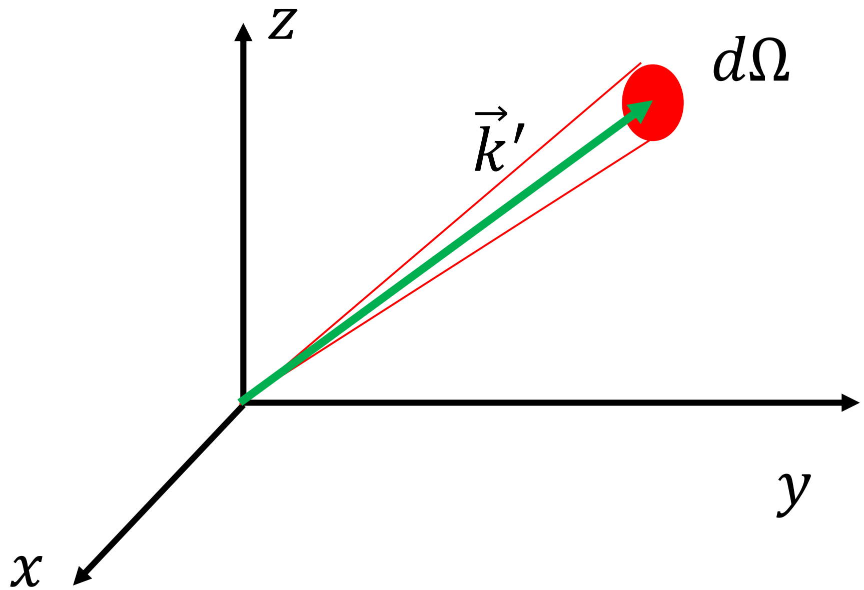
with the specification of the dispersion relation applicable for photons

$$\omega = ck$$

$$E = \hbar\omega = \hbar ck$$

Scattering geometry

- We will discuss the cross section for scattering in which the scattered photon has direction defined by the wave vector $\vec{k}'$ within an infinitesimal solid angle $d\Omega$



X-ray scattering cross section

- It can be proved that the differential cross section is

$$\frac{d\sigma}{d\Omega} = \frac{e^4}{16\pi^2\varepsilon_0^2 m^2 c^4}\left(\frac{\omega'}{\omega}\right)(\hat{\varepsilon}\cdot\hat{\varepsilon}')^2\left|\langle b|e^{-i\vec{q}\cdot\vec{r}}|a\rangle\right|^2$$

$$= r_0^2\left(\frac{\omega'}{\omega}\right)(\hat{\varepsilon}\cdot\hat{\varepsilon}')^2\left|\langle b|e^{-i\vec{q}\cdot\vec{r}}|a\rangle\right|^2$$

$r_0 = \frac{e^2}{4\pi\varepsilon_0 mc^2} \cong 2.82 \times 10^{-15}\ m$, the «classical electron radius» or «Thomson scattering length»

Scattering of radiation: general case

- In the general case (not only X-rays) one has to use both terms of the interaction Hamiltonian

$$H' = -i\hbar\frac{e}{m}\vec{A}\cdot\vec{\nabla} + \frac{e^{2}}{2m}\vec{A}^{2}$$

$$=$$

$$= \frac{e}{m}\vec{A}\cdot\vec{p} + \frac{e^{2}}{2m}\vec{A}^{2}.$$

Linear term: second order pertubation theory
Quadratic term: first order pertubation theory

Scattering of radiation: general case

- It can be demonstrated that in the dipole approximation the differential cross section is the Kramers – Heisenberg formula

$$\frac{d\sigma}{d\Omega} = r_0^2 \omega \omega'^3 \left| m \sum_n \left[\frac{(\hat{\varepsilon}' \cdot \vec{r}_{bn})(\hat{\varepsilon} \cdot \vec{r}_{na})}{(E_n^0 - E_a^0 - \hbar\omega)} + \frac{(\hat{\varepsilon} \cdot \vec{r}_{bn})(\hat{\varepsilon}' \cdot \vec{r}_{na})}{(E_n^0 - E_a^0 + \hbar\omega')} \right] \right|^2$$

with the condition that

$$E_a^0 + \hbar\omega = E_b^0 + \hbar\omega'$$

and the sum is over all atomic states n.

Scattering of radiation: general case

- $\frac{d\sigma}{d\Omega} = r_0^2 \omega\omega'^3 \left| m \sum_n \left[\frac{(\hat{\varepsilon}'\cdot\vec{r}_{bn})(\hat{\varepsilon}\cdot\vec{r}_{na})}{(E_n^0 - E_a^0 - \hbar\omega)} + \frac{(\hat{\varepsilon}\cdot\vec{r}_{bn})(\hat{\varepsilon}'\cdot\vec{r}_{na})}{(E_n^0 - E_a^0 + \hbar\omega')} \right] \right|^2$
- A «picture» of this equation
  - Scattering is due to the sum of «virtual» transitions to intermediate states.
  - Conservation of energy is valid only globally, not for transitions to intermediate «virtual» states