# Introduction to matter – radiation interaction

*Prof. Federico Boscherini*
Director, CNR – Istituto Officina dei Materiali, Trieste
federico.boscherini@cnr.it
https://iom.cnr.it/phonebook/federico-boscherini/

ISTITUTO OFFICINA DEI MATERIALI

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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
- 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
- X-ray scattering from a single electron, an atom and a solid

# 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)

# Dispersion and attenuation

- The dielectric function determines dispersion and attenuation of an EM wave propagating in matter
- In vacuum the dispersion relation for EM waves is

$$\omega = ck$$

$c$ is the speed of light *in vacuo*.

# Dispersion and attenuation

- In matter 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 propagation in matter is

$$e^{ikx} = e^{ik_1(\omega)\,x}\; e^{-k_2(\omega)\,x}$$

Propagation term | 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 propagates in matter
- $n_1(\omega)$: 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

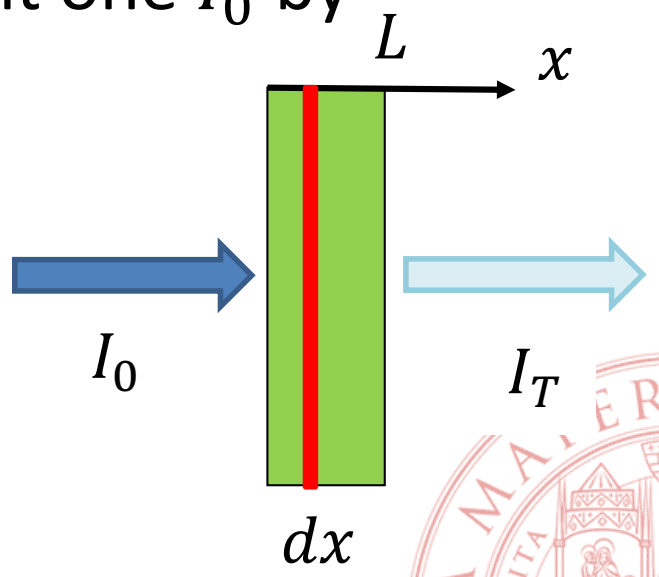
$$\mu = \frac{2\omega n_2(\omega)}{c}$$

- 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

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



# Model dielectric function

- Consider matter as an ensemble of damped harmonic oscillators
- The oscillators are the electrons, each of which is bound to a particular atom
- Simplify to the case of a set of identical atoms

# A medium as an ensemble of polarizable atoms

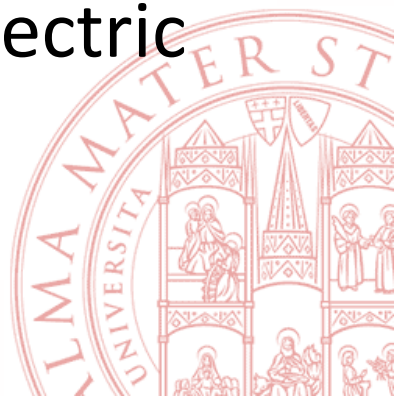
- If the (number) density of identical atoms is $\rho$

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

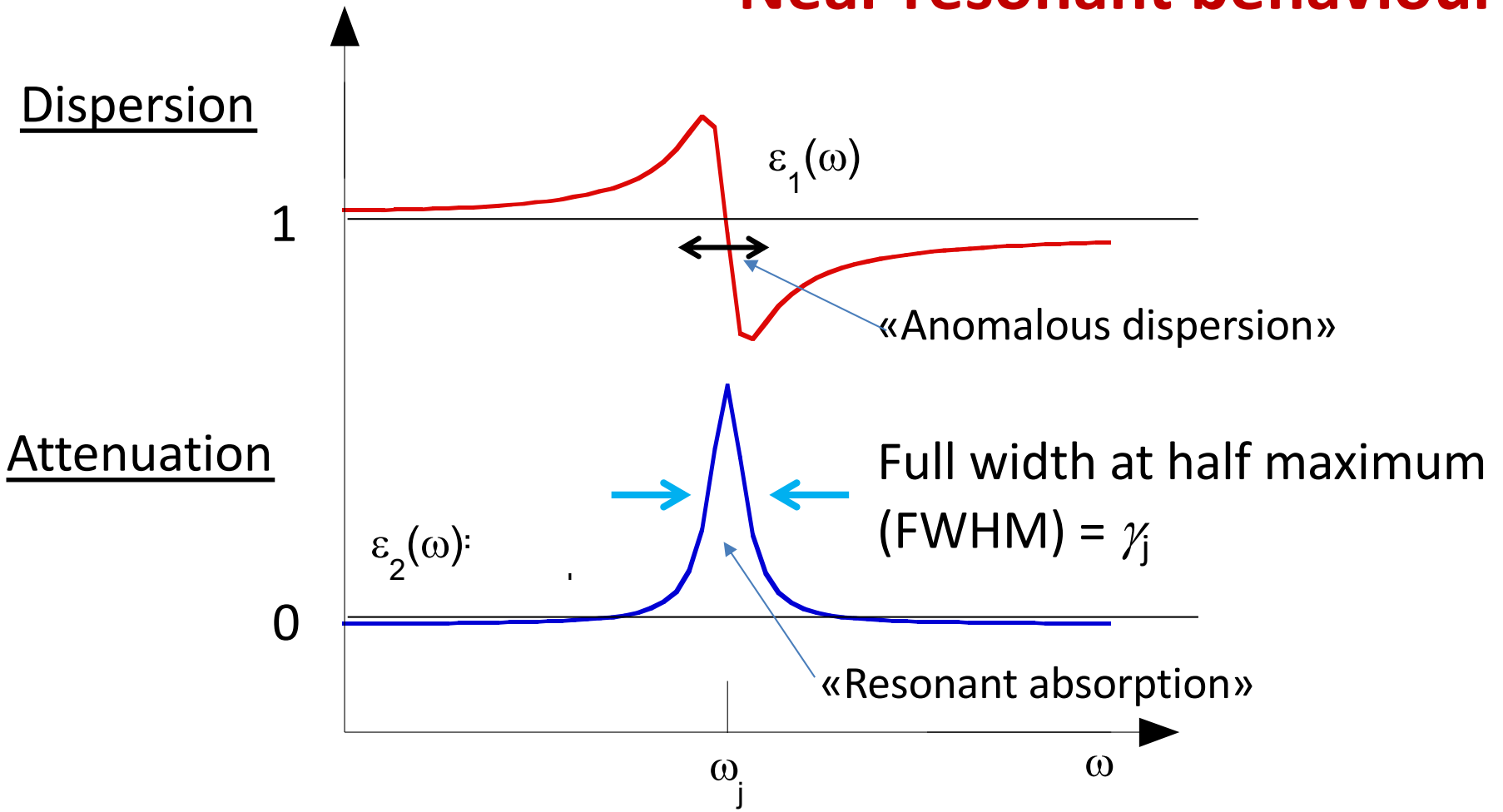
- $\varepsilon_1(\omega) = 1 + \frac{\rho e^2}{\varepsilon_0 m} \sum_{j=1}^{M} \frac{f_j\left(\omega_j{}^2 - \omega^2\right)}{\left[\left(\omega_j{}^2 - \omega^2\right)^2 + \left(\gamma_j\omega\right)^2\right]}$

- $\varepsilon_2(\omega) = \frac{\rho e^2}{\varepsilon_0 m} \sum_{j=1}^{M} \frac{f_j\gamma_j\omega}{\left[\left(\omega_j{}^2 - \omega^2\right)^2 + \left(\gamma_j\omega\right)^2\right]}$

- Kramers – Heisenberg or electric dipole dielectric function



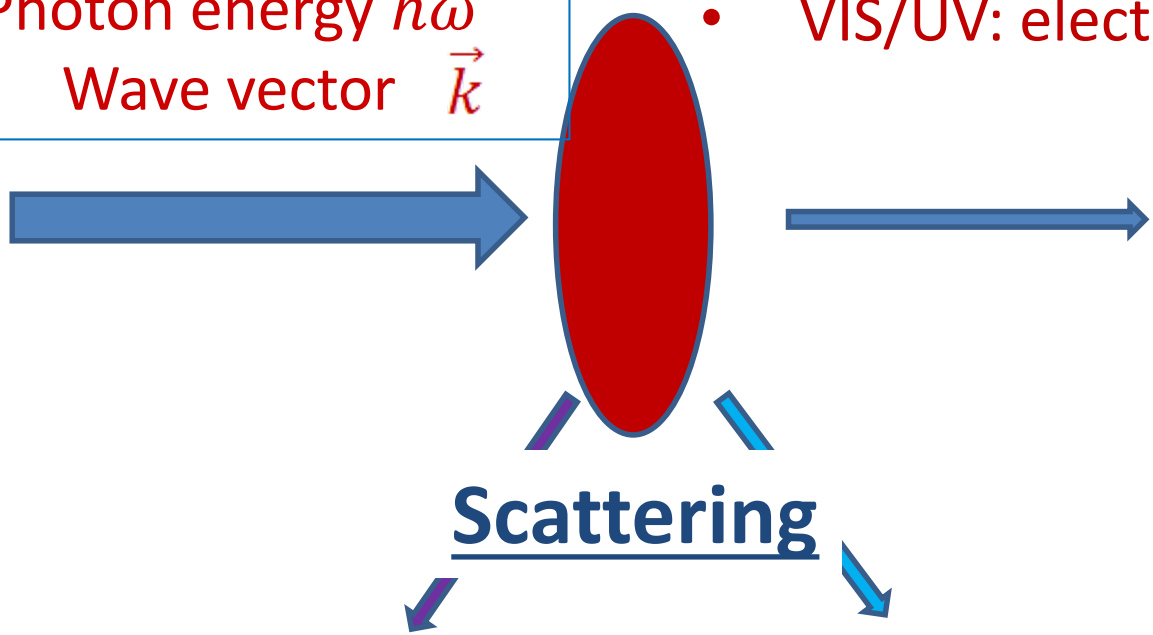
# Near resonant behaviour




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

# 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

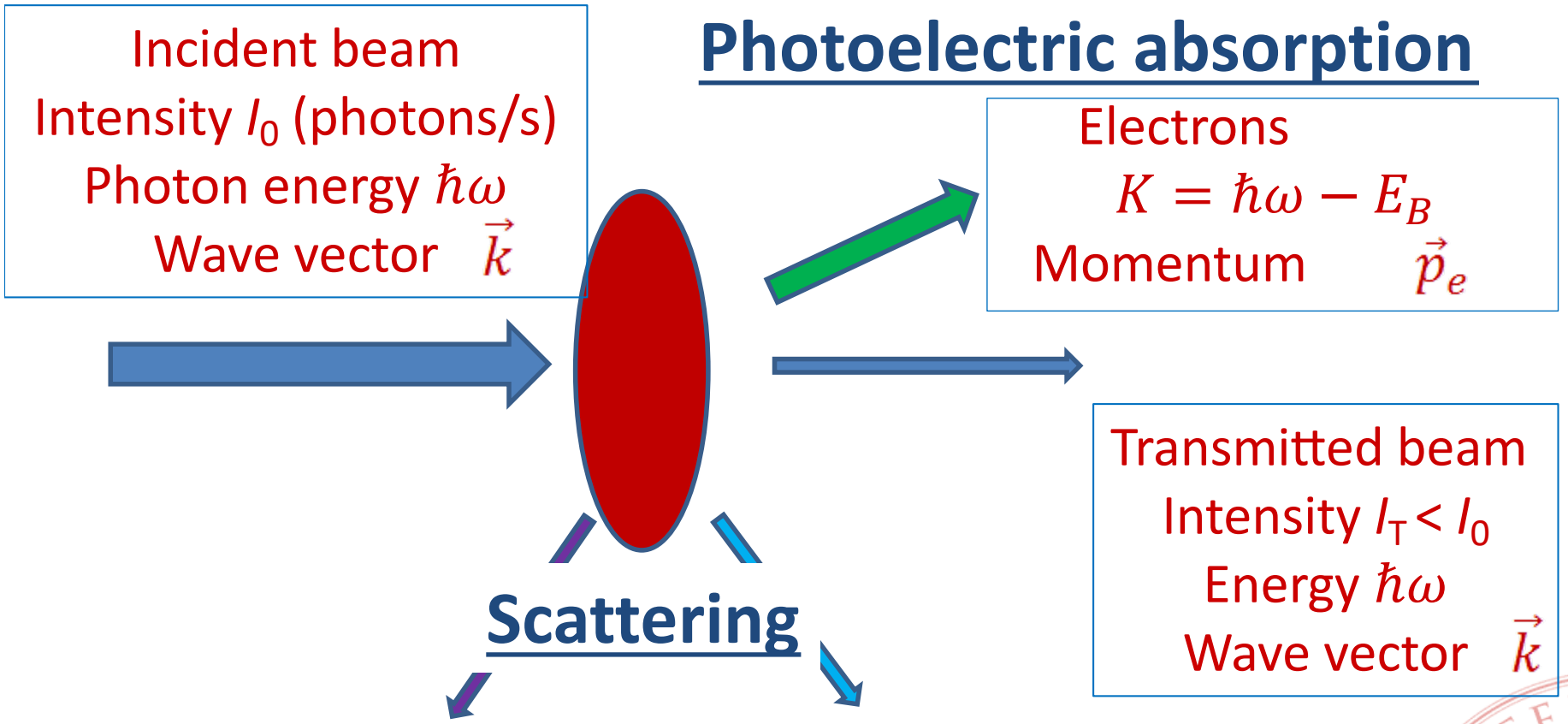
## Scattering

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

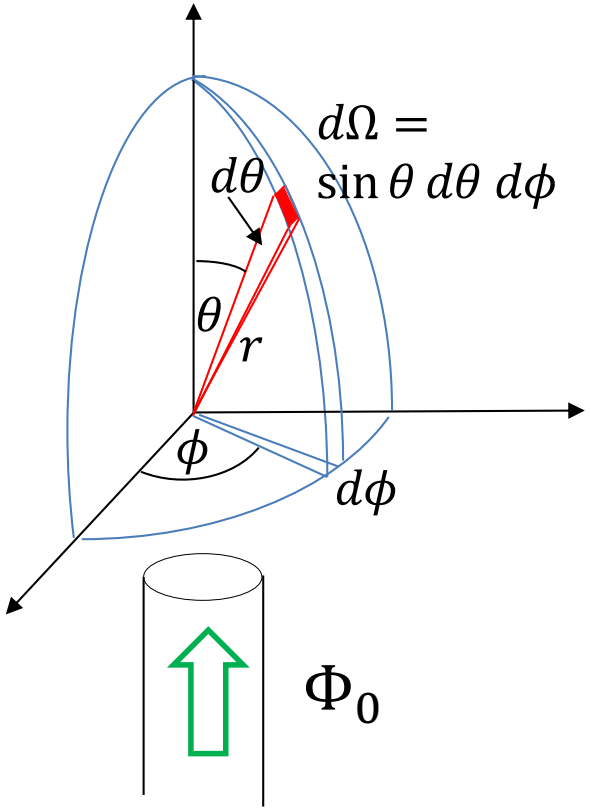
Inelastic
$\hbar\omega' \neq \hbar\omega \quad \vec{k}' \neq \vec{k}$

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

# Interaction: atomic approach (UV to X-rays)



# Cross section




Impinging beam of monochromatic photons, flux $\Phi_0$

$\Phi_0$=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$^2$

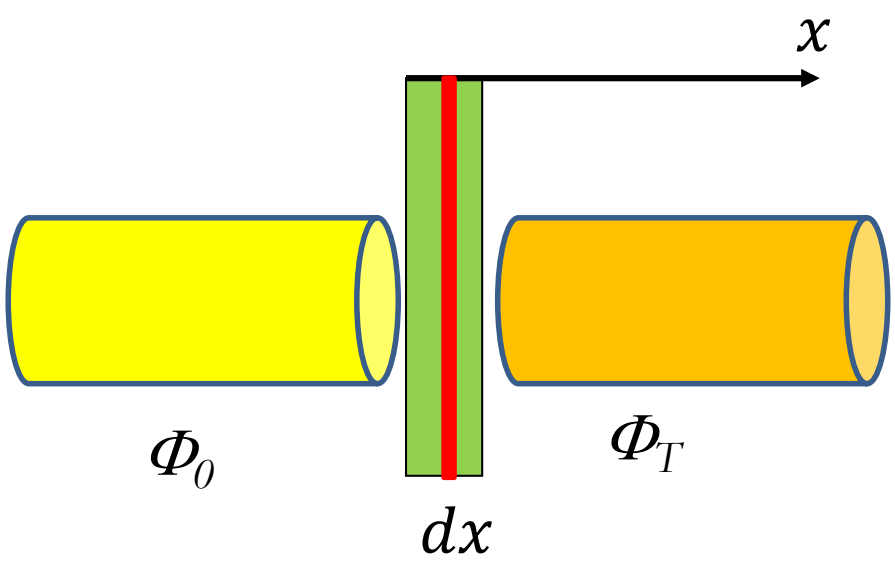
Ge, Z = 32, $\hbar\omega$ =10 keV

$\sigma_{photo} = 4 \times 10^3$ barn

$\sigma_{el} = 2 \times 10^2$ barn

$\sigma_{inel} = 1 \times 10^1$ barn

# Cross section & linear attenuation coefficient

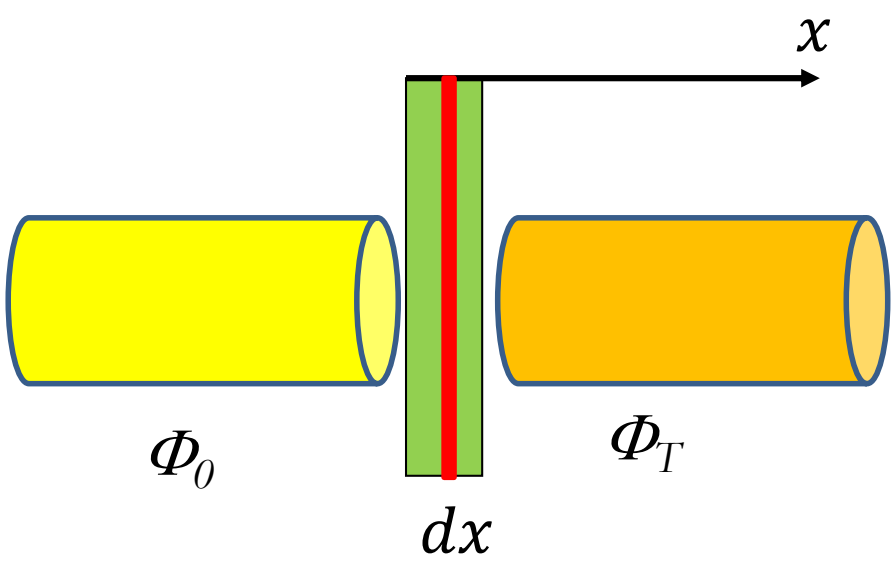



A homogeneous sample composed by identical atoms with density $\rho$ (atoms/cm$^3$)

- 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

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

# Cross section & linear attenuation coefficient




A homogeneous sample composed by identical atoms with density $\rho$

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

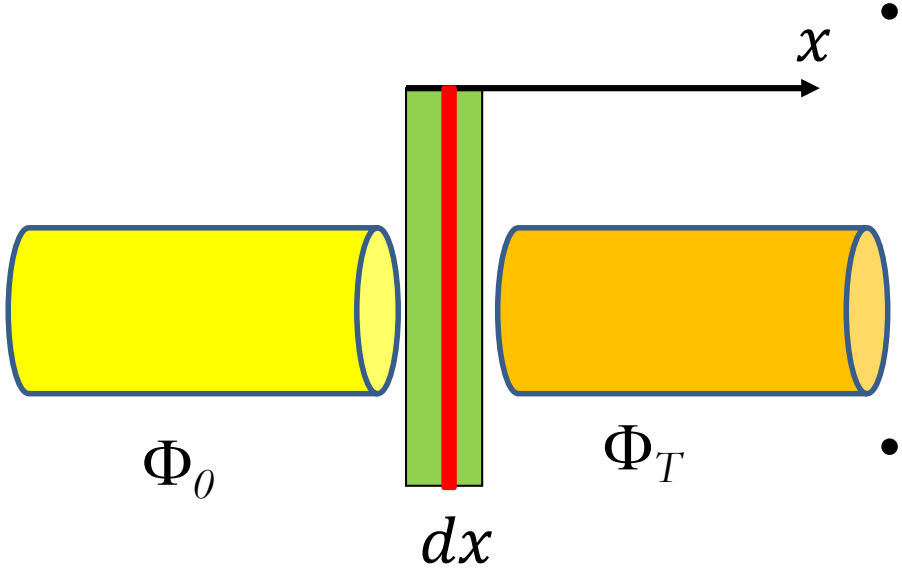
$$dN = -dI$$

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

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

$$\mu = \sigma\rho$$

# Cross section & linear attenuation coefficient



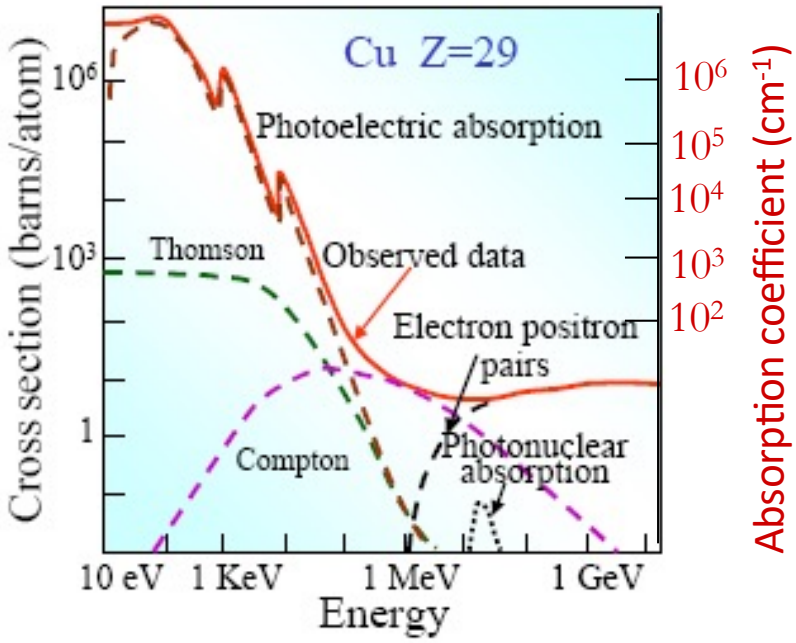

- If the sample is composed of different atoms with densities $\rho_i$ and cross sections $\sigma_i$ then

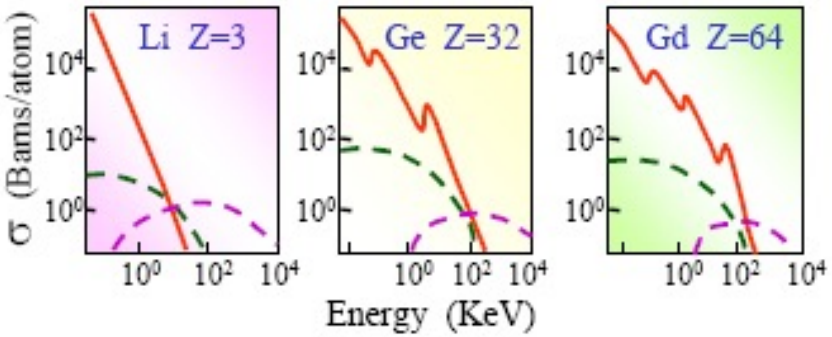
$$\mu = \sum_i \rho_i \sigma_i$$

- 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)

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

$$r_0 = \frac{e^2}{4\pi\varepsilon_0 mc^2} \cong 2.82\times10^{-15}\,\mathrm{m}$$

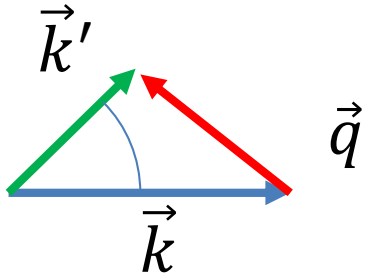
"Thomson scattering length"
or "classical electron radius"

Angle between the polarization vector and the scattered wave vector

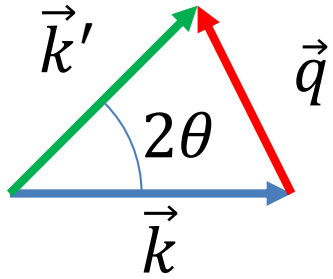
# The exchanged wave vector

- $\vec{q} = \vec{k}' - \vec{k}$
- 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 composed of a nucleus and $Z$ free electrons

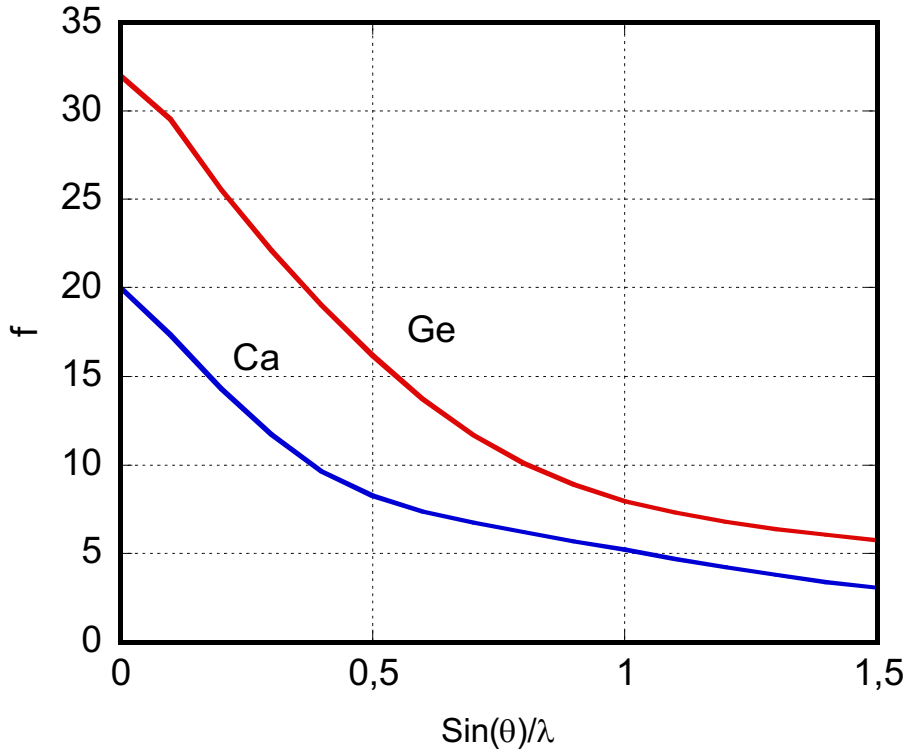
$$E(\vec{r},t) = -E_0 r_0 \left(\frac{e^{i(kr-\omega t)}}{r}\right) f(Z,\theta)\sin\theta$$

- $f(Z,\theta)$ is the «atomic form factor» or «scattering amplitude»; no physical dimensions
- Scattering is due only to the electrons, nuclei are fixed

# Elastic scattering from one atom

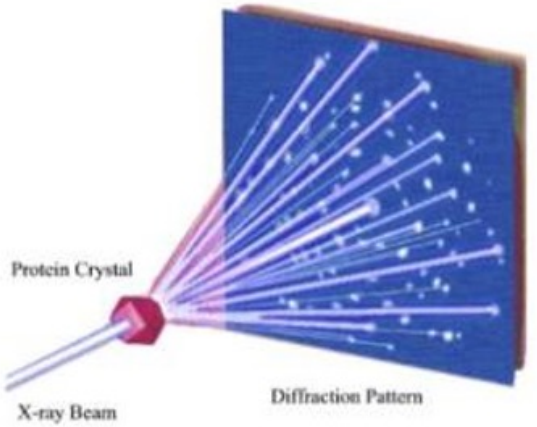
- The differential cross section $\frac{d\sigma}{d\Omega} = \frac{d\sigma_{electron}}{d\Omega}|f(Z,\theta)|^2$

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



# X-ray diffraction

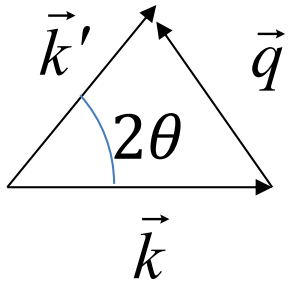
- Elastic X-ray scattering is at the base of X-ray scattering (XRD), a class of methods which are the premiere experimental methods to determine the atomic structure of condensed matter
  - ➢ Measure the intensity of x-ray beams scattered by a sample as a function of their deviation




Diffraction Process

# The exchanged wave vector («scattering vector»)

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



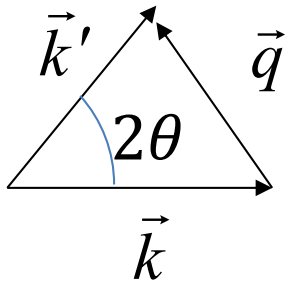

- The variation of (linear) momentum is $\hbar\vec{q}$
- In XRD literature the scattering angle is indicated as $2\theta$
- For elastic scattering

$$|\vec{k}'| = |\vec{k}| = k \qquad q = 2k\sin\theta = \frac{4\pi}{\lambda}\sin\theta$$

- The space defined by wave vectors is also known as «reciprocal space»

# Two ways to change the scattering vector

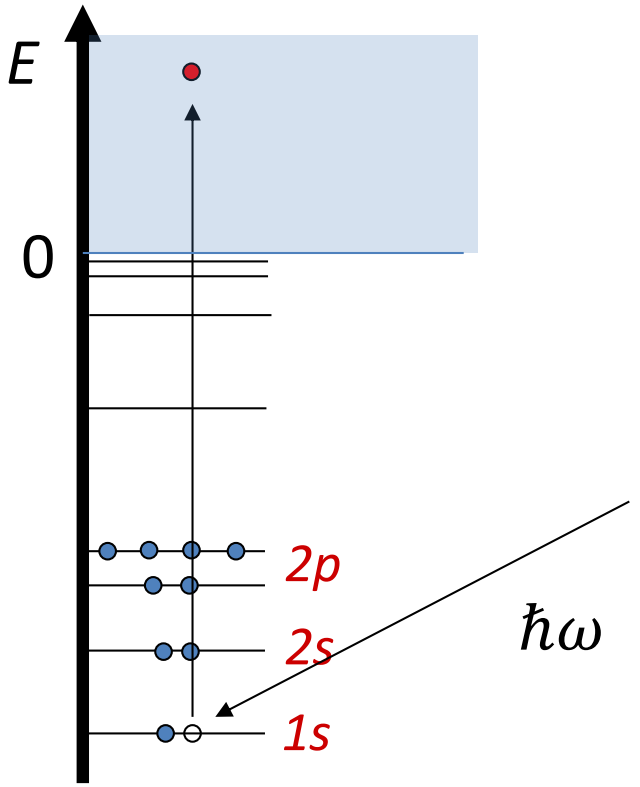
$$q = \frac{4\pi}{\lambda}\sin\theta \qquad \vec{q} = \vec{k}' - \vec{k}$$




- If $\lambda$ is constant (more common choice): measure as a function of $\theta$ (angular dispesion)
- If it is more convenient to keep $\theta$ constant: measure as a function of $\lambda$ (wavelength or energy dispersion)

# Photoelectric absorption

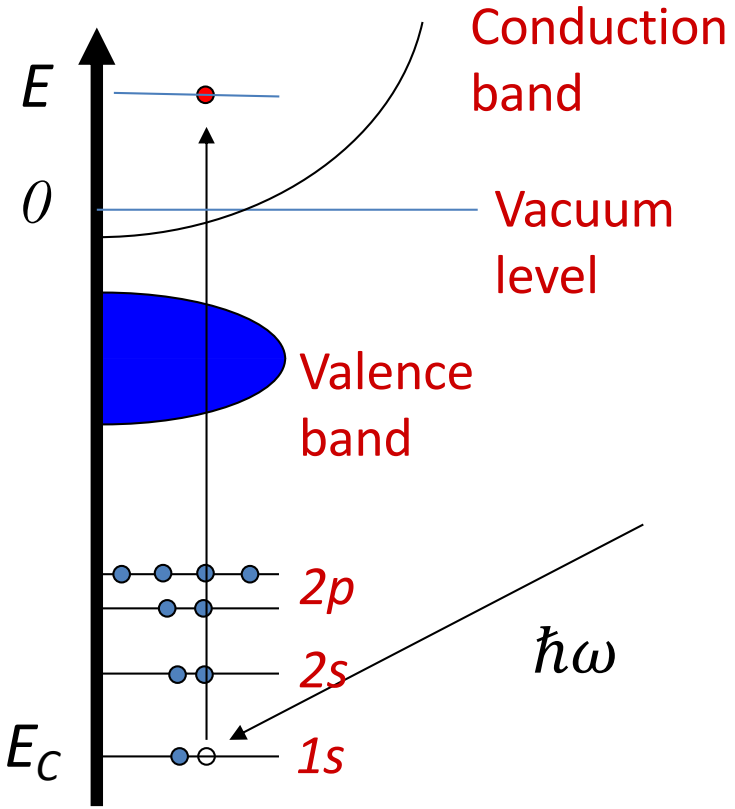
- A photon is absorbed and gives its energy to an electron.
- The electron makes a transition to
  - A bound state (excitation) <u>or</u>
  - An unbound state (ionization): a photoelectron is created




Energetics of photoelectric absorption in an atom (ionization)

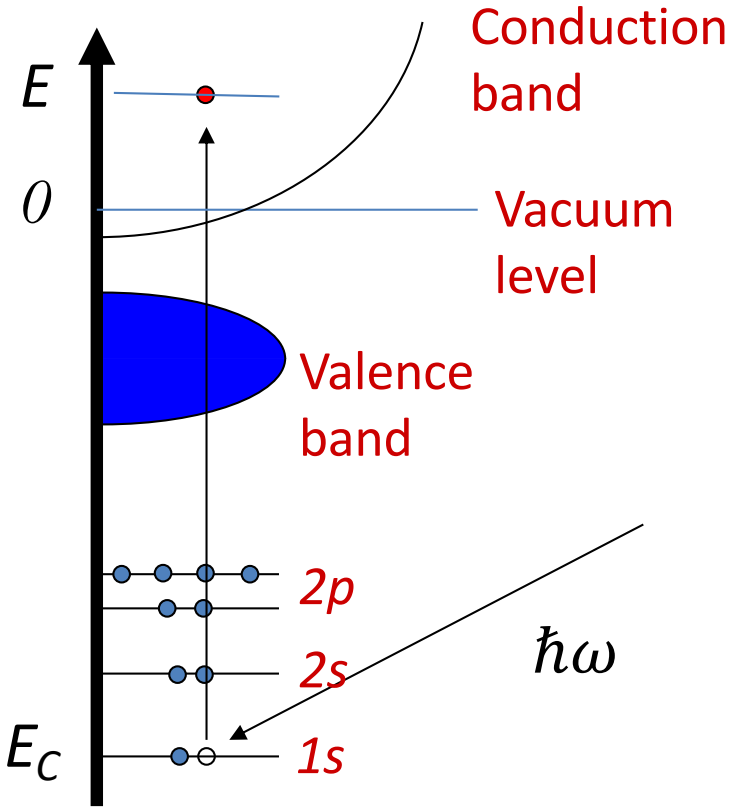
# Photoelectric absorption in solids

- 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:




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

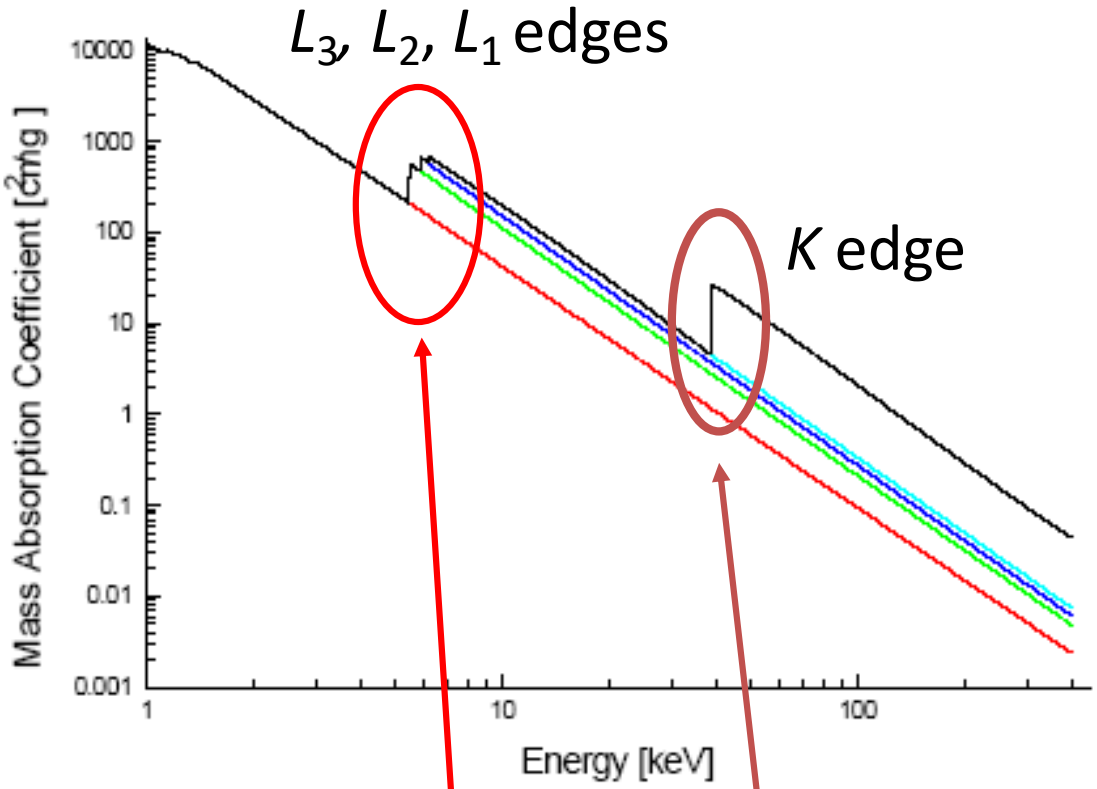
$$\text{Final state energy} = K$$

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

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

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

# Absorption coefficient: energy dependence

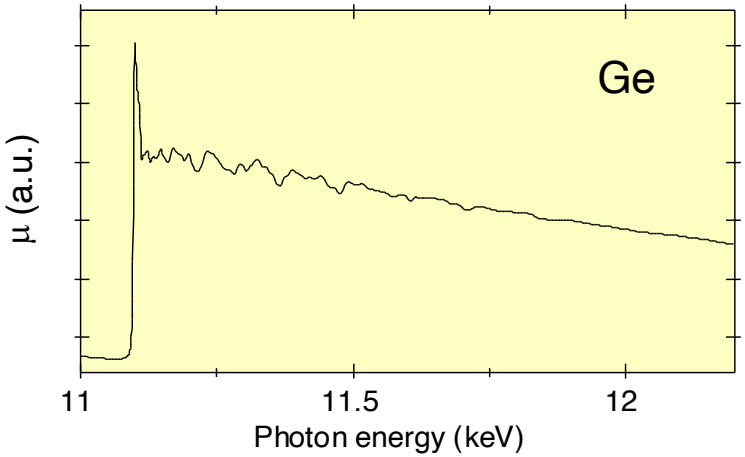


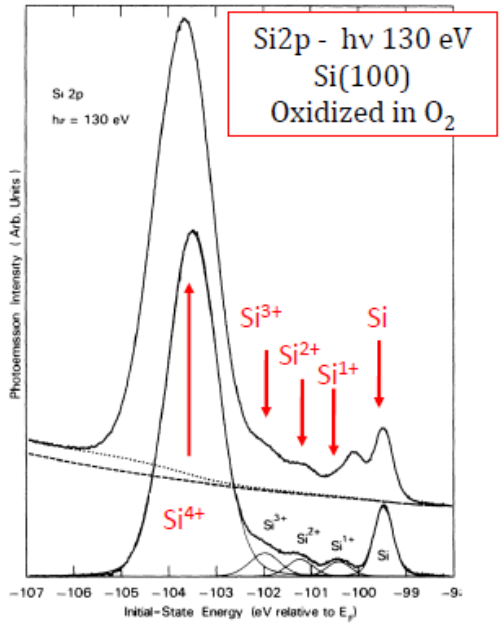

*Mass absorption coefficient of Lanthanum (Z=57) versus energy of incident photons split in its components.*

Absorption edges

# 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



# 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 $\rho$

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

- $n(\omega)$ 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 $\omega$: $f(\vec{q},\omega) = f^0(\vec{q}) + f'(\omega) - if''(\omega)$
  - $f^0(\vec{q})$: 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 $n_2(\omega) = \frac{2\pi r_0 \rho f''(\omega, q=0)}{k^2}$

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

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

# Interaction between a wave and an atom

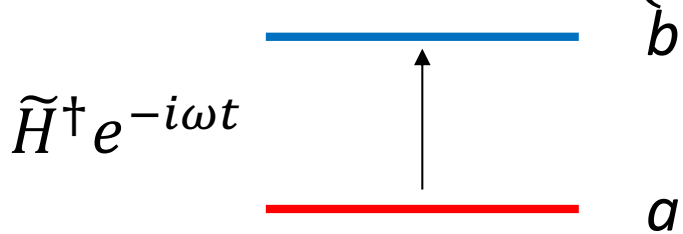
- The interaction is treated with time dependent pertubation theory
- The unperturbed atom's Hamiltonian is $H_o$
- The pertubation is an EM wave and the time dependent interaction Hamiltonian is $H'(t)$
- The EM wave has a harmonic dependence on time, thus it is expressed by an Hermitian operator of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

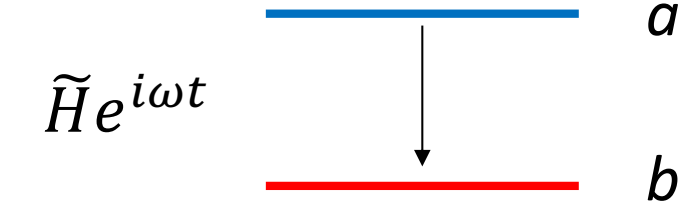
# Time dependent perturbation theory

- 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 $H'(t)$




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

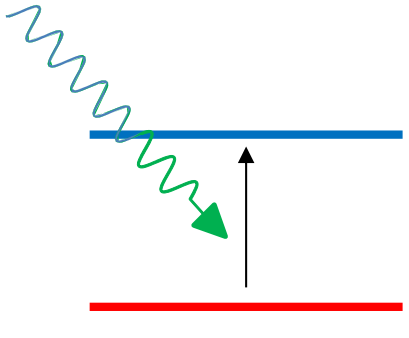
$$\hbar\omega = {E_b}^0 - {E_a}^0$$




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

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

# Time dependent perturbation theory

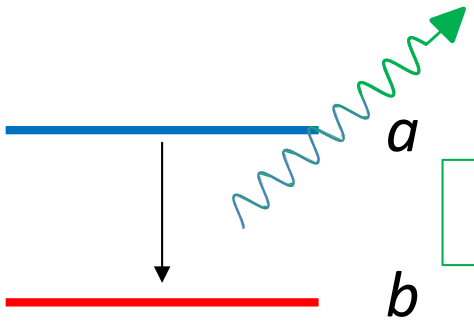



$$\tilde{H}^{\dagger} e^{-i\omega t}$$

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

Stimulated absorption

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




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

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

Stimulated emission

- 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

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

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

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

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

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

# Dipole approximation

- In deriving the cross section for photoelectric absorption a key element is the dipole approximation
- Call $d$ the spatial extent of the initial state wave function. At most, it is the atomic size $\sim 1$ Å.
- The dipole approximation is

$$2\pi d \ll \lambda$$

- Visible range: dipole approximation always valid
- For valence initial states the dipole approximation is valid up to the UV.
- For core level initial states of not too light atoms the dipole approximation continues to be valid even in the X-ray range.

# The cross section in the dipole approx.

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

- 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 $\delta$ 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 $\ell$ is

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

- 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

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

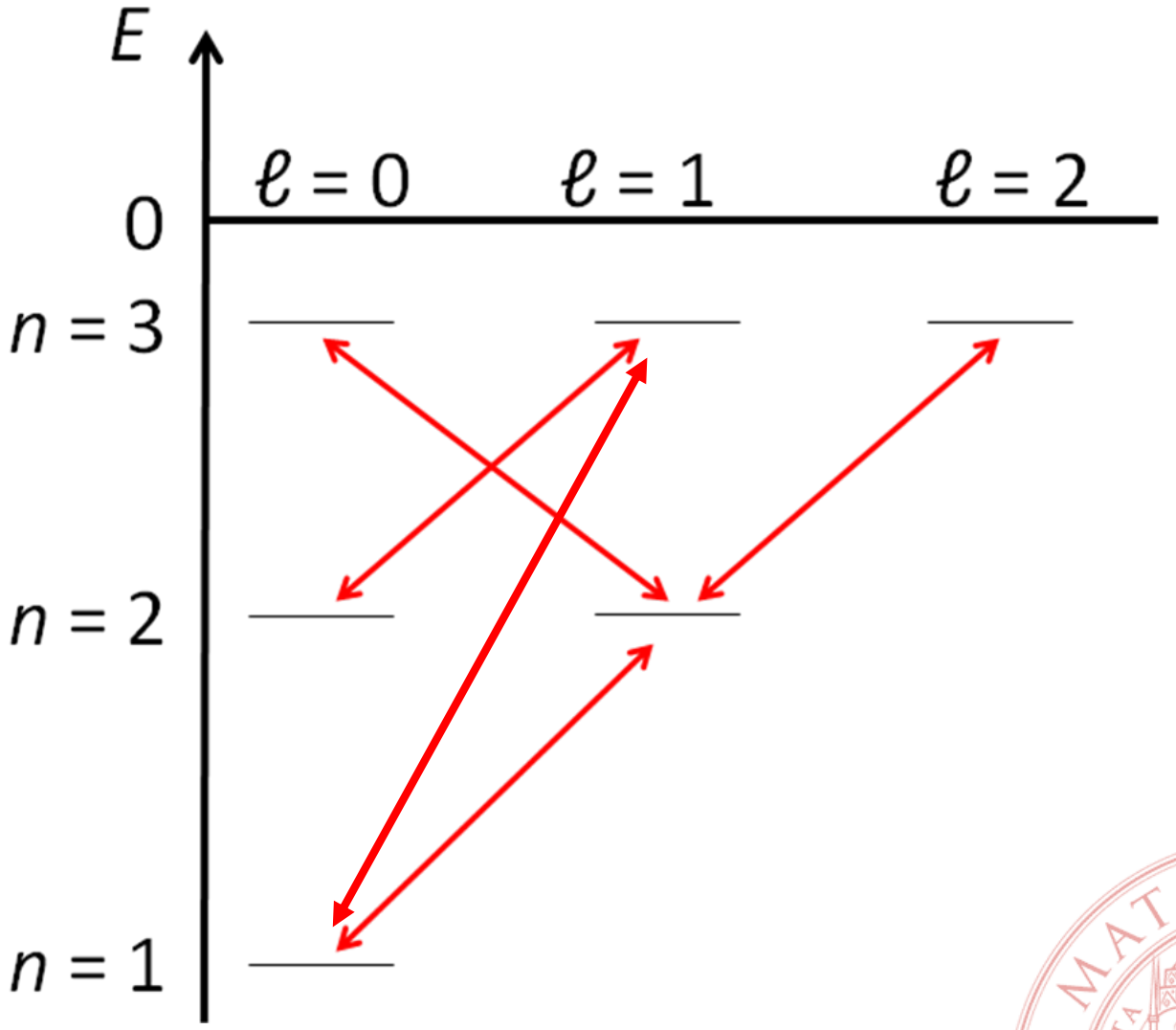
Conservation of angular momentum (modulus)

$$\Delta m = \pm 1$$

Conservation of angular momentum (quantization axis component)

# Selection rules

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



# 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 $\tau$ 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 spectral broadening
  - Transitions do not occur at a single photon energy

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

  - Transitions occur in a band centered around $\hbar\omega_{ba}$ with a broadening $\Gamma$ which can be estimated from the Heisenberg uncertainty principle
- From the energy – time Heisenberg uncertainty principle, interpret $\tau$ 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 $\tau_a$ and $\tau_b$ the Lorentzian half width at half maximum (HWHM) is

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

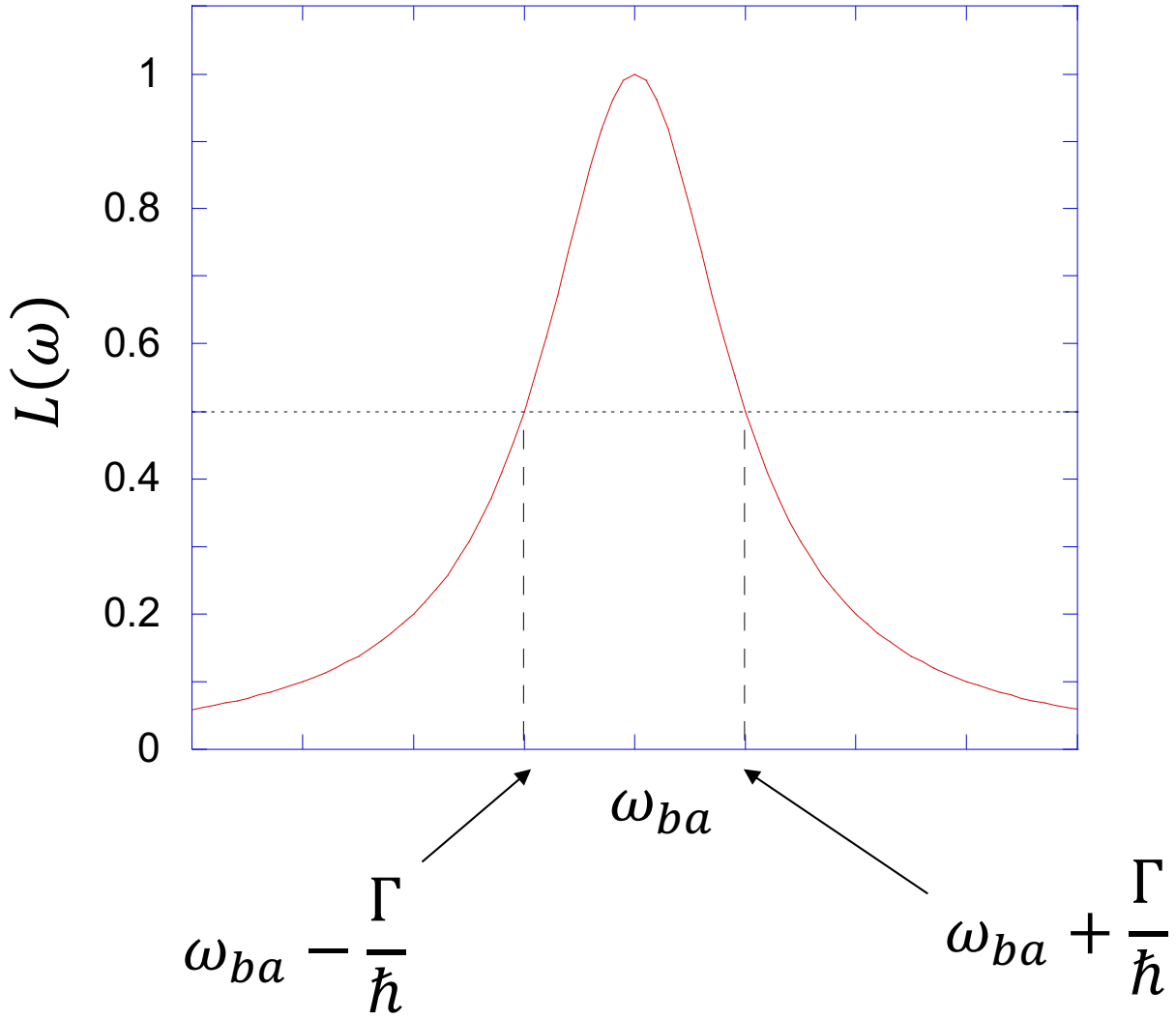
- The energy dependence of the cross section, the lineshape, is proportional to

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

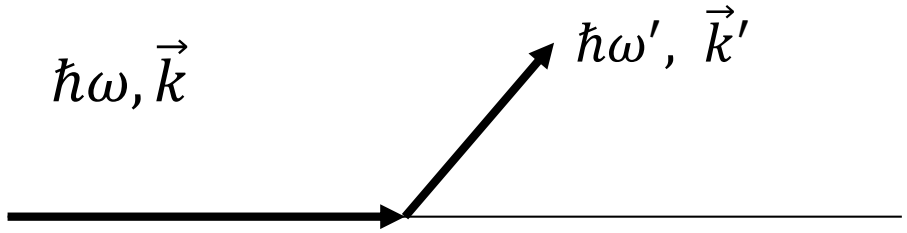
- This spectral broadening resolves the apparently unphysical result that the cross section is proportional to a $\delta$ function.

# Lifetime and lineshape

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



# Scattering of radiation



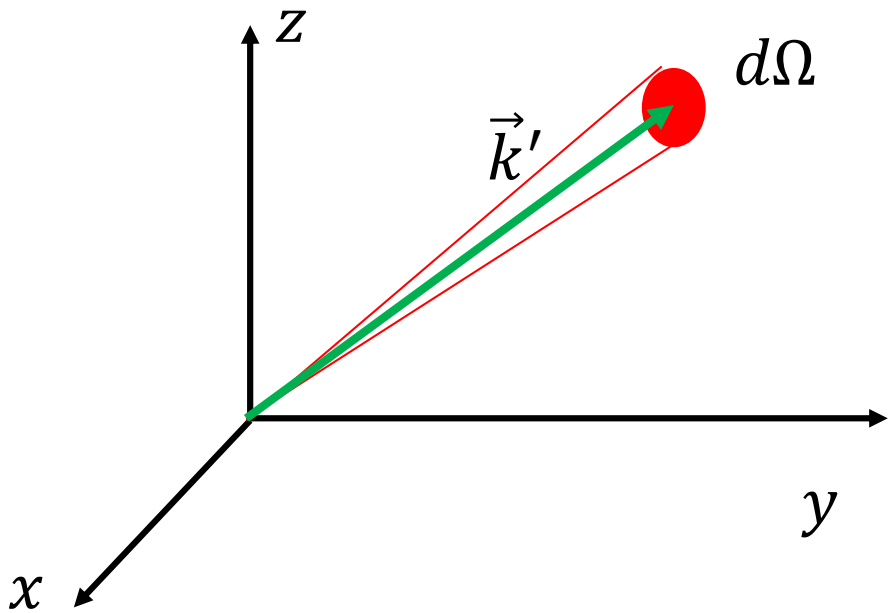

- From the particle point of view scattering is a 2 photon process: a photon is absorbed (destroyed) and another is emitted (created).
- The scattered photon in general has a different energy and different wave vector (modulus and/or direction)

- $\omega' = \omega$ : 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 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

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

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

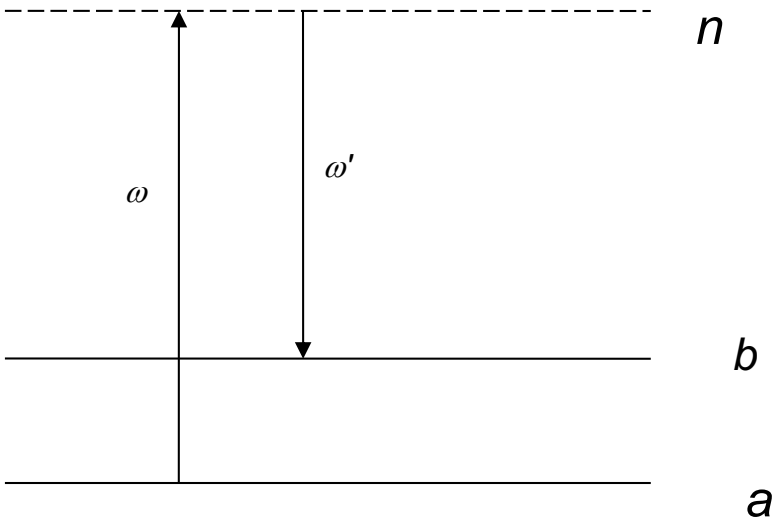
with the condition that

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

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



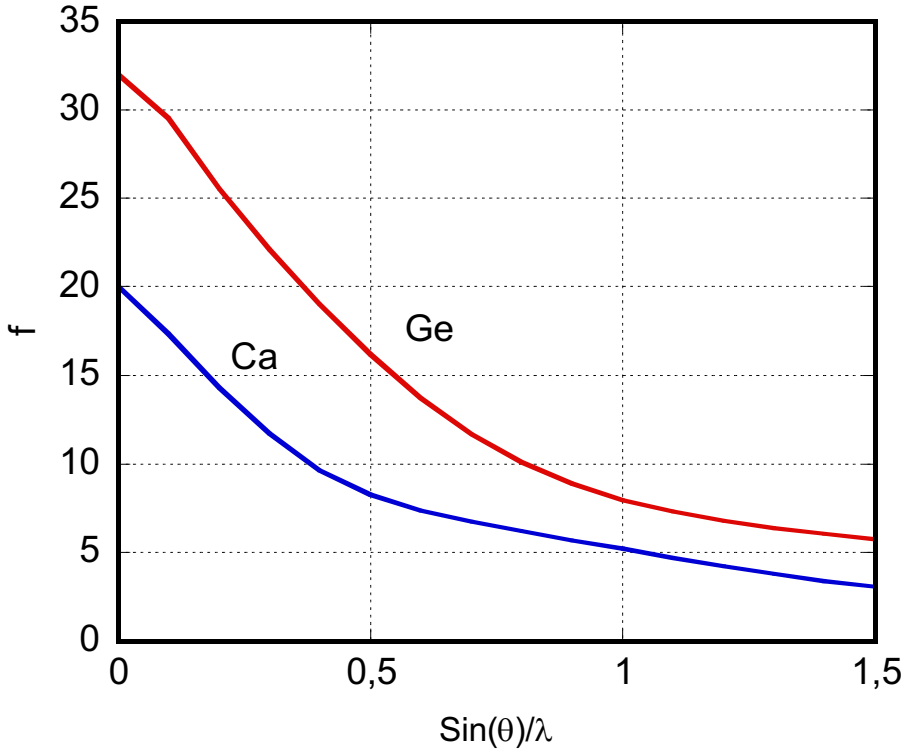
# “Anomalous” scattering

# Elastic scattering from one atom

- Recall the differential cross section

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

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



# The atomic form factor

- It can be shown that the form factor is the Fourier transform of the electronic density

$$f(\vec{q}) = \int_{V_{at}} d^3 r \rho_{e-at}(\vec{r}) \; e^{-i\vec{q}\cdot\vec{r}}$$

# «Anomalous» corrections to *f*

- More realistically, electrons are not free but bound to specific atoms. This introduces «anomalous» corrections to the atomic form factor, with a real and imaginary component

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

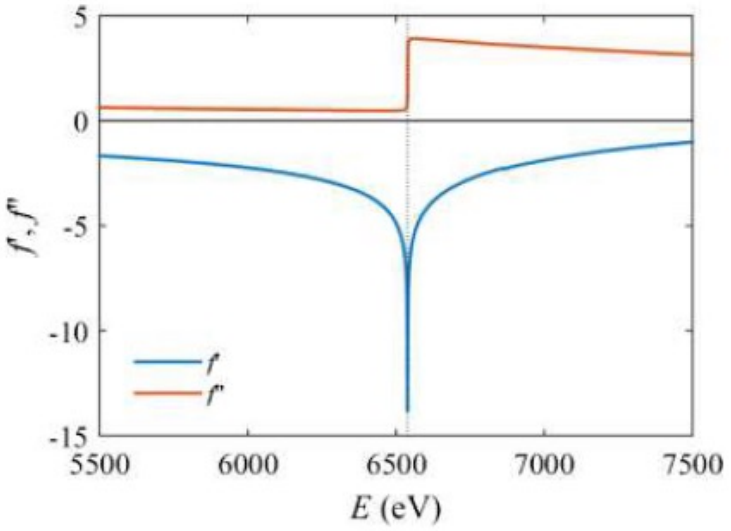
- These corrections are significant when the X-ray photon energy, $\hbar\omega$, is close to an absorption edge (resonance condition)

# «Anomalous" corrections to the form factor

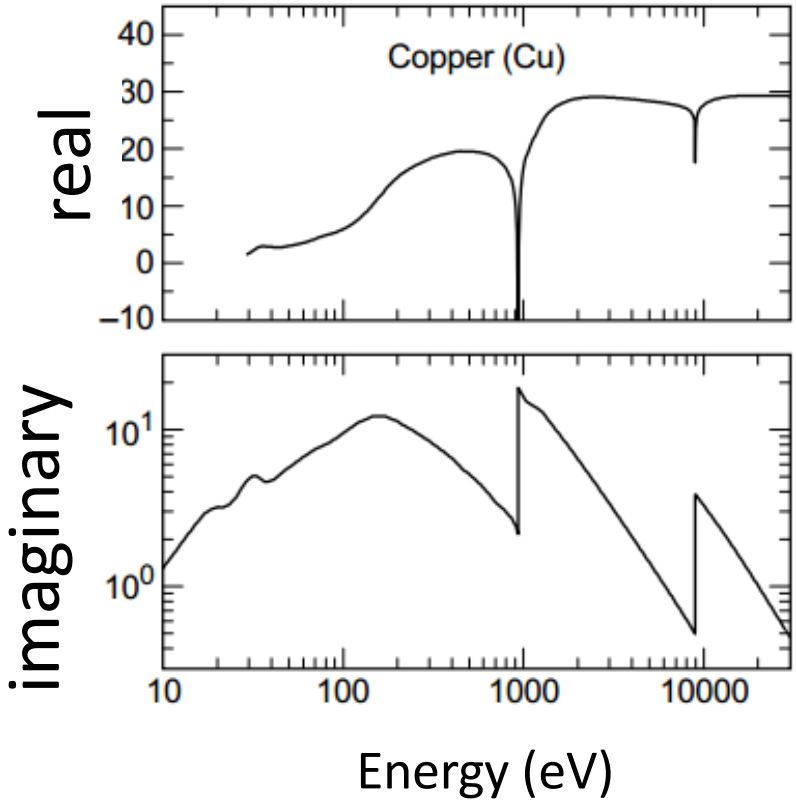
- It is common to separate the dependence on $\vec{q}$ and $\omega$: $f(\vec{q},\omega) = f^0(\vec{q}) + f'(\omega) + if''(\omega)$
  - $f^0(\vec{q})$: atomic scattering far from resonance frequencies / absorption edges
  - $f'(\omega)$: correction to dispersive part, important near resonance frequencies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

- Corrections to the form factor for Mn, as a function of the photon energy $\hbar\omega$

  Giannini et al, Prog. Mat Science, 112, 100667 (2020), © Elsevier



# Form factor of Cu




Optical theorem:

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

# Origin of "anomalous" corrections

- In the atomic approach: differential cross section for elastic scattering in the dipole approximation

$$\frac{d\sigma}{d\Omega} = r_0^2 m^2 \omega^4 \left| \sum_n \left[ \frac{(\hat{\varepsilon}' \cdot \vec{r}_{an})(\hat{\varepsilon} \cdot \vec{r}_{na})}{(E_n^0 - E_a^0 - \hbar\omega)} + \frac{(\hat{\varepsilon} \cdot \vec{r}_{an})(\hat{\varepsilon}' \cdot \vec{r}_{na})}{(E_n^0 - E_a^0 + \hbar\omega')} \right] \right|^2$$

- If $\hbar\omega \cong E^0{}_{n^*} - E^0{}_a$ one particular term will dominate the sum
- If $\Gamma$ is the lifetime of state $n^*$ it can be shown that

$$\frac{d\sigma}{d\Omega} = r_0^2 \omega^4 m^2 \frac{(\hat{\varepsilon}' \cdot \vec{r}_{an^*})^2 (\hat{\varepsilon} \cdot \vec{r}_{n^* a})^2}{(E_n^0 - E_a^0 - \hbar\omega)^2 + \frac{1}{4}\Gamma^2}$$

# Origin of "anomalous" corrections

- In the macroscopic approach: relation between the index of refraction and atomic form factor

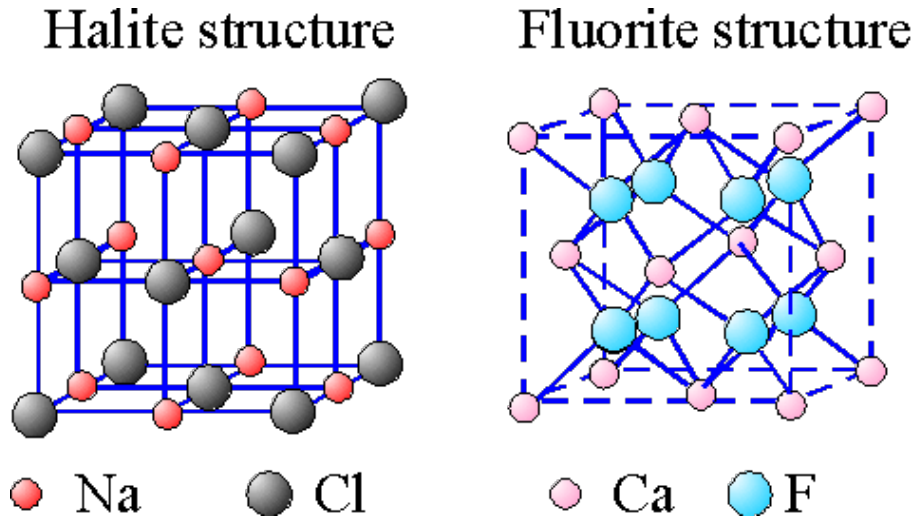
$$n(\omega) - 1 = -\frac{2\pi r_0 \rho f(\omega, q=0)}{k^2}$$

- Since $n$ has real and imaginary part so must $f$

# Diffraction from crystals: kinematic theory

# Kinematic diffraction theory

- Now consider scattering of x-rays from a crystal characterized by long range order with translational symmetry

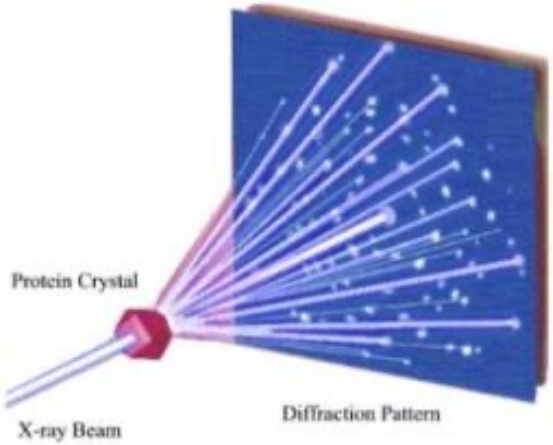


# Laue conditions

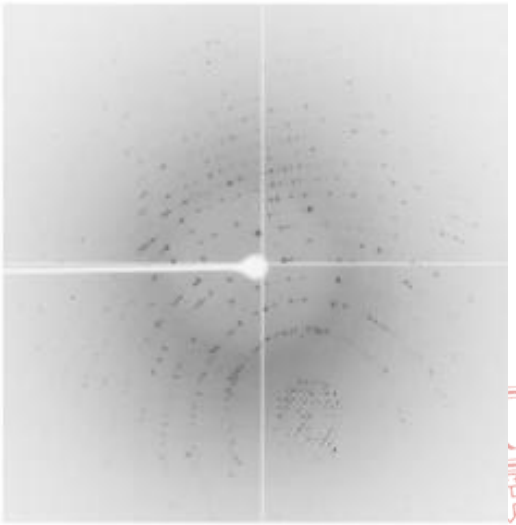
- There will be a maximum of intensity when the three «Laue conditions» are satisfied

$$\vec{q}\cdot\vec{a}_1 = h2\pi \quad \vec{q}\cdot\vec{a}_2 = k2\pi \quad \vec{q}\cdot\vec{a}_3 = \ell 2\pi\,; \qquad h,k,\ell = 0,\ 1,\ 2,\ldots..$$

- These are diffraction <u>peaks</u> or <u>reflections</u>




Diffraction Process

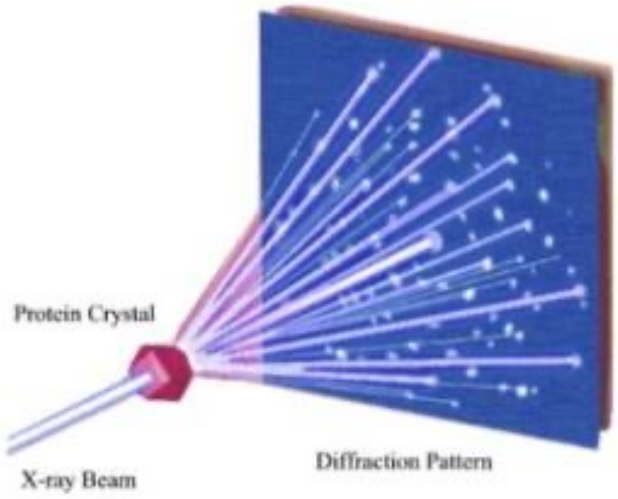


Diffraction Pattern from NSLS

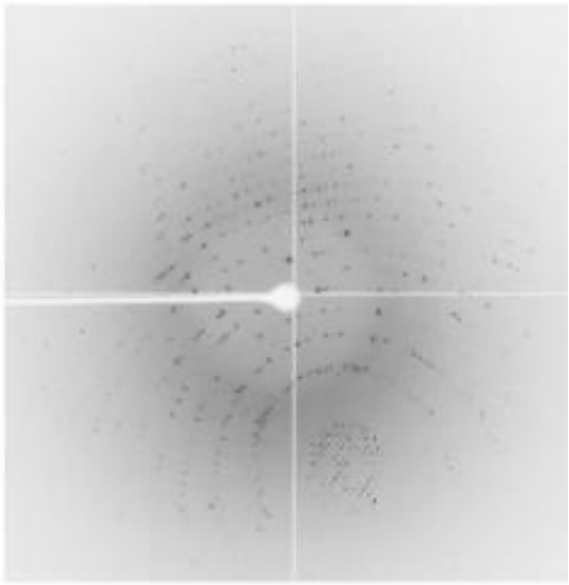
# Laue conditions

- Each peak is identified by three integers $(h\ k\ \ell)$

$$\vec{q}\cdot\vec{a}_1 = h2\pi \quad \vec{q}\cdot\vec{a}_2 = k2\pi \quad \vec{q}\cdot\vec{a}_3 = l2\pi \qquad h,k,\ell = 0,\ 1,\ 2,\ldots..$$




Diffraction Process

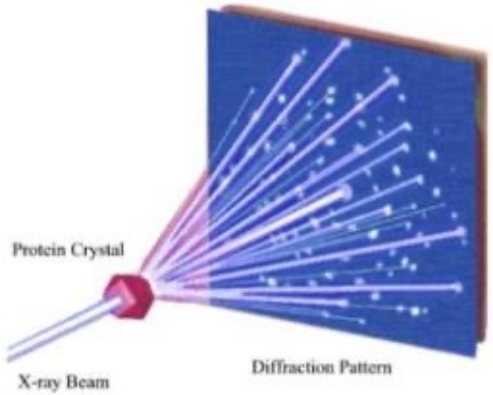


Diffraction Pattern from NSLS

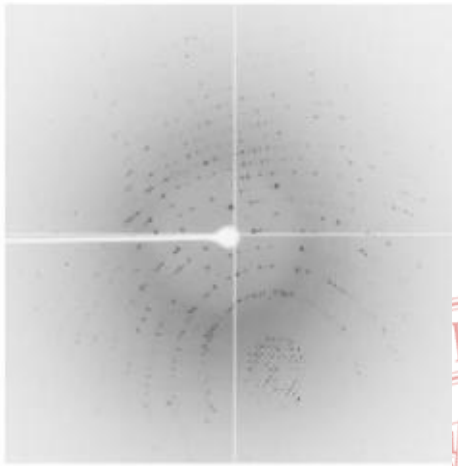
# Laue conditions

$$\vec{q}\cdot\vec{a}_1 = h2\pi \quad \vec{q}\cdot\vec{a}_2 = k2\pi \quad \vec{q}\cdot\vec{a}_3 = \ell 2\pi\,; \quad h,k,\ell = 0,\ 1,\ 2,\ldots..$$

- The position of peaks depends on the three primitive lattice vectors
- By measuring the position of the refections it is possible to determine the type of lattice, the lattice parameters and angles




Diffraction Process



Diffraction Pattern from NSLS

# Laue conditions

$$\vec{q}\cdot\vec{a}_1 = h2\pi \quad \vec{q}\cdot\vec{a}_2 = k2\pi \quad \vec{q}\cdot\vec{a}_3 = \ell 2\pi\,; \qquad h,k,\ell = 0,\ 1,\ 2,\ldots..$$

- Also reciprocal lattice vectors satisfy the same conditions, so we may also write

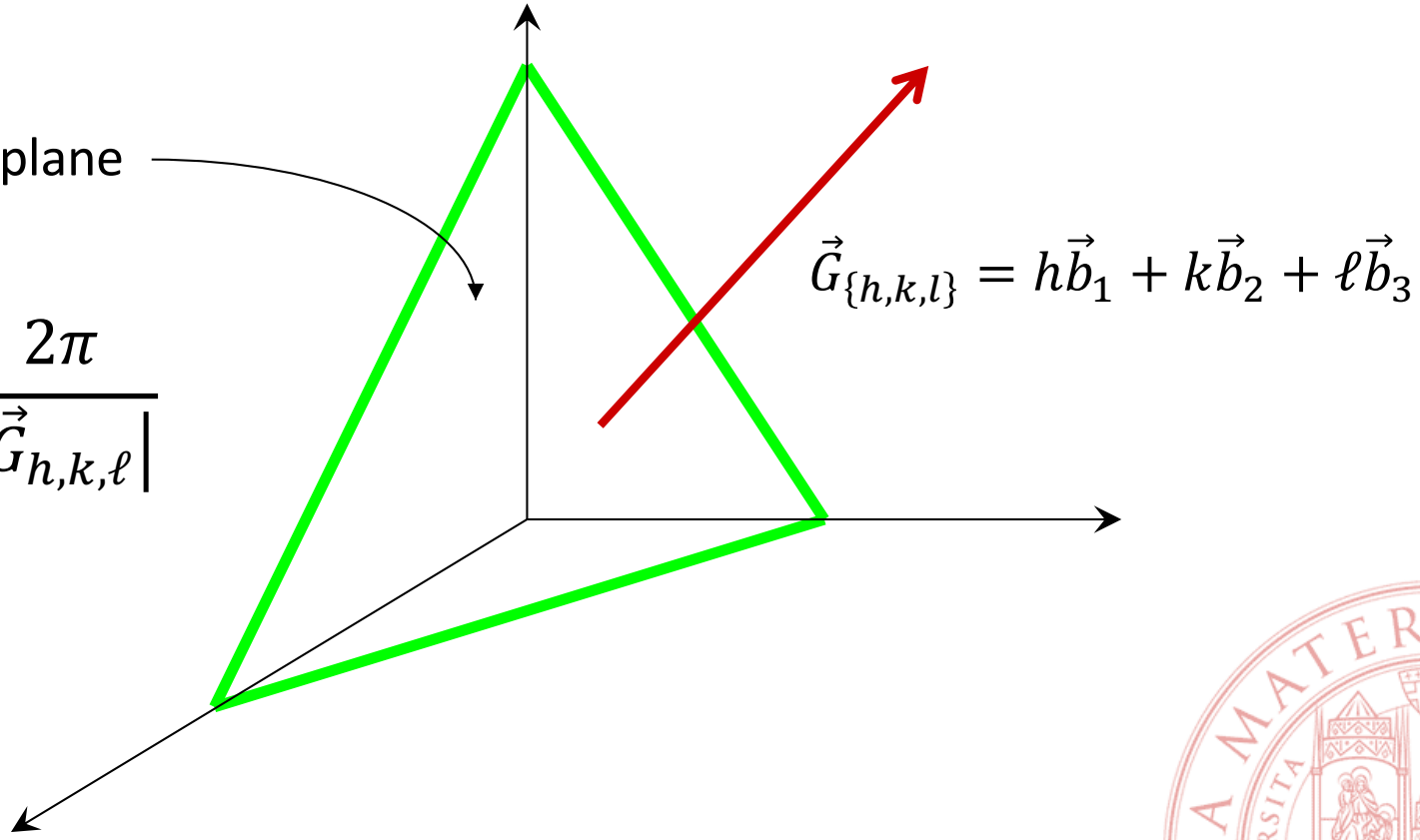
$$\vec{q} = \vec{G}_{h,k,\ell} = h\vec{b}_1 + k\vec{b}_2 + \ell\vec{b}_3$$

$$\vec{b}_i = 2\pi\frac{\vec{a}_j\times\vec{a}_k}{\vec{a}_i\cdot(\vec{a}_j\times\vec{a}_k)}$$

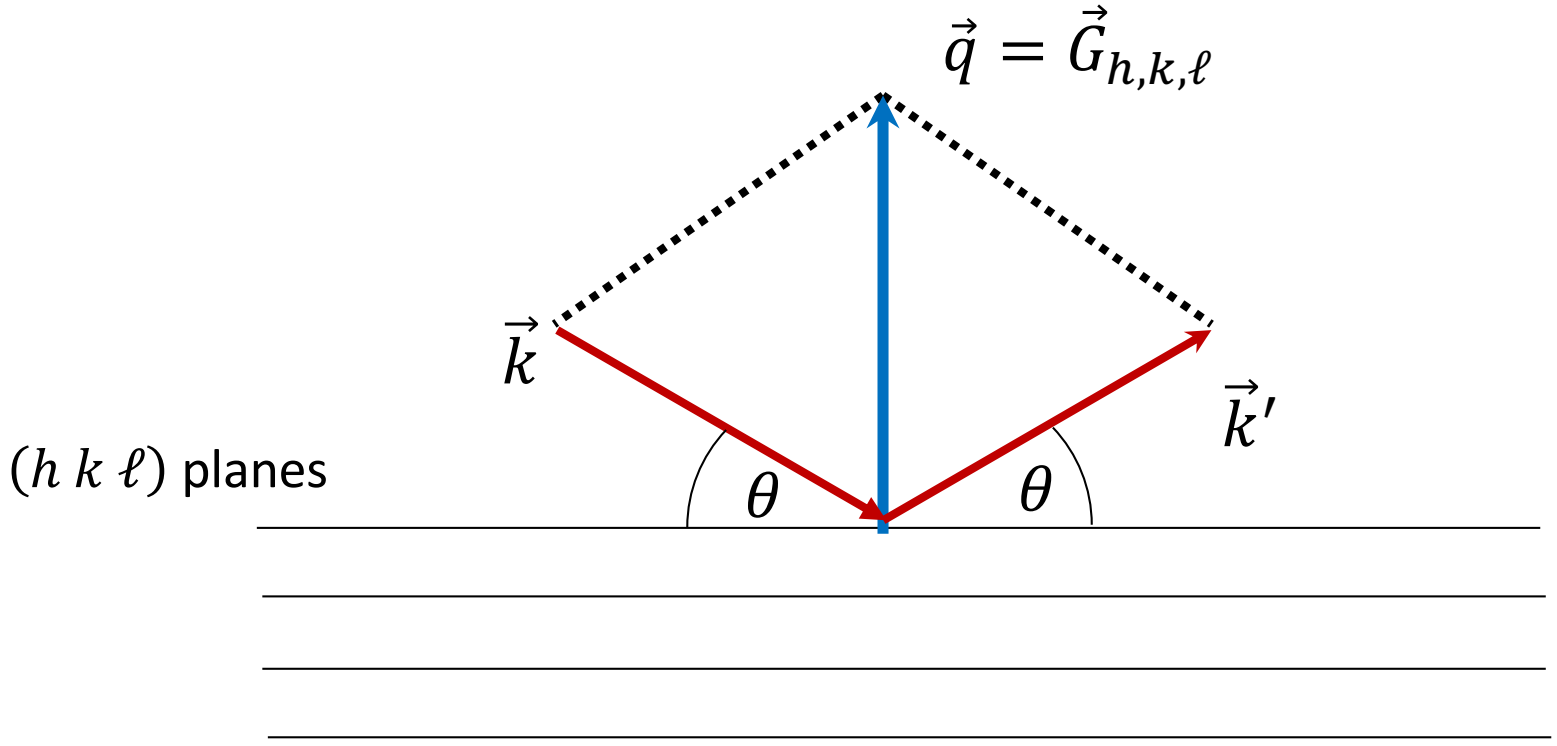
- A reciprocal lattice vector corresponds to each diffraction peak

# Lattice planes

- The reciprocal lattice vector $(h\ k\ \ell)$ is perpendicular to the lattice plane the Miller indeces of which are $(h\ k\ \ell)$
- The lattice plane distance is inversely proportional to the modulus of the reciprocal lattice vector

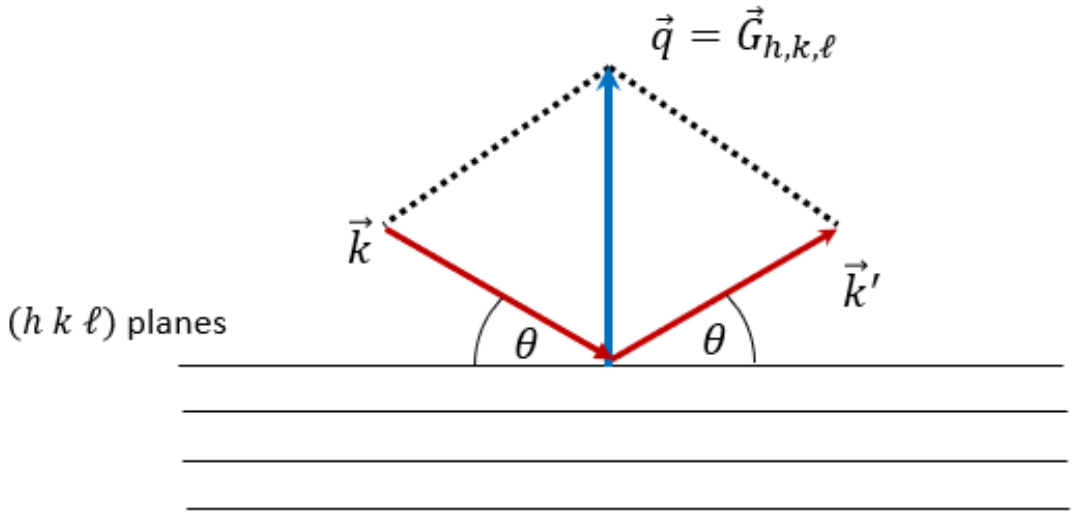


# “Reflections” from lattice planes




- Analogy with reflection from a surface

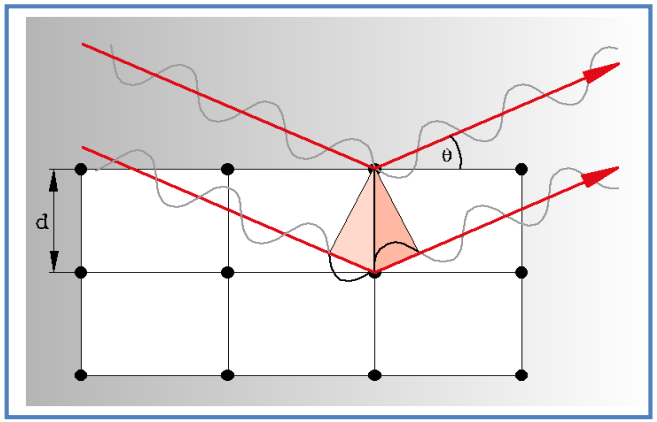
# Braggs' Law



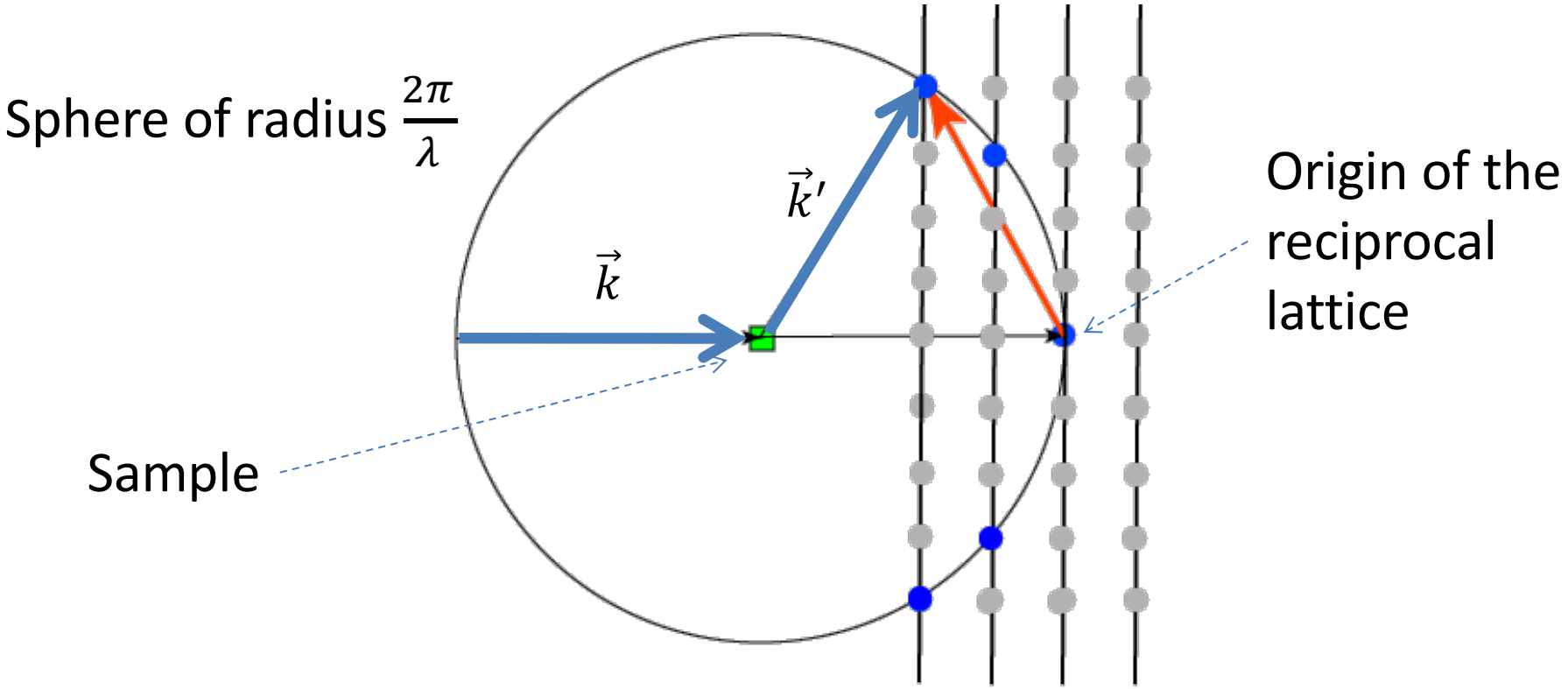

$$|\vec{q}| = |\vec{G}_{h,k,\ell}|$$

$$\frac{4\pi}{\lambda}\sin\theta = \frac{2\pi}{d_{h,k,\ell}}$$

$$\lambda = 2d_{h,k,\ell}\ \sin\theta$$

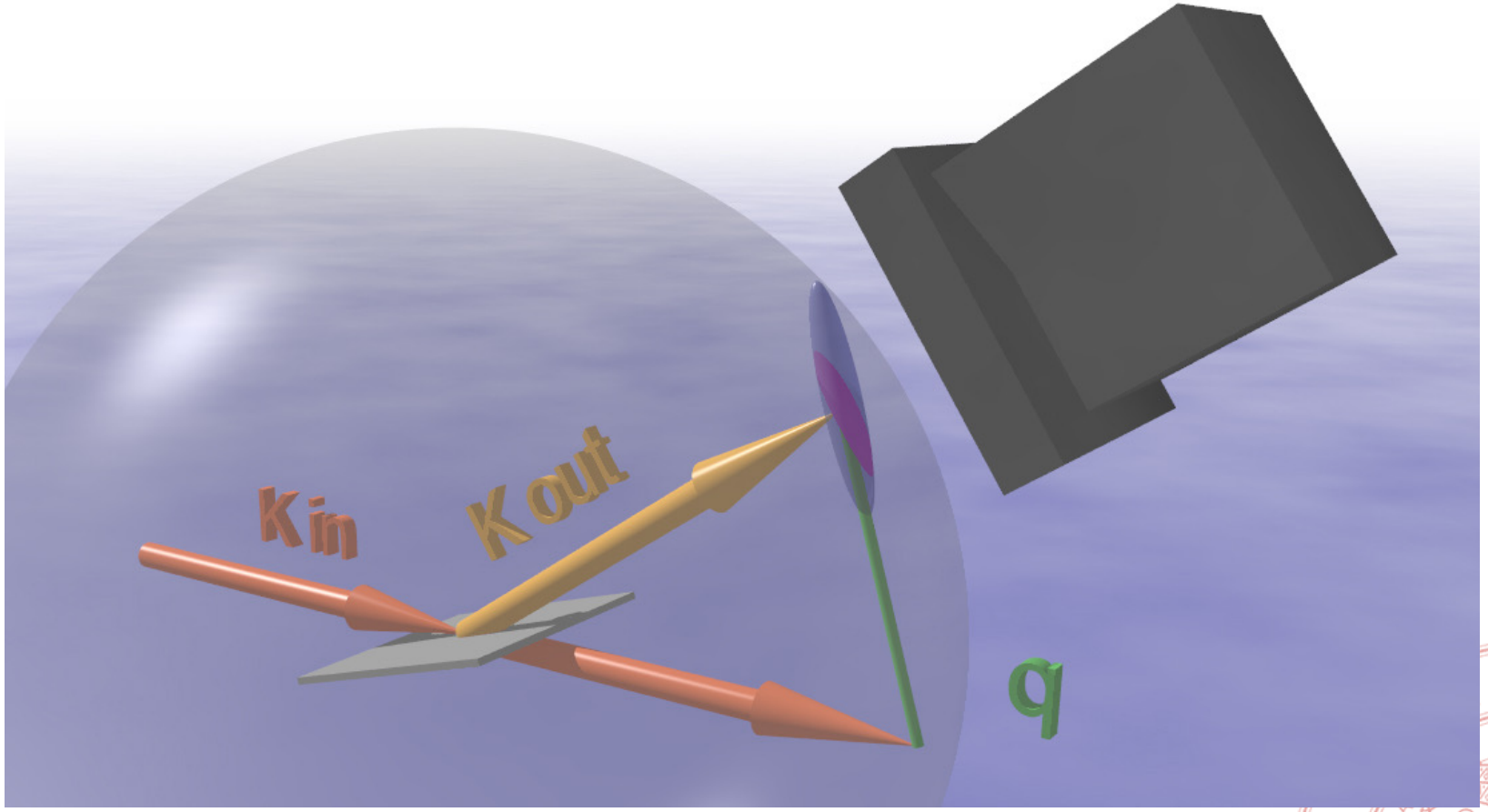


# Ewald's sphere




- When the sphere intersects a reciprocal lattice point a reflection will be observed

# Ewald's sphere



# Intensity of reflections

- When Laue conditions are satisfied the intensity is proportional to

$$I(\vec{q}) \propto |F(\vec{q})|^2, \qquad F(\vec{q}) = \sum_{j=1}^{Q} f_j(q)\, e^{-i\vec{q}\cdot\vec{r}_j}$$

- Since $\vec{q} = \vec{G}_{hk\ell}$ the notation used is

$$I_{hk\ell} \propto |F_{hk\ell}|^2, \qquad F_{hk\ell} = \sum_{j=1}^{Q} f_j(G_{hk\ell})\, e^{-i\vec{G}_{hk\ell}\cdot\vec{r}_j}$$

$$\vec{G}_{hk\ell} = h\vec{b}_1 + k\vec{b}_2 + \ell\vec{b}_3$$

# Intensity of reflections

- It is possible that $F_{hk\ell} = 0$ , in which case the diffraction peak/ reflection is absent
- Laue conditions are only necessary, they are not sufficient to observe a reflection
- When $F_{hk\ell} = 0$ for a set of $(h\ k\ \ell)$ the term "systematic extinctions" is used
- Simple rules can be derived which identify the type of lattice. E.g. $F_{hk\ell} \neq 0$ if:
  - FCC e ZB: $h\ k\ \ell$ same parity
  - BCC: $h + k + \ \ell$ = an odd number

# Intensity of reflections

- $F_{hk\ell}$ depends on the atomic positions within the unit cell: by measuring the intensity of a good number of reflections it is possible to determine them