Transmission Electron Microscopy

Part II: electron scattering

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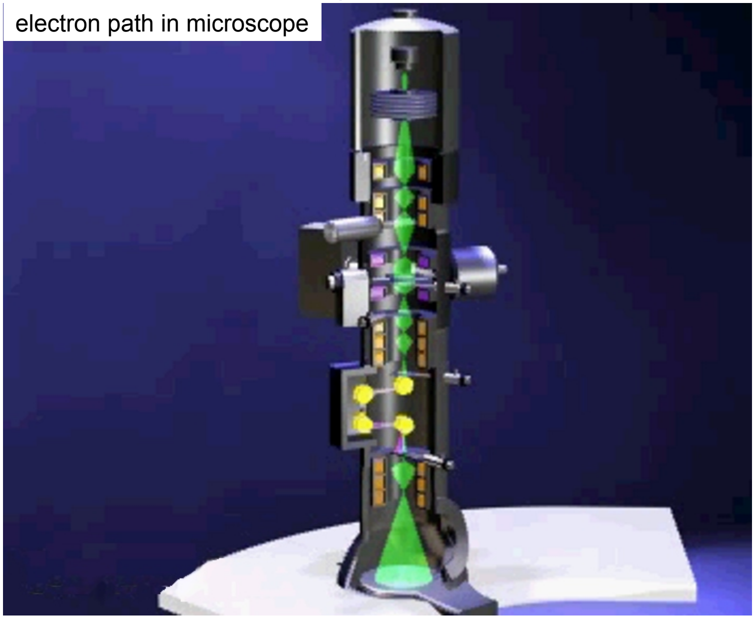
The TEM

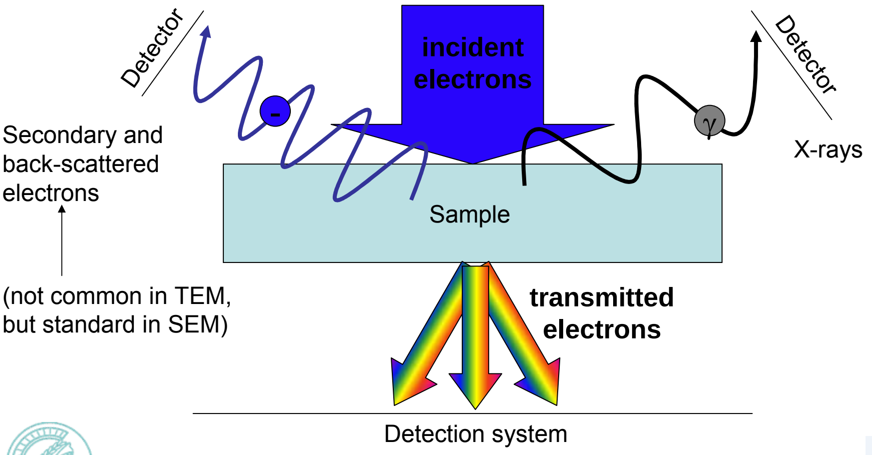


electron path in microscope

Image and animation: Carl Zeiss SMT

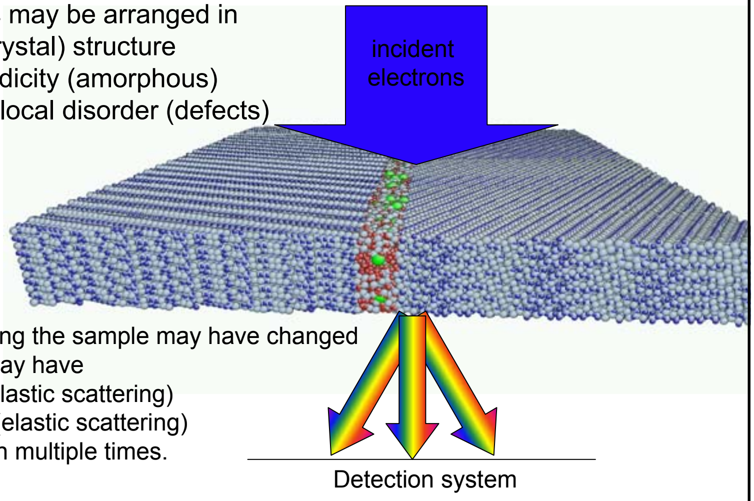
Transmission of the electron wave by the sample

Transmission electron microscopy involves sending electrons in a well-defined manner through a thin sample and collect the transmitted electrons (and in some cases also secondary electrons or photons).

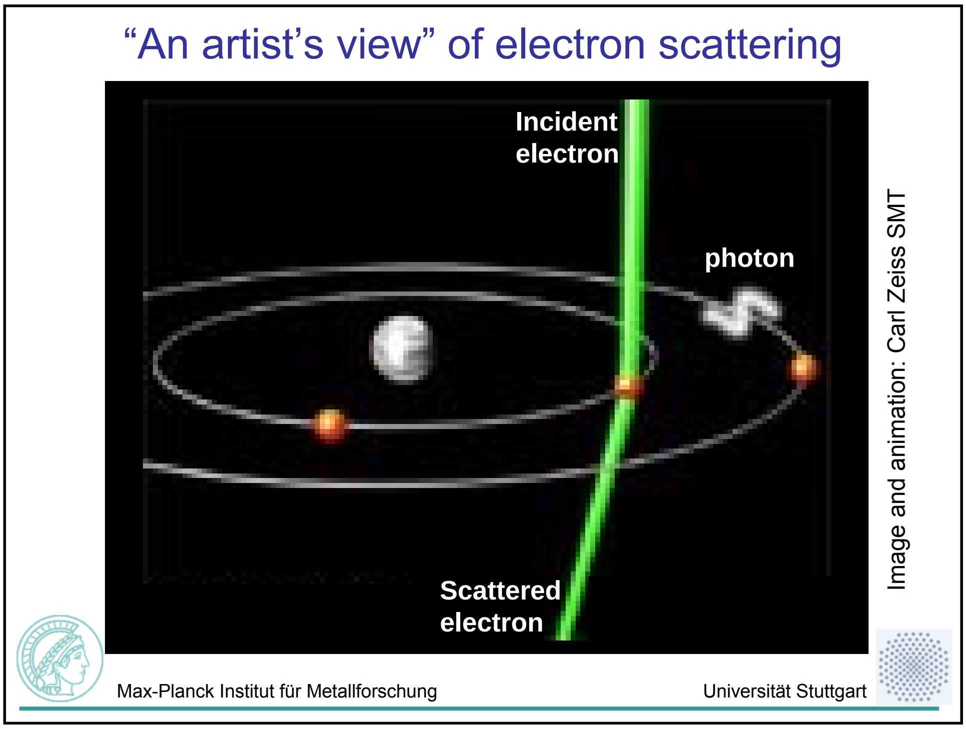


Scattering – an atomistic view

- The sample consists of atoms
- These atoms may be arranged in
  a) a periodic (crystal) structure
  b) without periodicity (amorphous)
  c) crystals with local disorder (defects)



- Electrons leaving the sample may have changed direction and may have
  a) lost energy (inelastic scattering)
  b) lost no energy (elastic scattering)
  c) done both, even multiple times.



"An artist's view" of electron scattering

Image and animation: Carl Zeiss SMT

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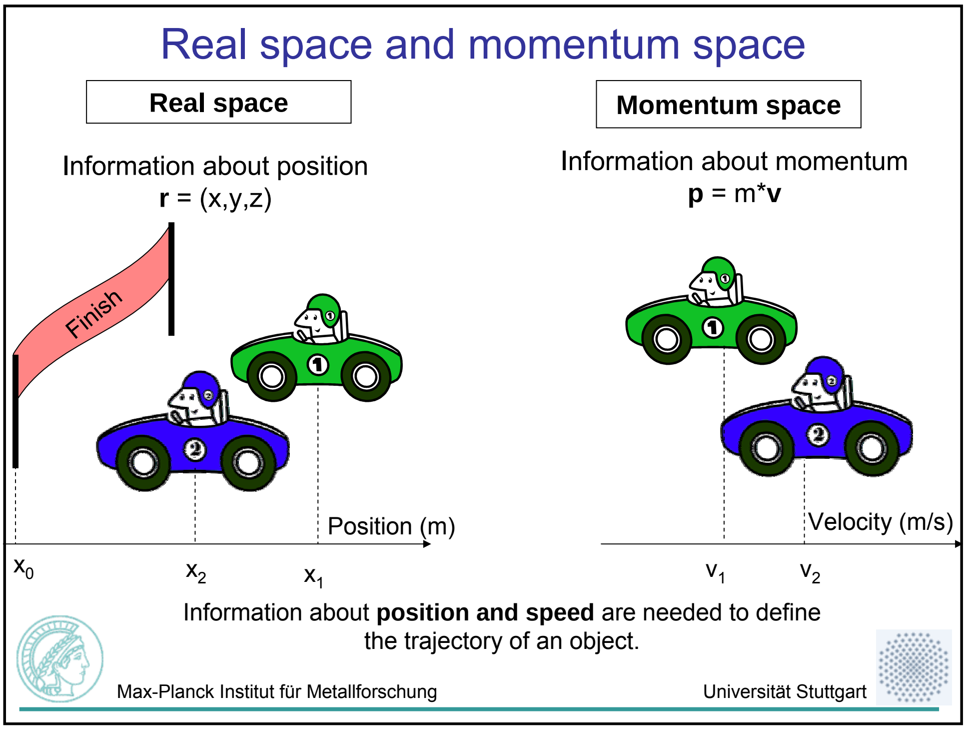

Real space and momentum space

Real space	**Momentum space**
Information about position **r** = (x,y,z)	Information about momentum **p** = m***v**

Information about **position and speed** are needed to define the trajectory of an object.

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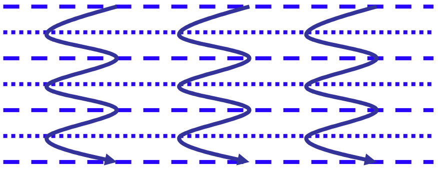
When the mass of the object gets smaller …

Real space

Momentum space



A **plane wave** extends infinitely and is defined by a momentum vector and origin.

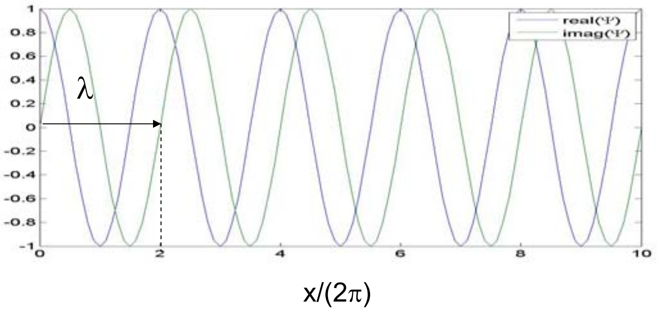
Electron trajectory with a very well defined momentum (**p**=$m_e \cdot$**v**)

Uncertainty relation:
(W. Heisenberg, 1927)

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi} = \frac{\hbar}{2}$$

Once we know the momentum of a particle very precisely, the wave function describing it becomes very large.

Plane waves



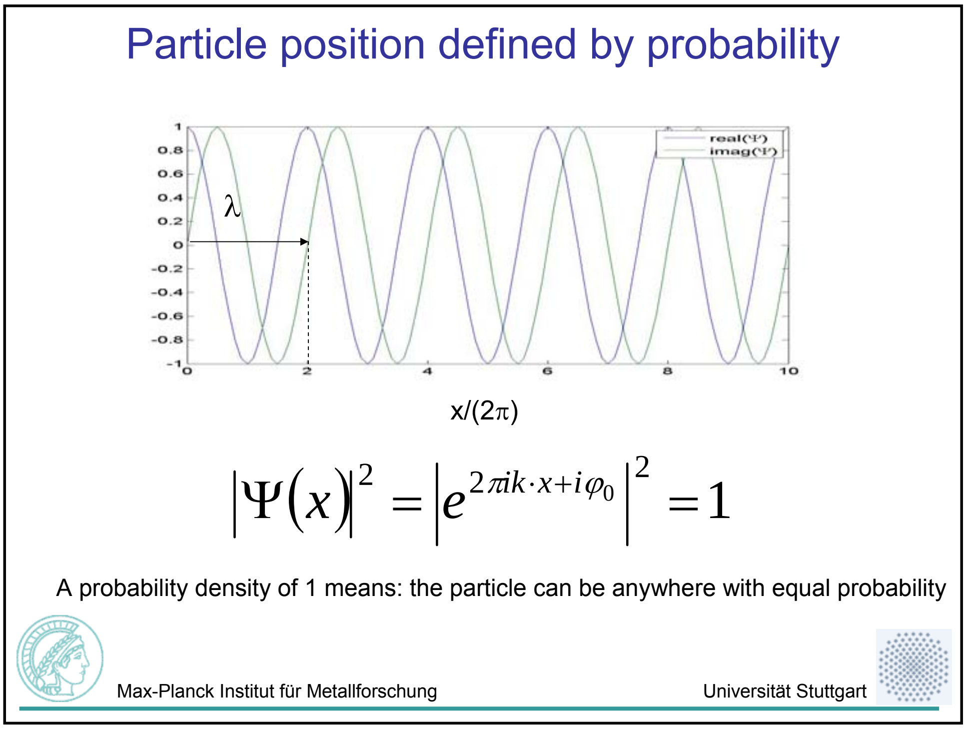
1D: $$\Psi(x) = e^{2\pi i k \cdot (x + x_0)} = e^{2\pi i k \cdot x + i\varphi_0}$$

3D: $$\Psi(x) = e^{2\pi i \vec{k} \cdot \vec{r} + i\varphi_0}$$

Phase shift

Wave number **k**=m**v**/h: |**k**|=1/λ

Momentum is given in 1/m => momentum space = reciprocal space



Particle position defined by probability

x/(2π)

$$\left|\Psi(x)\right|^2 = \left|e^{2\pi i k\cdot x+i\varphi_0}\right|^2 = 1$$

A probability density of 1 means: the particle can be anywhere with equal probability

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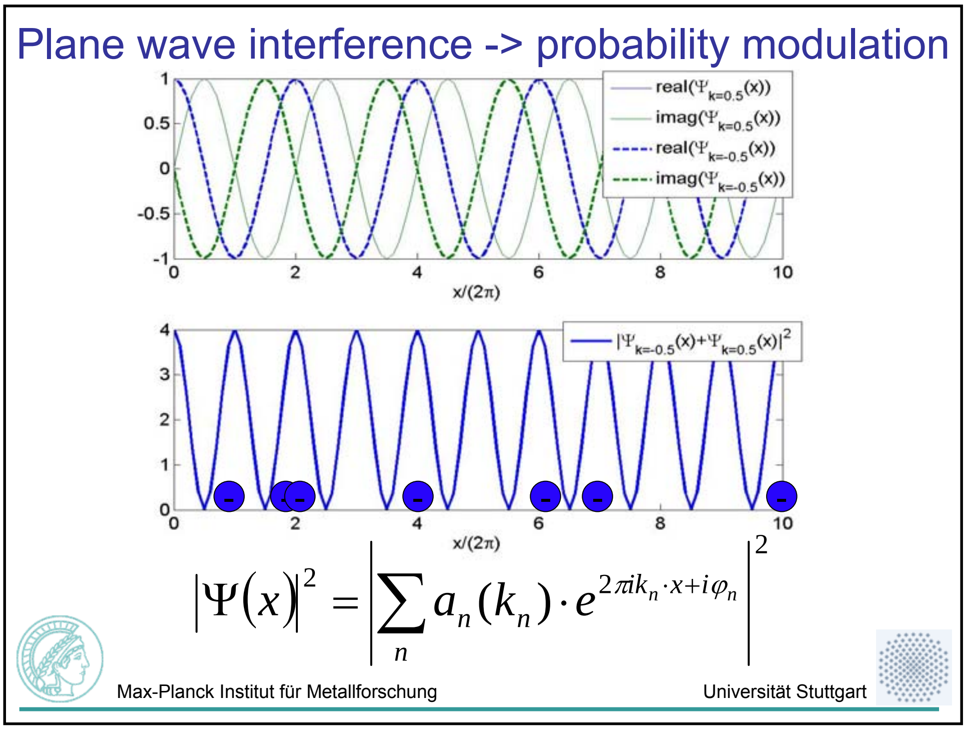

Plane wave interference -> probability modulation

$$\left|\Psi(x)\right|^2 = \left|\sum_n a_n(k_n)\cdot e^{2\pi i k_n\cdot x+i\varphi_n}\right|^2$$

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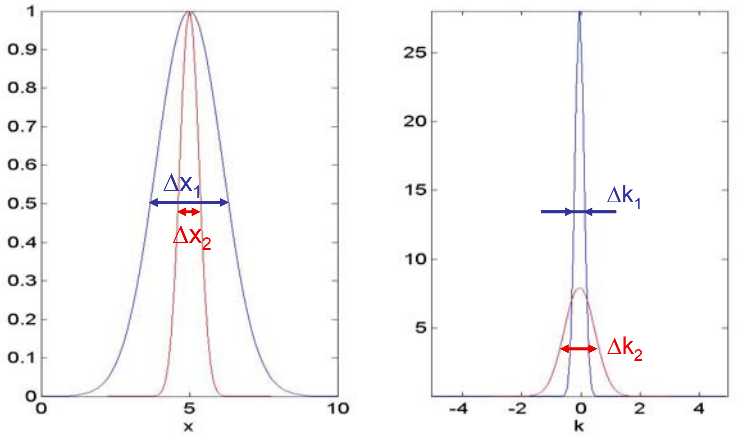
Definition of wave packets by plane waves

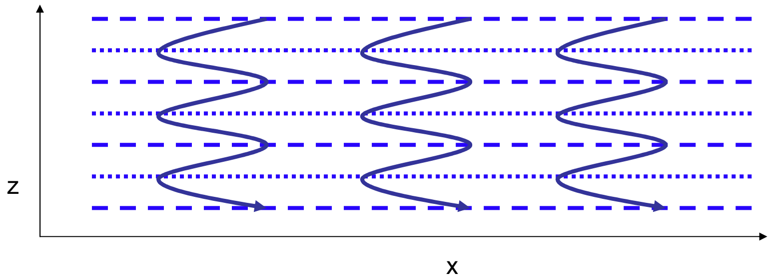


Wave packet defining the
position of a particle
in real space

Spectrum of wave numbers
needed to represent the same
wave packet.

Fourier uncertainty relation: $\Delta x \cdot \Delta k = 1/\pi$

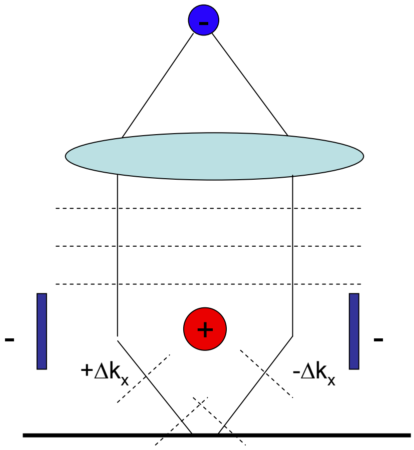
Plane wave traveling down the microscope column



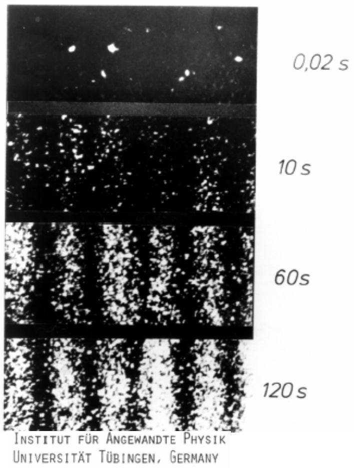
$$\Psi(x) = e^{2\pi i \vec{k} \cdot \vec{r}}$$

If k = (0,0,k_z) then the plane wave is infinite in x- and y-direction

Particle – Wave dualism



Detector
Waves interfere on the detector
Producing a probability distribution



Electrons choose a position on the detector according to a probability distribution

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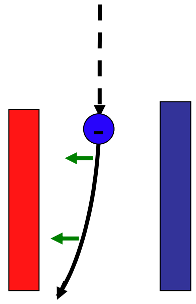
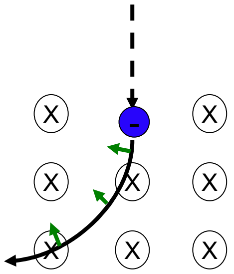
Elastic interactions in the sample



Electrostatic force



Lorentz force

$\mathbf{F}=q\mathbf{E}$

$\mathbf{F}=q\mathbf{v}\otimes\mathbf{B}$

These 2 forces govern the elastic interaction between sample and beam electron.
Since most materials are non-magnetic, the Lorentz force will be neglected for this part of the lecture.

Potential of atomic nuclei

Electrons are also deflected by the scalar potential Φ produced by atoms.
The potential produces the electric field

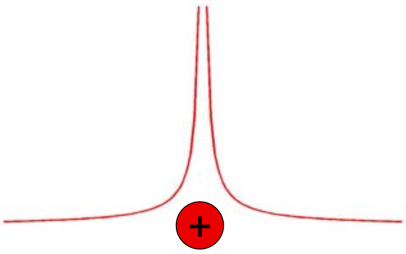
$$\vec{E} = -\vec{\nabla}\Phi$$

The potential of a point charge at position r_0 is

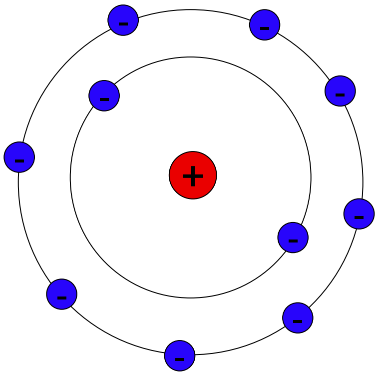
$$\Phi(\vec{r}) = \frac{1}{4\pi\varepsilon_0} \frac{q}{\left|\vec{r} - \vec{r}_0\right|}$$

This means:
Positively charged atomic nuclei (q=Ze) produce a positive electrostatic potential.
Negatively charged electrons (q=-e) are attracted by positively charged nuclei.

Atomic potential



Potential of nucleus decays
as 1/distance



Electrons around the nucleus screen the
core potential,
making it decay even faster

Comparison: light vs. electron wave

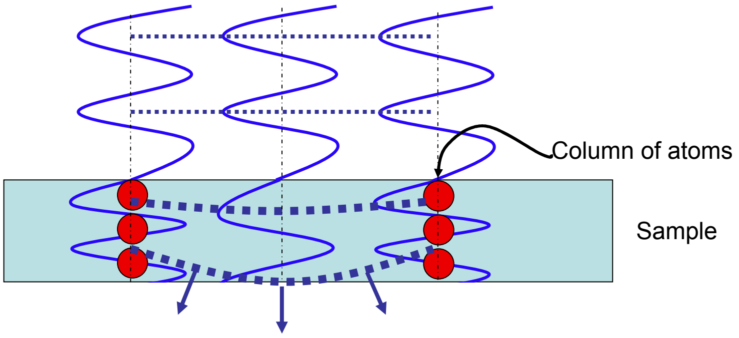
Light wave	Electron wave
$m_0 = 0$	$m_0 = 9.1 \cdot 10^{-31}$ kg
$\lambda = hc/E_{photon}$	$\lambda = h/(2m_0\, eV_r)^{1/2}$ $V_r = V_0 + (e/(2m_0c^2))^2 V_0^2$
$n = \lambda_{vacuum} / \lambda_{material}$	$n \approx 1 + \Phi_0/V_0$

$h = 6.625 \cdot 10^{-34}$ Js
$c = 3 \cdot 10^8$ m/s
$h/(2m_0e)^{1/2} = 1.2264$

V_0 = accelerating voltage (typ. few 10^5V)
V_r = relativistic acc. voltage (if V_0>50kV)
n = refractive index
Φ_0 = mean inner potential

Refractive index at atomic scale

incident electron wave



Variations in the projected potential produce local relative phase shifts of the electron wave.

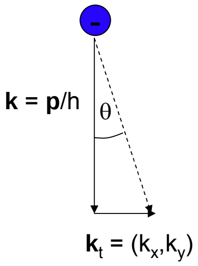
The wave front therefore bends as wave travels through medium

Atomic scattering factor

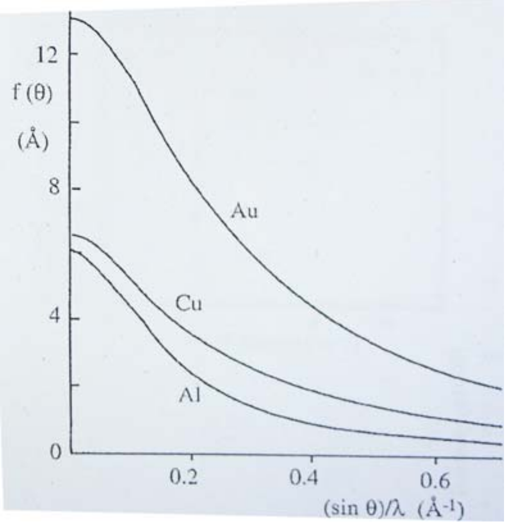
Normally the reciprocal space representation of the potential decay is given.

$$\Phi(x) \rightarrow \Phi(k)$$

For electrons of known momentum **p** (de Broglie: |**p**|=m|**v**|=h/λ)
a change in transverse momentum is equivalent to scattering by a certain angle θ



Atomic scattering factor f(θ) (a.k.a. “form factor”)



- f(θ) decreases with increasing θ
- f(θ) decreases with decreasing λ (i.e. with increasing acc. voltage)
- f(θ) increases with increasing atomic number Z
- f(θ)^2 is proportional to the scattering intensity I(k) = |Ψ(k)|^2, i.e. the probability for an electron to be deflected by angle θ

Scattering factors tabulated by Doyle and Turner as well as others
(P.A. Doyle and P.S. Turner, Acta Cryst. A24, (1968), 390-397)

Electron scattering and X-ray scattering

Electrons are scattered by the object's potential distribution $\Phi(x)$
Photons are scattered by the objects charge density distribution $\rho(x)$

Bethe – Mott formula: $$f(\vartheta)=\frac{1+E/E_0}{8\pi^2 a_0}\left(\frac{\lambda}{\sin(\vartheta)}\right)^2\left(Z-f_X(\vartheta)\right)$$

Bohr radius: $$a_0=\frac{\varepsilon_0 h^2}{\pi m_0 e^2}=0.0529nm$$

Electron rest energy: $E_0 = 511\text{keV}$

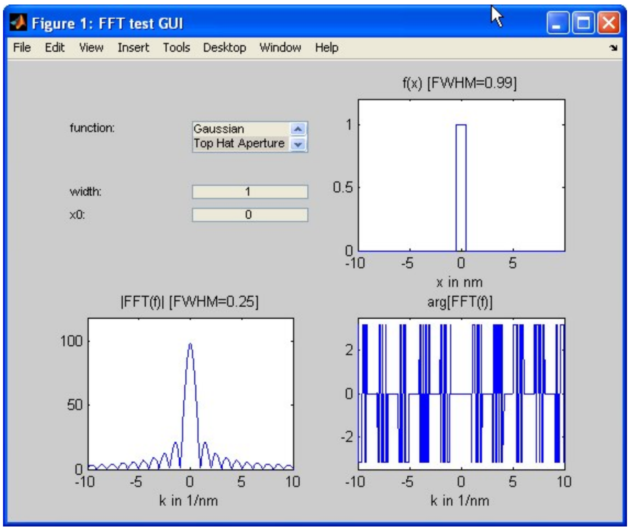
Homework: real - and reciprocal space

Use Matlab (or your favorite Math-capable visualization tool)
to plot **amplitude and phase** of the FFT of the following functions:

- Gaussian: $$f(x)=e^{\left(-\pi\left[\frac{x-x_0}{w}\right]^2\right)}$$
- Top hat aperture: $$f(x)=\begin{cases}1, if\ |x-x_0|<w/2\\0, if\ |x-x_0|\geq w/2\end{cases}$$

Use different values for w and x_0

Discussion of Homework



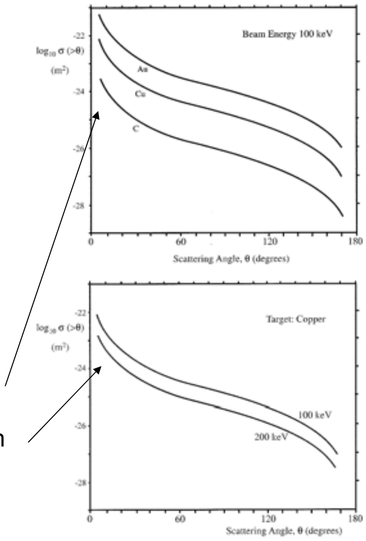
function: Gaussian / Top Hat Aperture

width: 1

x0: 0

Solution: http://hrem.mpi-stuttgart.mpg.de/koch/Vorlesung/

Scattering factor: Low angle scattering much more likely than high-angle scattering

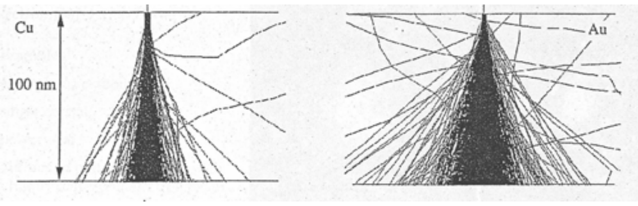


Elastic scattering increases with *Z*

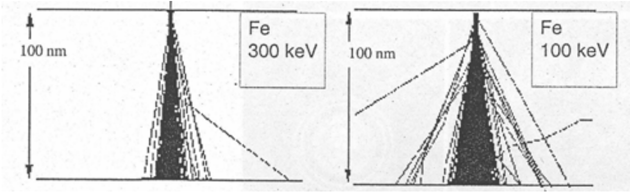
Elastic scattering decreases with accelerating voltage

Small scattering angles are much more likely

Scattering cross section ~ # of scattering events

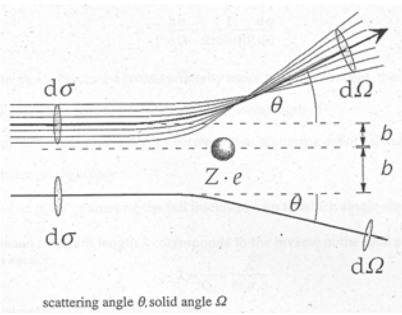


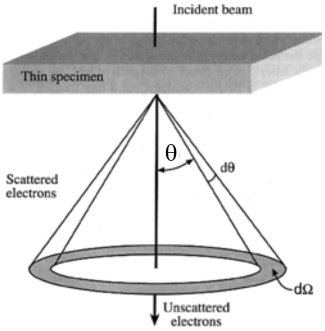
Monte Carlo simulation of electron scattering in Cu and Au
⇒ Heavier atoms (higher Z) scatter stronger.



Monte Carlo simulation of electron scattering in Fe at 100 and 300kV
⇒ Higher voltage reduces scattering cross section

Scattering Cross-section

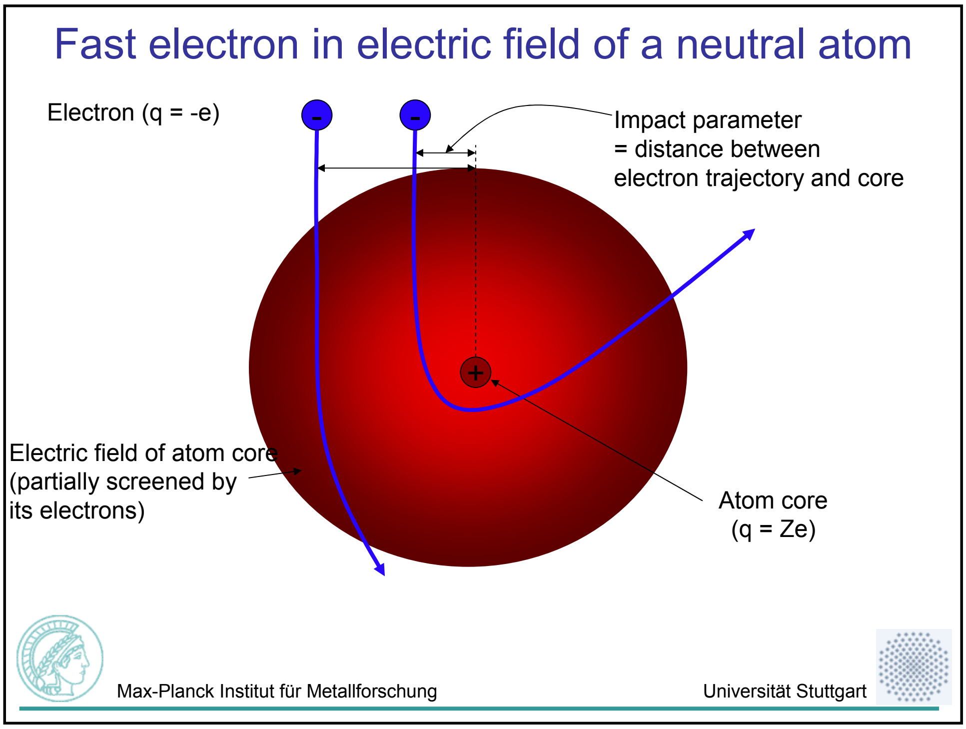




Probability of scattering into a solid angle dΩ is described by the **differential scattering cross-section** dσ/dΩ.

Most single-atom scattering events are azimuthally symmetric, so that dσ/dΩ is defined independent of azimuthal angle.

The **total cross section**, σ, is obtained by integrating over all scattering angles θ



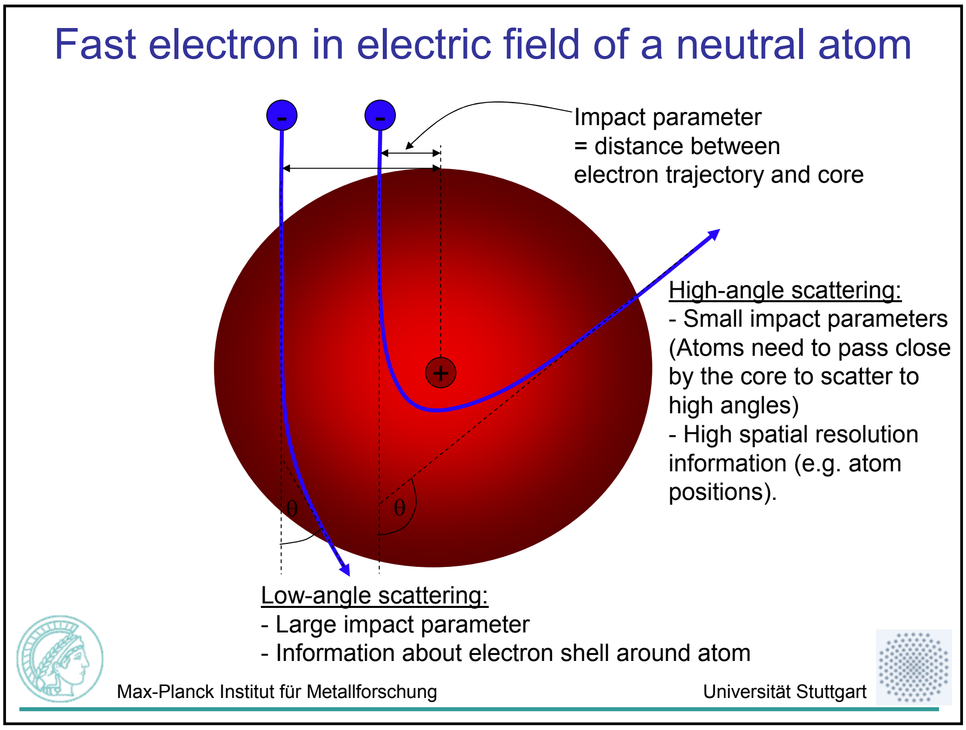
Fast electron in electric field of a neutral atom

Electron (q = -e)

Impact parameter
= distance between
electron trajectory and core

Electric field of atom core
(partially screened by
its electrons)

Atom core
(q = Ze)



Fast electron in electric field of a neutral atom

Impact parameter
= distance between
electron trajectory and core

High-angle scattering:
- Small impact parameters
(Atoms need to pass close
by the core to scatter to
high angles)
- High spatial resolution
information (e.g. atom
positions).

Low-angle scattering:
- Large impact parameter
- Information about electron shell around atom

Rutherford (elastic high-angle) scattering

Rutherford scattering describes the scattering off a point charge

Differential cross section: $$\frac{d\sigma}{d\Omega} = \frac{e^4 Z^2}{16E^2 \sin^4 \frac{\theta}{2}}$$

Z – atomic number
E – Electron kinetic energy

More scattering in heavy materials (Z)

Images using high-angle scattered electrons give high intensity at positions where heavy atoms are located (Z contrast imaging).

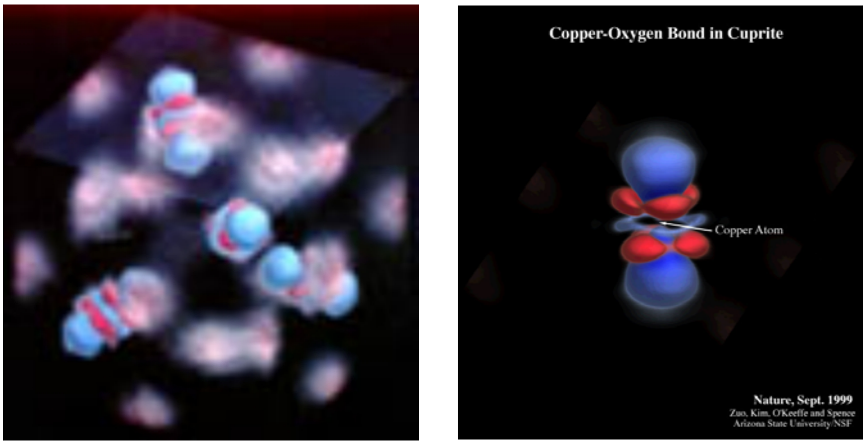
More scattering at low kinetic energies of the electrons (E)

Imaging of light elements (biological material) easier at lower E

(Because of screening of the nuclear charge and due to spin effects the Rutherford cross-section has to be modified→ Mott cross-section)

Low-angle elastic scattering

Contains information about charge density distribution within crystal unit cells



Charge density maps of Cu_2O obtained from convergent-beam electron diffraction data (Zuo et al., Nature **401** (1999) 49).

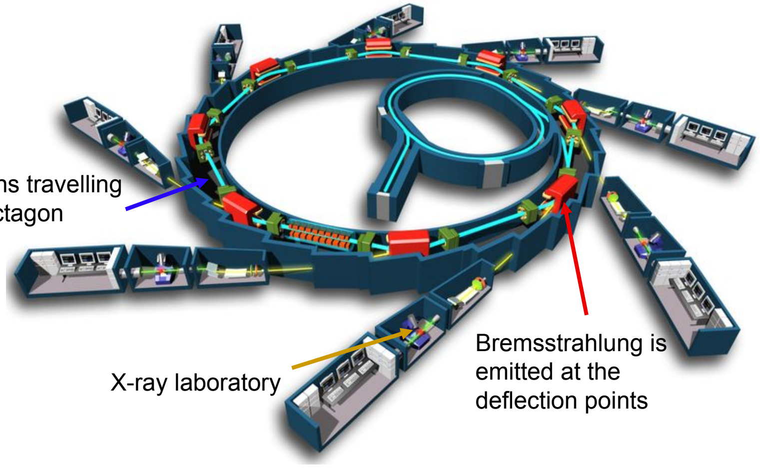
Inelastic scattering

Interaction of the fast electron with …

- single atom core
- single atomic electron (orbital)
- molecular bonding electron orbitals
- Phonons (collective vibrational states of all the atoms)
- Plasmons (collective vibrational states of electrons in conduction- and valence band)

Bremsstrahlung

Fast electrons that are accelerated (i.e. forced to change direction or velocity) emit photons -> so called "Bremsstrahlung"



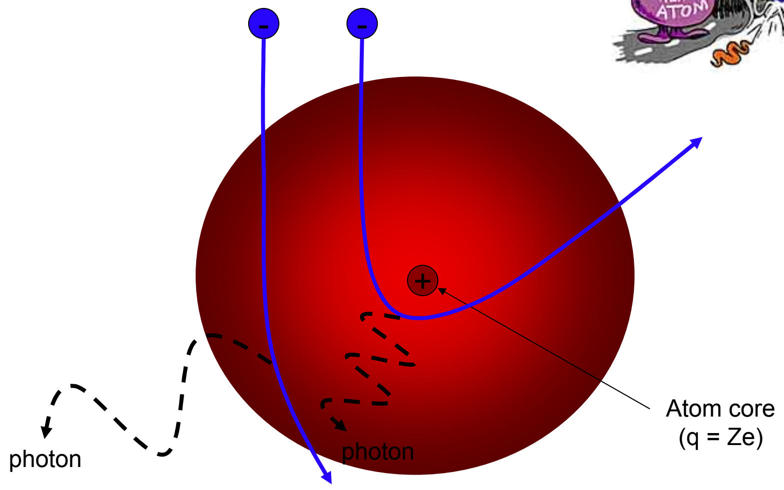
Electrons travelling in an octagon

X-ray laboratory

Bremsstrahlung is emitted at the deflection points

(Synchrotron Soleil, GIF-sur-YVETTE, France)

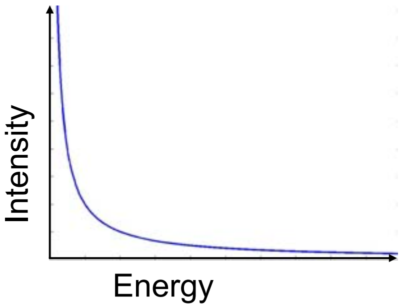
Bremsstrahlung



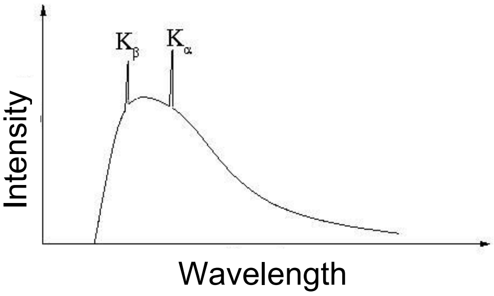
Bremsstrahlung is emitted when electrons are accelerated,
i.e. forced to change direction of speed of motion.

Bremsstrahlung

Radiation emitted by accelerated electrons



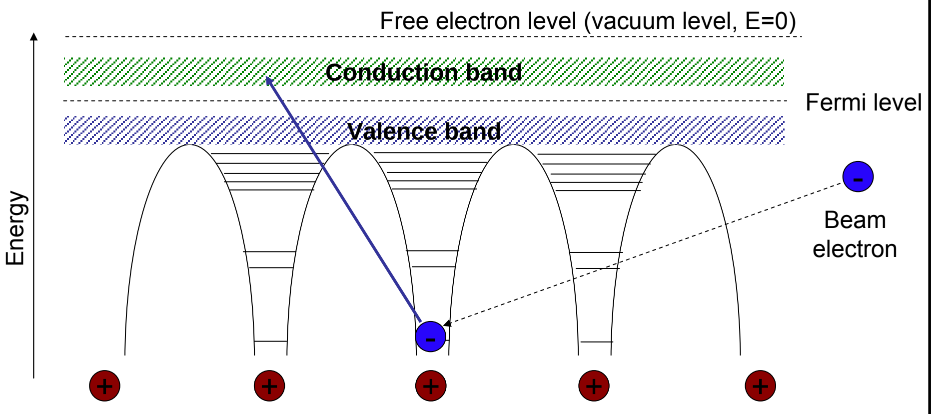
Spectrum of Bremsstrahlung
in a TEM (e.g. V_0=200kV)



Typical spectrum of an X-ray tube:
Bremsstrahlung has a continuous spectrum.

$$I_{Bremsstrahlung}(E) = KZ\frac{eV_0 - E}{E}$$

Electronic excitations



Fast beam electrons may catapult electrons within the material to higher energy levels

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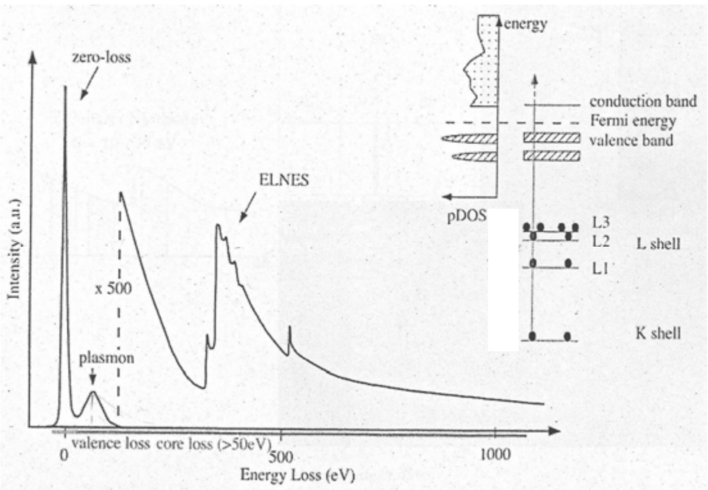
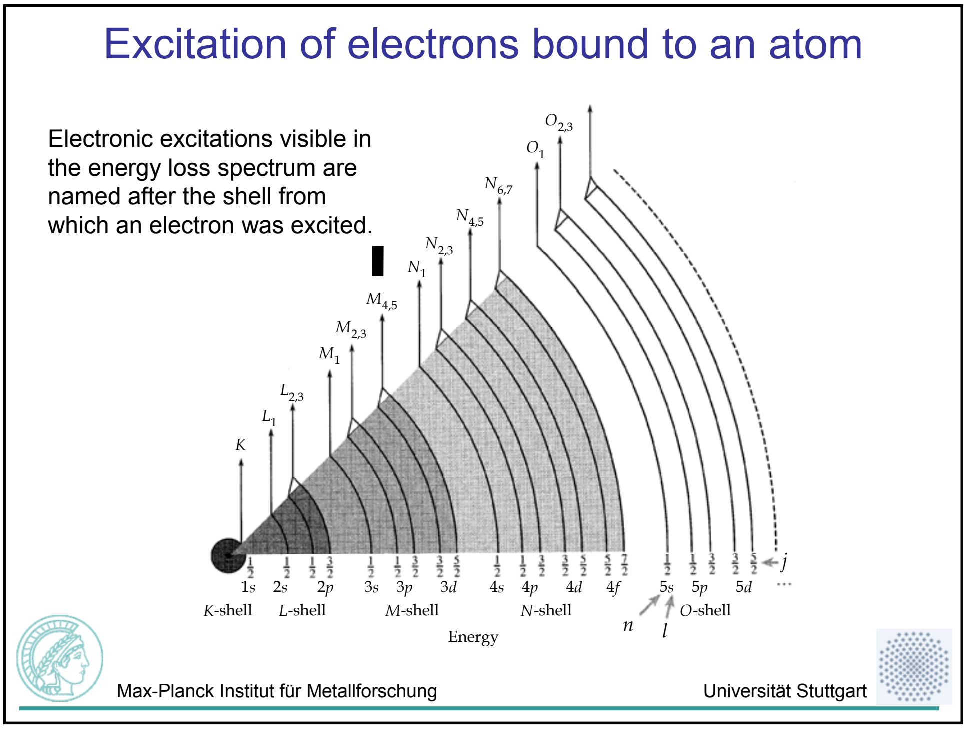
Excitation of electrons bound to an atom

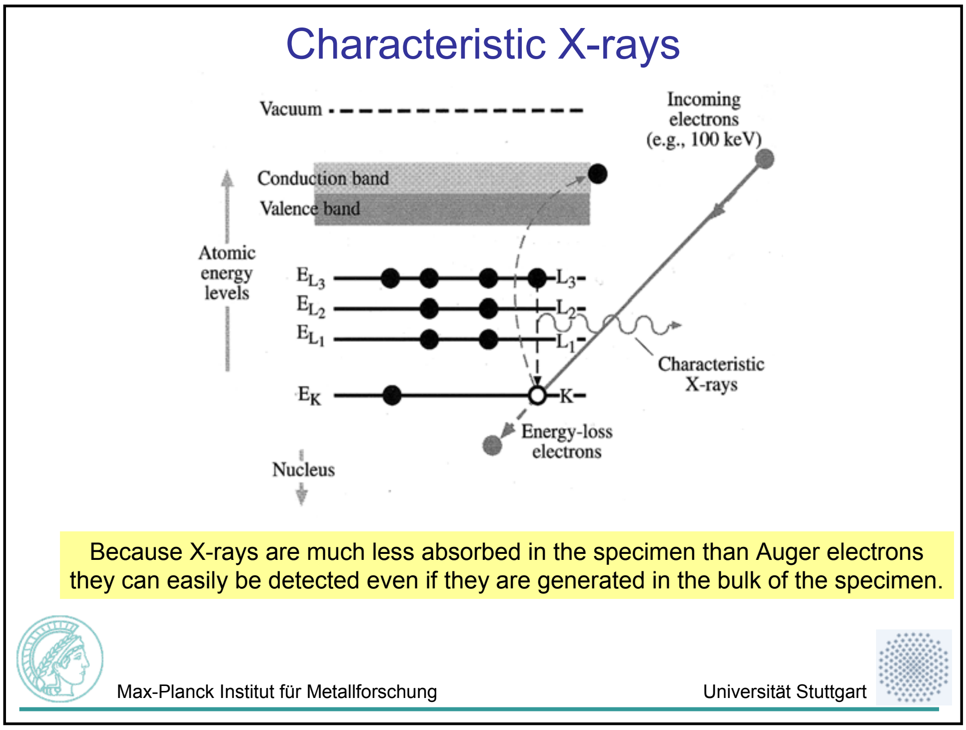


Low loss excitations: valence → conduction band (**interband transitions**)
within conduction band (**intraband transitions**)
High energy loss excitations: core levels → conduction band



Excitation of electrons bound to an atom

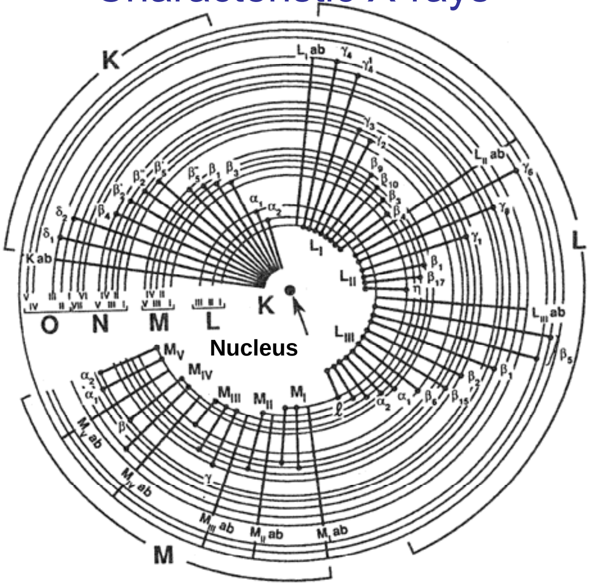
Electronic excitations visible in the energy loss spectrum are named after the shell from which an electron was excited.



Characteristic X-rays

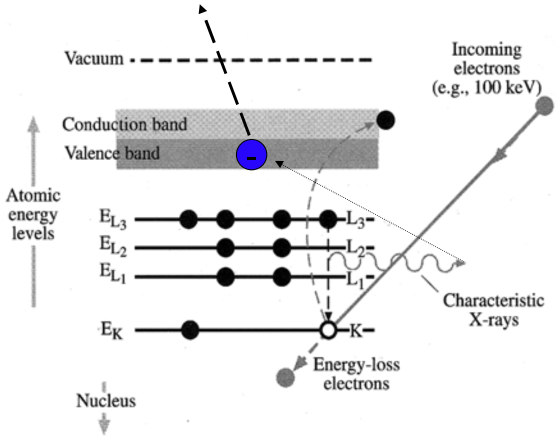
Because X-rays are much less absorbed in the specimen than Auger electrons they can easily be detected even if they are generated in the bulk of the specimen.

Characteristic X-rays



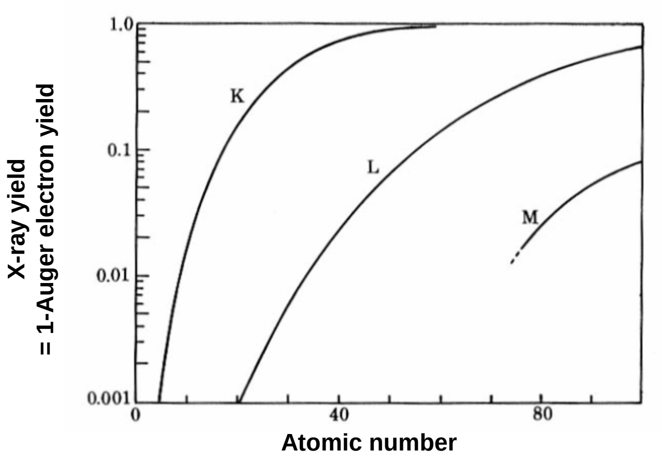
Possible electron transitions giving rise to K, L, M characteristic X-rays

Auger electron scattering



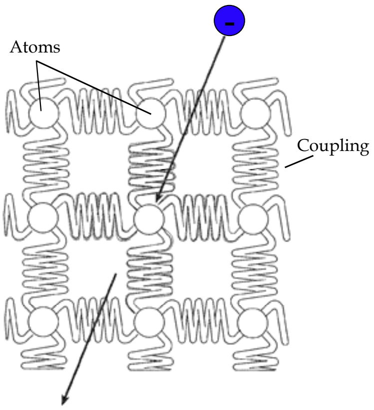
Characteristic X-rays may excite loosely bound electrons (Auger electrons)
[nach Pierre Auger 1899 – 1933, Auger-effect: 1929]

Auger electrons vs. characteristic X-rays



Probability of relaxation of excited atoms by X-ray emission.
Auger electrons are emitted otherwise.

Phonon scattering



The primary electron may create or anihilate quantized vibrational states in the target, called „phonons".

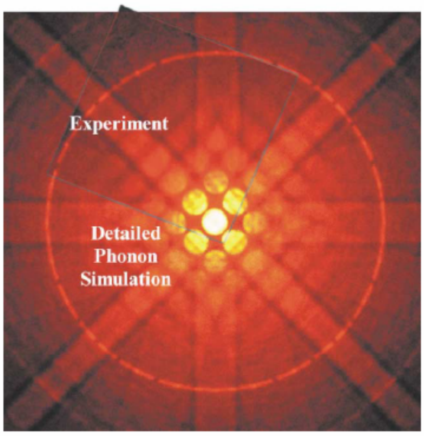
The energy required to create a phonon is very small (≤ 0.2 eV) and hardly measurable in the TEM („quasielastic").

Note: it is also possible for the electron to gain energy by anihilating (destroying) a phonon quantum. The probability for anihilation is always less than the chance for creating a phonon.

Electrons may also scatter elastically off phonons already present because of the finite sample temperature.

Phonon scattering

D.A. Muller et al. / Ultramicroscopy 86 (2001) 371–380

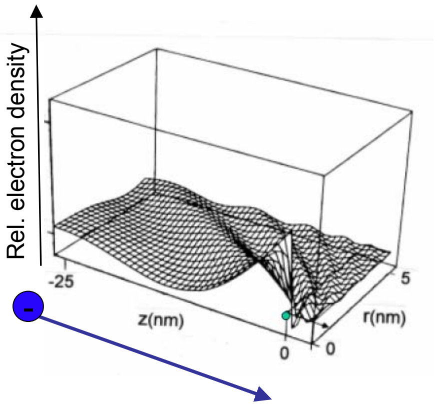


The momentum transfer of phonon scattering is comparatively large. This leads to a diffuse background in diffraction patterns at almost all scattering angles.
At large scattering angles the phonon scattering cross section exceeds the elastic scattering cross section.

Scattering is stronger
…at heavy atoms (proportional to $Z^{3/2}$)
…at higher temperatures (more phonons present)

The creation of phonons causes the specimen to heat up.

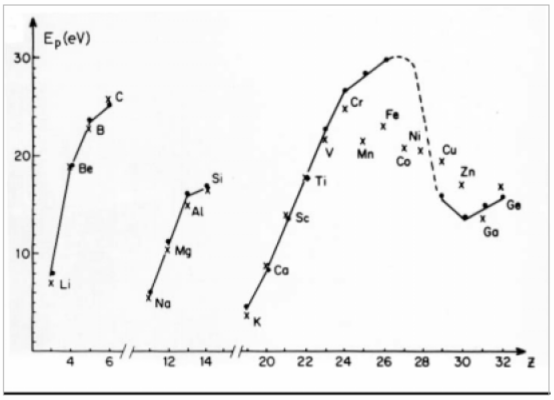
Plasmon excitation



- Because the primary electron is a charged particle, it produces a travelling electromagnetic field during its passage through the specimen.
- This field causes oscillations in the local density of electrons in the **valence and/or conduction bands**: charge density waves (**plasmons**).
- The energy of the plasmon depends on the electron density in the material. It is typically in the range between 10 and 30 eV.

Plasmon excitation

Plasmon energies of different materials



The plasmon energy can be used for material analysis

Dielectric formulation of energy loss

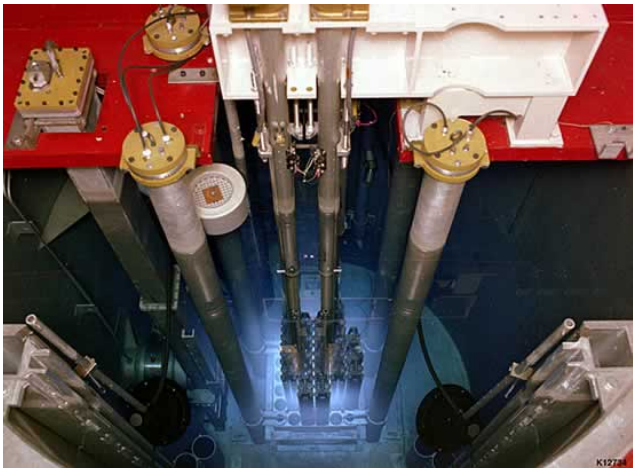
The entirety of energy losses can be considered as a response of the material on the impact of the swift electron.

The response function is called **energy-loss function** and can be written as Im $(1/\varepsilon(q,\omega))$

$\varepsilon(q,\omega)$ is the dielectric function of the material.

⇒The EELS spectrum contains the full information about the dielectric function, including optical properties of the material.

Cherenkov Radiation

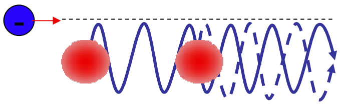


260keV electrons, products of nuclear fission, exceed the speed of light in water (refractive index n_{Water}=1.3 => $c_{Water} = 3.0\cdot10^8$m/s / 1.3=$2.3\cdot10^8$m/s), producing a characteristic “blue glow” in nuclear reactors.

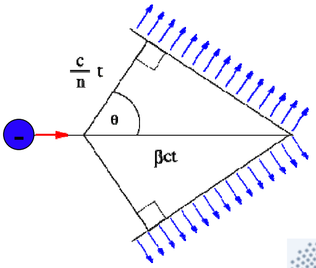
Cherenkov Radiation

- As a fast electron travels through an insulating (finite dielectric constant) material, it polarizes atoms along its path. As the atoms relax back, they may emit light.
- For low electron speeds, the emitted light interferes **destructively**.
- If an electron exceeds the phase velocity ($v_p=\omega/k$) of light in this dielectric medium, the light emitted into a certain direction interferes **constructively**.

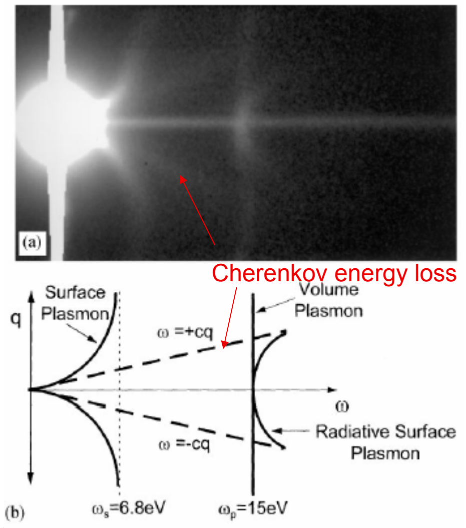
$V_{electron} < c_{Medium}$



$V_{electron} > c_{Medium}$



Cherenkov Radiation



Cherenkov energy loss

P.A. Midgley / Ultramicroscopy 76 (1999) 91–96

- The energy loss is in the range of a few eV
- The intensity is weak unless the specimen is very thick
- The fast electron is scattered under very small angles (< 0.1 mrad)

Dispersion curve (energy loss as function of momentum transfer) in Al.

Beam damage

The transfer of energy by fast moving electrons to the specimen may either directly of indirectly change the atomic arrangement, thus changing the object being investigated during investigation.

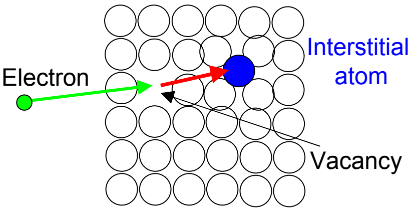
Beam damage mechanisms include:
- Ballistic knock on damage: transfer of kinetic energy from the fast electron to the atom exceeds its binding energy
- Radiolysis: Ionization and breaking of bonds causes atomic clusters to re-arrange

Quantification is complicated by:
- In addition to electrons, fast Ions may also be created in the electron gun. These have a much greater mass and may therefore damage strongly by knock-on processes.
- Surfaces may be damaged much more easily than bulk material.

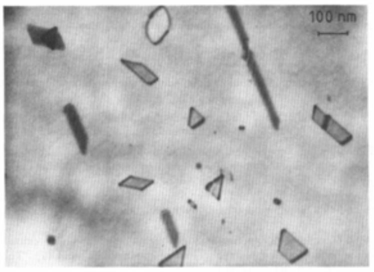
Knock-on damage

If the transfered energy exceeds the threshold for atom displacement the atom is displaced from its original site and becomes an interstitial atom. Together with the vacancy left behind it forms a Frenkel pair (interstitial and vacancy)).

Vacancies and/or interstitials can migrate in the crystal and form agglomerates
Typical: Dislocation loops, stacking-fault tetrahedra, voids



Creation of a Frenkel pair



Faulted dislocation loops in silver after electron irradiation