X-ray Properties and Atoms

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Fundamentals of X-ray Absorption Fine-Structure
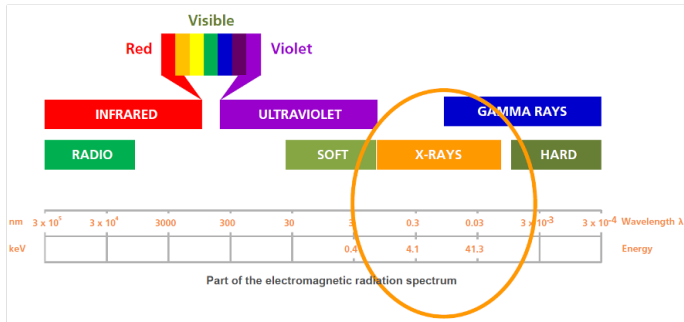
Virtual XAFS School at Illinois Institute of
Technology and Advanced Photon Source

X-rays are light with wavelength $\lambda : [0.05 : 50]$ Å or energy $E : [0.25 - 250]$ keV.

X-rays are used in many scientific fields for studying:

- interior micro-structure of materials.
- atomic-scale structure of materials.
- chemical composition of materials.
- chemical state of elements.

Part of the electromagnetic radiation spectrum

Why we use X-rays to study atoms

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X-rays have 3 main properties:

Property	Behavior	Use
Interact weakly with electrons	penetrate deeply into matter, with strong contrast in atomic number Z.	Imaging, Tomography
Energy	comparable to binding energies of core electrons in atoms.	Spectroscopy
Wavelength	comparable to distances between atoms in solids and liquids.	Scattering, Diffraction

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X-rays from synchrotron sources also have these properties, that can be useful for many applications:

- highly *polarized* in the horizontal plane.
- highly *collimated* and so possible to focus to beams at μm or nanometer scale.
- partially *coherent* - being "in phase" with other X-rays.

> We will focus on the Energy property of X-rays.

X-ray Penetration and Imaging

X-rays penetrate deeply into matter, with strong dependence on X-ray energy and material composition.

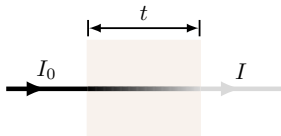X-rays are *attenuated* by matter as

$$I = I_0 e^{-\mu t}$$

Where

I X-ray intensity after material

I_0 X-ray intensity before material

t material thickness

μ absorption coefficient

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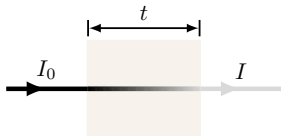
Early X-ray image of hand with wedding ring (1896).

Wilhelm Conrad Roentgen: discovered X-rays (1895).

X-rays penetrate flesh.
X-rays are partially stopped by bone.
X-rays are almost completely stopped by metal ring.

The X-ray Attenuation Coefficient: μ in $I = I_0 e^{-\mu t}$

Three processes cause attenuation: 1) Rayleigh (elastic) scattering, 2) Compton (inelastic) scattering, and 3) the photo-electric effect or *X-ray absorption*.

For heavy elements and moderate X-ray energies, photo-electric absorption dominates.

The photo-electric portion of μ, depends linearly on density, ρ, and very strongly on

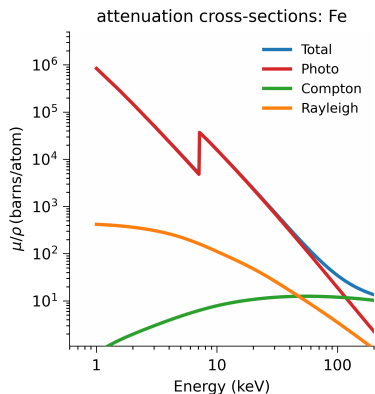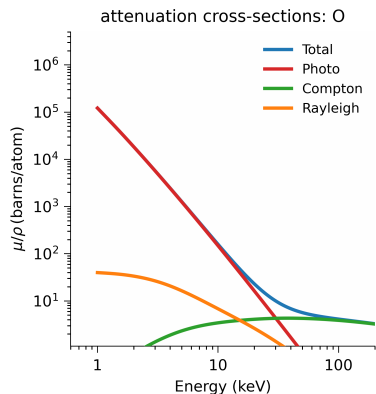- atomic number, Z.
- X-ray energy, E.

$$\mu \sim \frac{\rho Z^4}{E^3}$$

μ has sharp *Absorption Edges* at the characteristic core-electron energy levels of each atom.

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For light elements at high energy Compton scattering can dominate.

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X-rays are absorbed by all matter through the *photo-electric effect*:

An atom absorbs an x-ray when the x-ray energy is transferred to a core-level electron (K, L, or M shell).

The atom is left in an *excited state* with a *core hole* – an empty electronic level.

Any excess energy from the x-ray is given to an ejected *photo-electron*.

A. Einstein, Nobel Prize, 1921 "For his services to Theoretical Physics, and especially for his discovery of the law of the photoelectric effect".
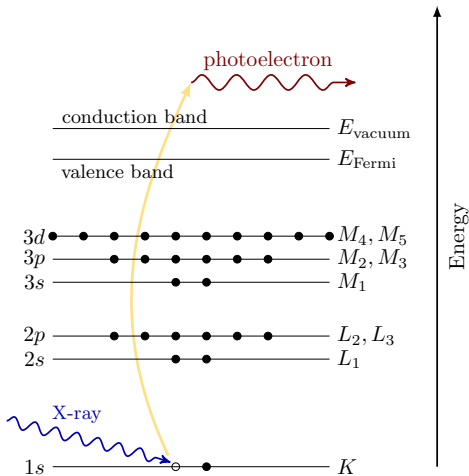
After X-ray absorption, the excited atom relaxes to the ground state. A higher level electron fills the core hole, and a *fluorescent X-ray* or *Auger electron* is emitted.

X-ray Fluorescence: Emit an X-ray with energy given by core-levels energies.
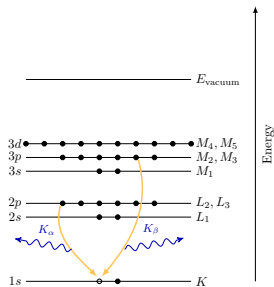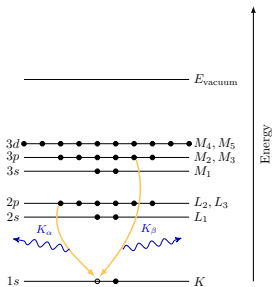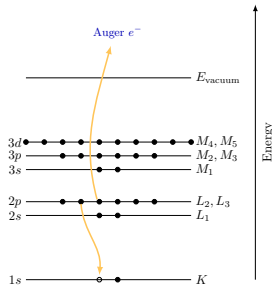

Charles Barkla, Nobel Prize, 1917 "discovery of the characteristic Röntgen radiation of the elements"

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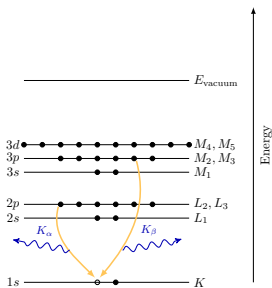
Lise Meitner, no Nobel Prize, first to discover Auger effect, explained nuclear fission.
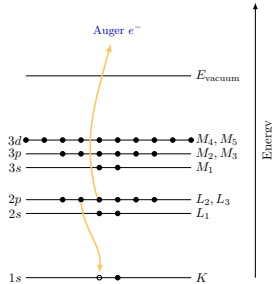
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X-ray fluorescence and Auger emission have discrete energies, characteristic of the absorbing atom – very useful for identifying atoms!

X-ray Fluorescence (XRF) Spectroscopy

The fluorescence X-rays at characteristic energies from different elements can be used to identify element and to quantify elemental abundances often down to ppm levels.
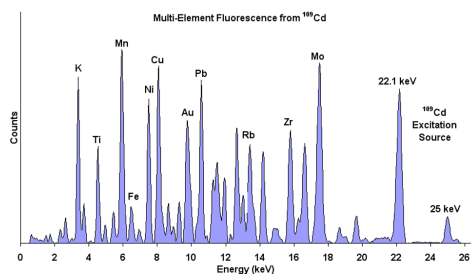
In a modern electron-probes and X-ray microprobe beamlines, XRF spectra are collected fast enough to make elemental maps in a few hours.
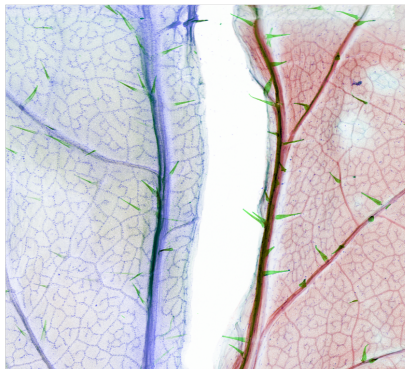
K / Mn / Zn from a hyper-accumulating plant grown in two different conditions.

Map size: 10 x 9 mm, pixel size: 5 μm.
15 ms per pixel.

X-ray Absorption Spectroscopy (XAS) is the modulation of the X-ray absorption coefficient at energies at and above an X-ray absorption edge.

XAFS	X-ray Absorption Fine-Structure Spectroscopy ($=$ XAS)
XANES	X-ray Absorption Near-Edge Spectroscopy
EXAFS	Extended X-ray Absorption Fine-Structure

These contain information about an element's chemical state (XANES) and local atomic environment (EXAFS).
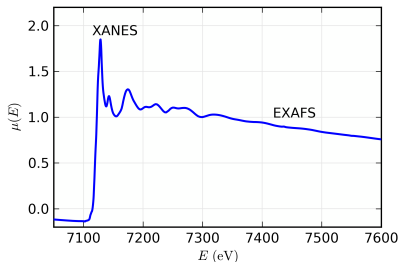
Fe K-edge XAFS for FeO.

Main XAS Characteristics:

- local atomic coordination
- valence, oxidation state
- applies to any element ($Z > 2$) .
- works at low concentrations (ppm, μM)
- minimal sample requirements.
- independent of crystal structure, isotope.
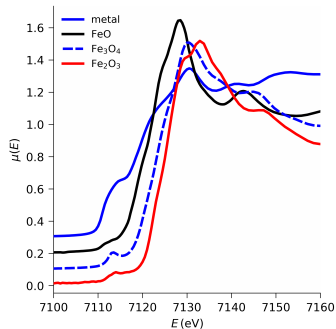
Within ~100eV of the absorption edge, the X-ray Absorption Spectra is highly sensitive to the chemical state and formal valence of absorbing element:
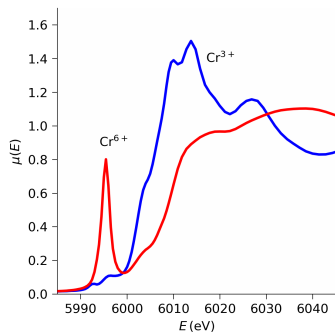
Cr^{3+} and Cr^{6+}
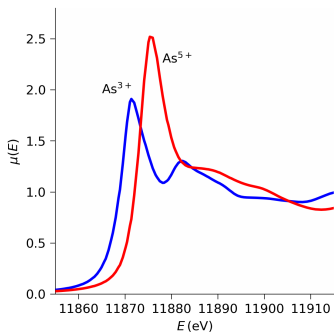
As^{3+} and As^{5+}

Fe metal and oxides.

The oxidation state and local atomic coordination environment strongly affect the lowest unfilled electronic levels of an absorbing atom.

what are the unoccupied electronic states that the photo-electron can fill?
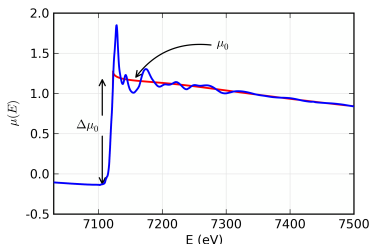
EXAFS: Extended X-ray Absorption Fine Structure

Even far above the edge, there are oscillations in $\mu(E)$ that are sensitive to the positions and types of atoms neighboring the absorbing atom.
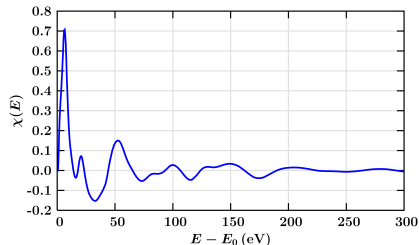
We define the EXAFS as:

$$\mu(E) = \mu_0(E)[1 + \chi(E)] \qquad \chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu_0(E_0)}$$

We subtract off a smooth *"bare atom" background* $\mu_0(E)$, and divide by the *"edge step"* $\Delta\mu_0(E_0)$ to get χ, the EXAFS oscillations:
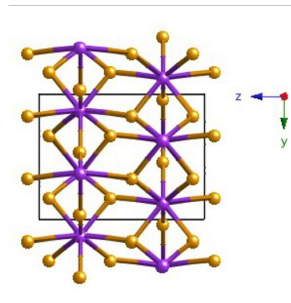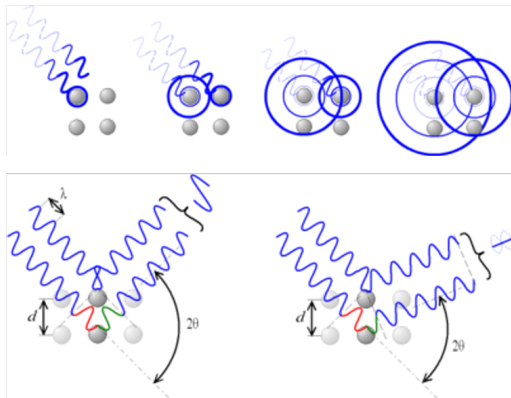

$\mu(E)$ and $\mu_0(E)$ for FeO

$\chi(E)$ for FeO, with $E_0 = 7122$ eV.

The spacing between atoms in most molecules, solids, and liquids is typically 1 to 10 Å.

X-rays have the right wavelengths to scatter (Rayleigh or elastic scattering) from planes of atoms coherently.

When the X-ray are at the right angle, the scattered X-rays with constructively interfere to diffract.

This can be used to tell the spacing between atoms.

Diffraction is the most common use of synchrotron X-rays

X-rays with the right wavelengths and angle of incidence to a crystal can diffract according to Bragg's law:
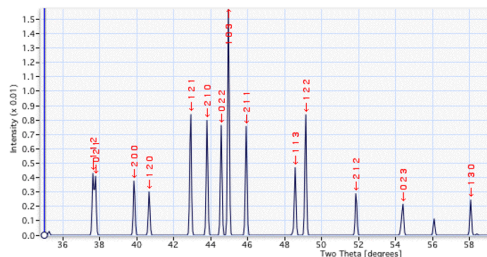
$$n\lambda = 2d\sin(\theta)$$

Where

λ X-ray wavelength

d spacing between atomic planes

θ scattering angle

X-ray diffraction pattern for Fe3C

William L. Bragg (son)

William H. Bragg (father)

All Nobel prize winners for work on X-ray diffraction.


Max von Laue

These days, X-ray diffraction at synchrotrons is done on

- very large molecules (proteins).
- on samples at extreme conditions (high pressure, high temperature).
- on very disordered materials (liquids, surfaces, interfaces).
- at very high speed to see dynamics.
- at very small scales and high-precisions to measure strain.
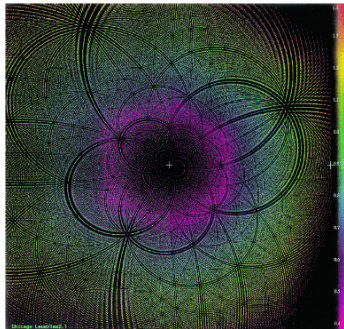
X-ray Diffraction Pattern from Macro-molecule.
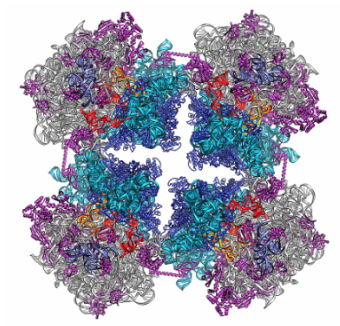
Molecular structure solved with X-ray Diffraction.

Light is generated by accelerating charge.

Accelerating low energy electrons gives low energy light:

An AC current in a radio tower produces radio waves: $\lambda \sim 1$m, $E \sim 1\mu$eV.

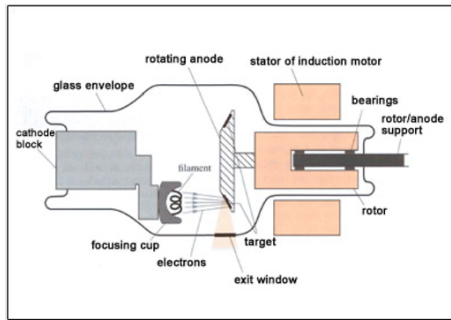X-rays have $\lambda \sim 10^{-10}$m, $E \sim 10$keV.

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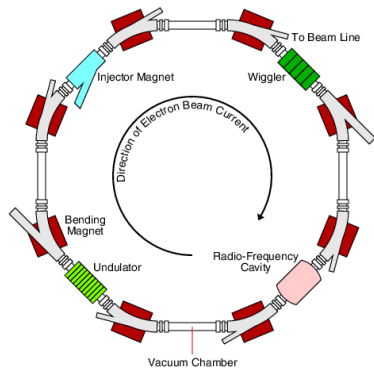X-rays have $\lambda \sim 10^{-10}\mathrm{m}$, $E \sim 10\mathrm{keV}$.

An X-ray tube (lab, dentist office) slams electrons into a metal target.

X-rays are produced from both X-ray fluorescence of the metal (discrete energies), and from the deceleration of the electrons.

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Synchrotron: a modern X-ray source

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4. insert alternating magnet poles (*wigglers* or *undulators*) in straight sections between the bending magnets, bends the electron beam many times, giving beamlines with more and brighter X-rays!
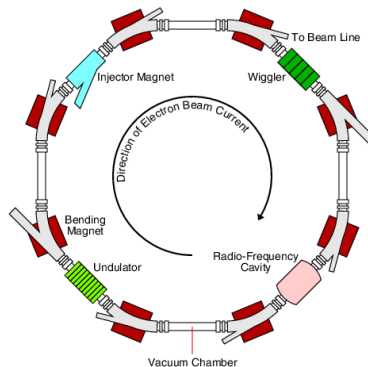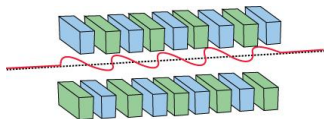
A *synchrotron* or *storage ring*, with many beamlines running simultaneously.

US DOE runs 4 synchrotrons as User Facilities, with many more around the world.
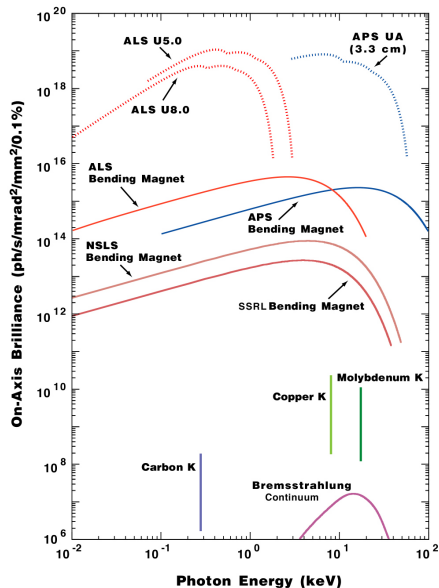
Brilliance: flux of monochromatic X-rays in a highly collimated beam.

Synchrotron beams are high flux **and** highly collimated.
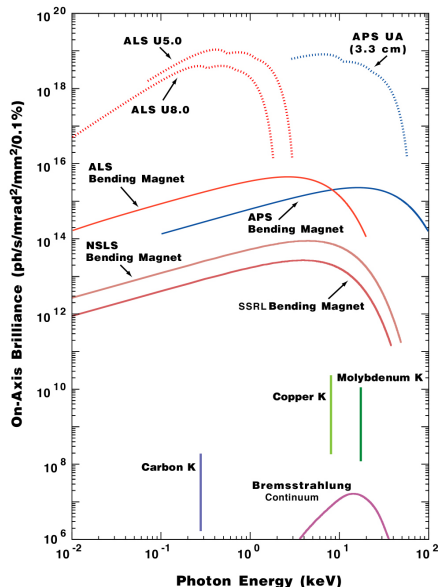
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Modern synchrotrons are large ($\sim 1\,\mathrm{km}$ circumference), with dozens of beamlines
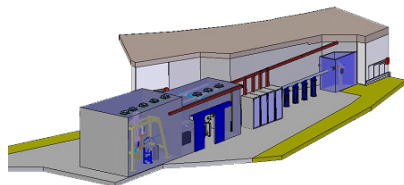

Advanced Photon Source (APS) at Argonne National Lab: $\sim$ 60 simultaneous, independent X-ray beamlines, each doing different science experiments.

The APS has 35 Sectors, each with:

- 1 Bending Magnet and 1 Undulator (high brightness) beamline.
- 200 days of beamtime per year.
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A beamline: Pb enclosures (hutches) hold X-ray optics (monochromators, mirrors, slits) and experimental equipment, and protect people from radiation.

Experiments happen at $\sim$ 40m from the X-ray source.

Most beamlines dedicated to a technique or scientific discipline.

Most beamlines run by ANL, some by outside groups.

Conclusions for X-ray Properties and Atoms:

X-rays – especially from synchrotrons – are useful in many scientific disciplines: biology, chemistry, geology, physics, archeology, material science, energy sciences, environmental science.

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More information on X-rays and X-ray Absorption Spectroscopy:

https://xafs.xrayabsorption.org/

Fundamentals of XAFS M. Newville, Reviews in Mineralogy & Geochemistry **78**, 2014.

Introduction to XAFS G. Bunker, Cambridge Univ Press, 2010.

XAFS for Everyone S. Calvin, CRC Press, 2013.

Elements of Modern X-ray Physics J. Als-Nielsen & D. McMorrow, John Wiley & Sons. 2001