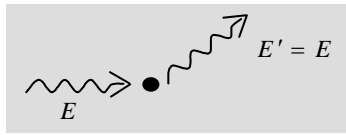# X-ray Absorption

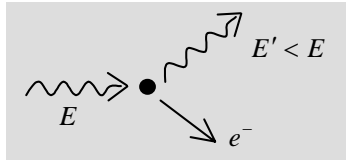## *Summary: interactions of X-rays with matter*
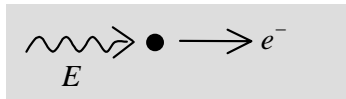
- elastic scattering
  (Thompson or Rayleigh
  scattering)

  $E' = E$

  E

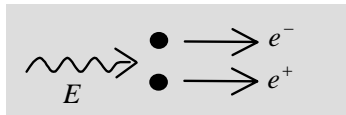- inelastic scattering
  (Compton scattering)

  $E' < E$

  E

  e^-

- photoelectric
  absorption

  E $\longrightarrow e^-$
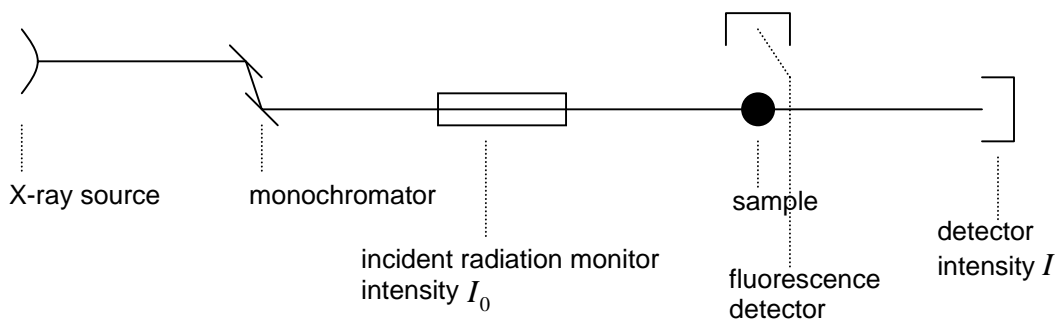
- pair creation

  e^-

  e^+

  E

So far, we have dealt exclusively with Thompson scattering.

Understanding X-ray absorption is important for
- X-ray radiography (e.g. medical X-rays, baggage screening)
- accurate description of X-ray diffraction ("dispersion corrections",
  "anomalous scattering")
- absorption spectroscopy (e.g. identification of elements and valence
  states in materials)

Basic experimental setup for X-ray absorption measurements

X-ray source   monochromator   sample

incident radiation monitor
intensity I_0

fluorescence
detector

detector
intensity I

Complementary experiment: monitor energy and direction of emitted
photoelectron (photoemission spectroscopy) $\Rightarrow$ next semester.

x

I_0 I
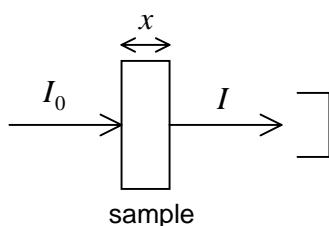
sample

$\dfrac{I}{I_0} = e^{-(\mu/\rho_a)x}$, where $\dfrac{\mu}{\rho_a}$ is the **mass attenuation coefficient** and ρ_a is the mass density.

All four processes above contribute to the attenuation of the incident beam inside the sample, and hence to $\dfrac{\mu}{\rho_a}$, and three regimes can be distinguished:
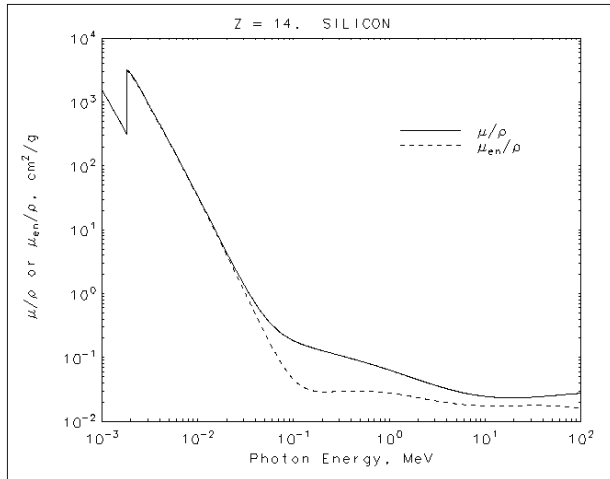
Mass attenuation coefficient for silicon
http://physics.nist.gov/PhysRefData/XrayMassCoef/tab3.html

$\hbar\omega < 100\,keV$	photoelectric absorption dominates
$100\,keV < \hbar\omega < 1MeV$	Thompson and Compton scattering dominate
$\hbar\omega \gtrsim 1MeV\left(= 2m_e c^2\right)$	pair production dominates

In the regime dominated by photoelectric absorption, there are prominent "absorption edges" characteristic of the binding energies of electrons in specific atoms (or ions).
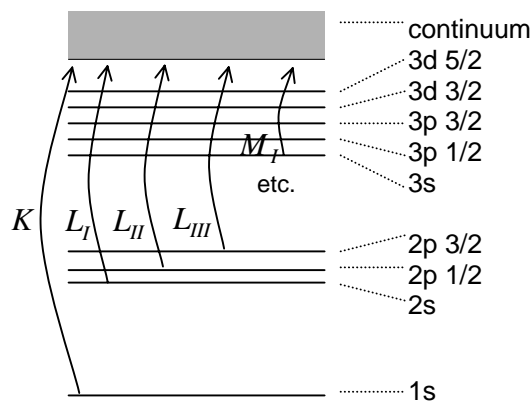
Examples:
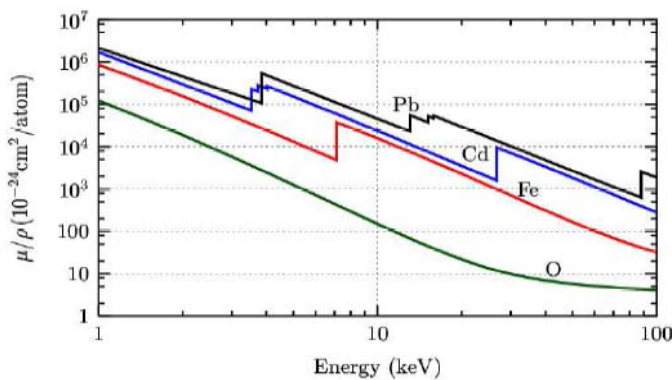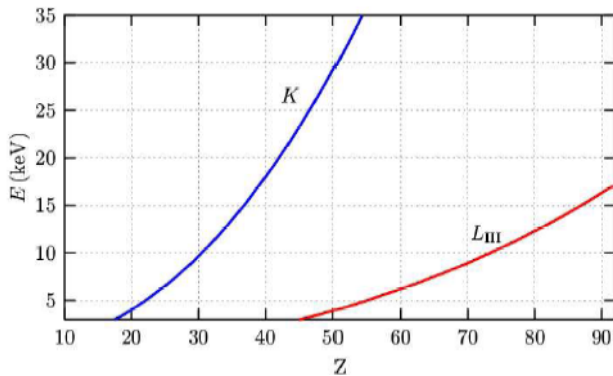
**Absorption edges and mass attenuation coefficients for various elements**
http://prins00.ethz.ch/Teaching/XAS1.pdf

Main features:
– **energy** of absorption edge is characteristic of specific element.
  E.g. for K-edge: $E_K \sim Z(Z-1) \times 13.6 eV$, where Z = nuclear charge.
  The second factor $Z-1$ is reduced to approximate the shielding of the
  nuclear charge by the second s-electron.
– strong **energy dependence** of absorption coefficient. This is the origin of the
  diminishing relative importance of photoelectric absorption with increasing
  energy.
– **absolute magnitude** of $\dfrac{\mu}{\rho_a}$ depends strongly on Z. This effect underlies
  X-ray radiography.

X-ray absorption spectra also contain information about the **valence state** of
elements in materials. If the element is present as anion (cation), the absorption
edge is shifted to lower (higher) photon energy because of the lower (higher)
ionization potential.

Example from frontier research:
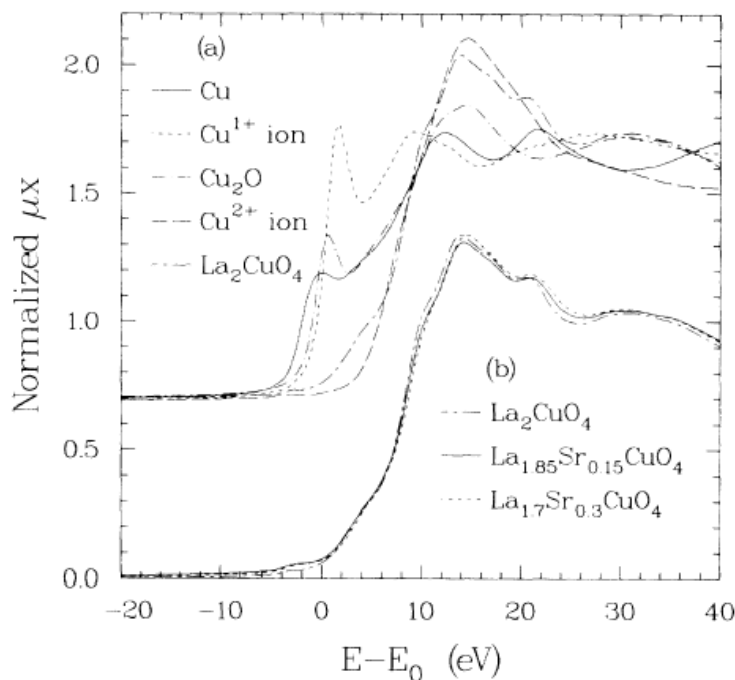
Determination of the copper valence state in high temperature superconductors by x-ray absorption at the Cu K-edge (E_0 = 8.98 keV)
Tranquada et al., Phys. Rev. B **35**, 7187- (1987)

High temperature superconductivity was discovered in 1986 in $La_{2-x}Ba_xCuO_4$. The "parent compound" of the high temperature superconductors, La_2CuO_4 is insulating, and superconductivity appears as La^{3+} is replaced by Ba^{2+}. The valence state of Cu is crucial for microscopic models of superconductivity. By comparison to reference materials, X-ray absorption experiments showed that copper is divalent in La_2CuO_4 (Cu^{2+}, electron configuration $[Ar]3d^9$). Cu is therefore the only element in La_2CuO_4 with an unfilled shell (both La^{3+} and O^{2-} have filled shells) and is thus of crucial importance for the electronic and magnetic properties. Interestingly, the Cu absorption spectrum hardly changes when the material becomes superconducting through Ba^{2+} (or Sr^{2+}) substitution. This is because the additional holes that drive the material superconducting move predominantly on the oxygen atoms.

Finally, high resolution spectroscopy near the absorption edge reveals a "fine structure" that contains information about the chemical environment of the atom or ion in the solid:

Plot of a raw data set (from HASYLAB, X1)

http://prins00.ethz.ch/Teaching/XAS1.pdf
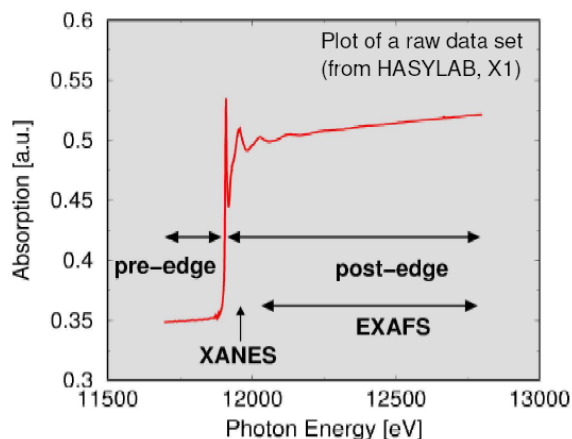
The "X-ray absorption near edge structure" (XANES) is due to transitions into unoccupied bound states below the edge of the continuum. The "Extended X-ray absorption fine structure" (EXAFS) above the edge is due to backscattering of the photoelectron to the emitting atom:
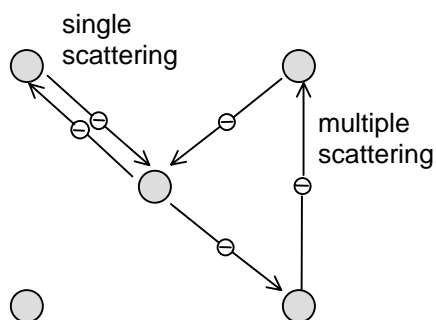
The backscattered waves interfere with the original electron wave and give rise to the wiggles above the edge.

The discrete energy level structure leading to the absorption edges is a quantum mechanical effect, and a quantitative description of X-ray absorption can only be obtained in a quantum-mechanical calculation. However, a classical calculation in the spirit of the calculation of the Thompson cross section is instructive to illustrate some qualitative features. In contrast to the earlier calculation, consider re-radiation by an electron **bound** to the nucleus. For simplicity, consider a harmonic potential:

$$\vec{E}_{in} = E_0 \hat{x} e^{-i\omega t}$$

equation of motion for electron:

$$\ddot{x} + \Gamma \dot{x} + \omega_0^2 x = -\frac{eE_0}{m} e^{-i\omega t}$$

In this simple driven harmonic oscillator model, the restoring force increases with distance, and the electron always remains bound. The model therefore only describes (qualitatively) transitions into unoccupied bound states. In quantum mechanics, the damping term Γ corresponds to the spontaneous decay rate of the excited state.

$$x = x_0 e^{-i\omega t}$$

Amplitude of wave re-radiated by bound electron:

$$E_{rad} = \frac{e}{4\pi\epsilon_0 R c^2}\, \ddot{x}\left(t - \frac{R}{c}\right)$$

$$= \frac{e}{4\pi\epsilon_0 R c^2}\, \frac{\omega^2}{\omega_0^2 - \omega^2 - i\omega\Gamma}\, \frac{eE_0}{m}\, e^{-i\omega t}\, e^{ikR}$$

$$\frac{E_{rad}}{E_0} = -r_0\, \frac{\omega^2}{\omega^2 - \omega_0^2 + i\omega\Gamma}\, \frac{e^{ikR}}{R} \equiv f(\omega)\, r_0\, \frac{e^{ikR}}{R}$$

with $r_0 = \dfrac{e^2}{4\pi\epsilon_0 m c^2} = 2.8\times 10^{-15}\,m$ as before

Form factor $f = 1$ frequency independent for single **free** electron

$$\frac{d\sigma}{d\Omega} = |f|^2\, r_0^2\, \mathcal{P} \qquad \mathcal{P} = \text{polarization factor}$$
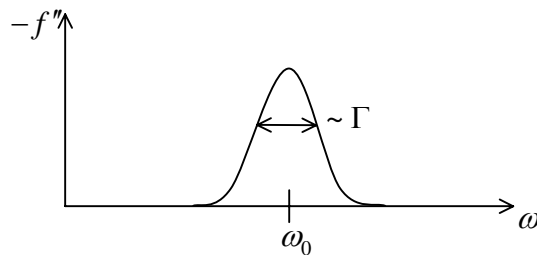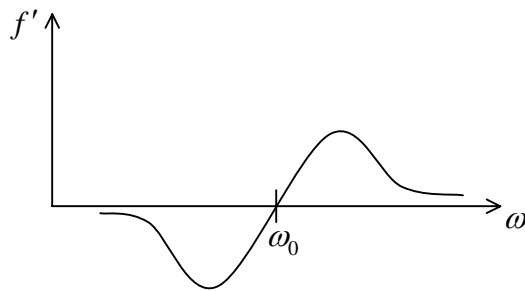
angle dependence not of interest for absorption.

$$\sigma_{total} = \frac{8\pi}{3}\, r_0^2\, |f|^2 = \frac{8\pi}{3}\, r_0^2\, \frac{\omega^4}{\left(\omega^2 - \omega_0^2\right)^2 + (\omega\Gamma)^2}$$

$$\to \frac{8\pi}{3}\left(\frac{\omega}{\omega_0}\right)^4 r_0^2 \text{ for small } \omega \text{ (Rayleigh's law)}$$

$$f = \frac{\omega^2}{\omega^2 - \omega_0^2 + i\omega\Gamma} \equiv f' + if''$$

$$f' = \frac{\omega^2\left(\omega^2 - \omega_0^2\right)}{\left(\omega^2 - \omega_0^2\right)^2 + \omega^2\Gamma^2}$$

$$f'' = \frac{-\omega^3\Gamma}{\left(\omega^2 - \omega_0^2\right)^2 + \omega^2\Gamma^2}$$

The relationship between f' and f'' is actually much more general than this simple calculation suggests. As these two quantities are related by the so-called "Kramers-Kronig relations", their qualitative behaviour in passing through a resonance is quite well described by this calculation.

The "anomalous" frequency dependence of the form factor near an absorption edge leads to so-called "dispersion corrections" to the scattering cross section

$$f(Q,\omega) = \underbrace{f_0(Q)}_{} + f'(Q,\omega) + i\,f''(Q,\omega)$$

contribution of electrons with
characteristic frequencies
different from ω_0

The dispersion corrections are required to obtain an accurate description of the Bragg diffraction pattern and can be exploited in "resonant" or "anomalous" scattering experiments at synchrotrons.

Examples:
– MAD (multiple wavelength anomalous diffraction)
  In protein crystallography, the X-ray energy is tuned through the absorption edges of specific (normally heavy) elements to extract their contribution to the diffraction pattern. Locating these elements helps solve the structure of complex protein molecules with thousands of atoms.
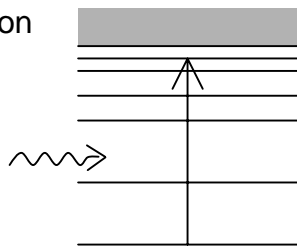– Resonant magnetic X-ray scattering
  (discussed later)

f'' is related to the contribution of absorption to the mass attenuation coefficient. The amplitude of the electromagnetic wave in the material is

$$E = E_0\,e^{inkx} \quad \text{with} \quad n = 1 - \frac{2\pi\rho r_0 f}{k^2} \equiv n - \delta + i\beta \qquad \rho = \text{electron number density}$$
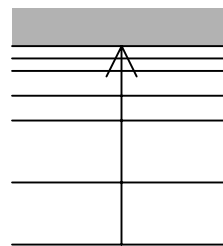
$$\Rightarrow \frac{I}{I_0} = e^{-\frac{\mu}{\rho_a}x} \quad \text{with} \quad \frac{\mu}{\rho_a} = 2k\beta = \frac{4\pi\rho r_0}{k} f''$$

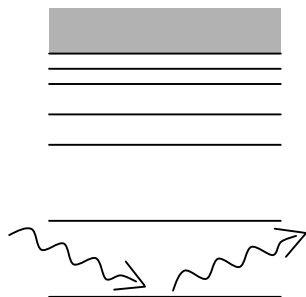## Quantum mechanical treatment

– absorption
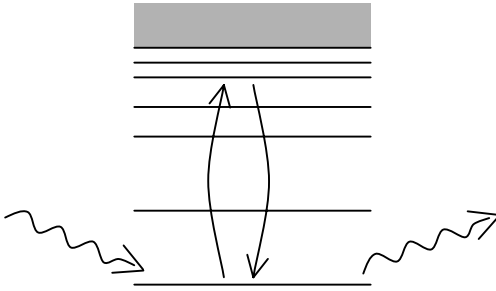

transition into
unoccupied
bound state

transition into
continuum

– Thompson scattering

– resonant (or "anomalous") scattering

Photoelectric absorption and Thompson scattering are described by first order time-dependent perturbation theory, resonant scattering is described by second-order TDFT.

In analogy to scattering cross section, define absorption cross section

$$\sigma_a = \frac{W}{\Phi_0}$$

W = transition rate $[\sec^{-1}]$

Φ_0 = incident flux $\left[\dfrac{\#\ \text{of photons}}{cm^2\ \sec} \right]$

Relationship to mass attenuation coefficient discussed earlier:

$\dfrac{\mu}{\rho_a} = \rho \sigma_a$ where ρ = electron density, ρ_a = mass density

In first-order time-dependent perturbation theory, W is described by Fermi's Golden Rule:

$$W = \frac{2\pi}{\hbar} \underbrace{\left| M_{fi} \right|^2}_{\substack{\text{matrix} \\ \text{element}}} \underbrace{\rho\left(E_f \right)}_{\substack{\text{density of} \\ \text{final states}}}$$

with $M_{fi} = \left\langle f \left| H_{\text{int}} \right| i \right\rangle$

Hamiltonian of electron / photon system:

$$H = H_e + H_{rad} = \frac{\vec{p}^2}{2m} + H_{rad}$$

with $\vec{p} \rightarrow \vec{p} - e\vec{A} = \dfrac{\hbar}{i}\vec{\nabla} - e\vec{A}$: canonical electron momentum in the presence of

electromagnetic field. $\vec{A}$ is the vector potential, and $\vec{E} = -\dfrac{\partial \vec{A}}{\partial t} = -i\omega \vec{A} = \hat{\varepsilon} E$ is the electric field of the electromagnetic wave.

$$H = \frac{\vec{p}^2}{2m} + H_{rad} + \underbrace{\frac{e}{m}\vec{A}\cdot\vec{p} + \frac{e^2\vec{A}^2}{2m}}_{\text{interaction Hamiltonian, } H_{\text{int}}}$$

The first term of H_{int} corresponds to absorption, the second term to Thompson scattering. This is most readily seen by writing $\vec{A}$ in quantized notation:

$$\vec{A} = \hat{\varepsilon}\sqrt{\frac{\hbar}{2\epsilon_0 V \omega}}\left(a_k^+ e^{-i\vec{k}\cdot\vec{r}} + a_k e^{i\vec{k}\cdot\vec{r}}\right)$$

annihilation operator

photon creation

This expression can be obtained by considering all possible electromagnetic waves in a large volume V with periodic boundary conditions, analogous to the generalization of the expression for the position of the *1D* harmonic oscillator to a three-dimensional crystal discussed before. The creation and annihilation operators act on the photon wave function $|n_k\rangle$ where n_k is the occupation number of the photon with wave vector $\vec{k}$.

Example: *K*-absorption edge of atom with nuclear charge *Z*.

Since *1s* electrons are tightly bound, they are well described by hydrogen-like wave functions with quantum numbers *n, l, m = 1,0,0..*

$$|i\rangle = |i\rangle_{photon}|i\rangle_{electron} = |1\rangle\,\Psi_{100}(\vec{r})$$

with $\Psi_{100}(\vec{r}) = \dfrac{1}{\sqrt{\pi}}\left(\dfrac{Z}{a_B}\right)^{3/2} e^{-Zr/a_B}$

Now distinguish two cases:

① *Transitions into unoccupied bound state*

$$|f\rangle = |f\rangle_{photon}|f\rangle_{electron} = |0\rangle\,\Psi_{nlm}(\vec{r})$$

For many bound excited states, hydrogen-like wave functions are still good approximations. The density of final states $\rho(E_f)$ is sharply peaked around E_{nlm}, with a width determined by the lifetime of the excited state

With $\dfrac{\hbar}{i}\vec{\nabla}\Psi_{100}(\vec{r}) = \dfrac{\hbar}{i}\dfrac{\hat{r}}{\sqrt{\pi}}\left(\dfrac{Z}{a_B}\right)^{5/2} e^{-Zr/a_B}$:

$$M_{fi} = \frac{e\hbar}{im}\sqrt{\frac{\hbar}{2\epsilon_0 V \omega}}\underbrace{\langle 0|a_k|1\rangle}_{=1}\frac{Z}{a_B}\int d\vec{r}\,\Psi_{nlm}^{*}(\vec{r})\,(\hat{\epsilon}\cdot\vec{r})e^{i\vec{k}\cdot\vec{r}}\Psi_{100}(\vec{r})$$

In the electric dipole approximation, the spatial variation of the $\vec{E}$-field over the volume of the atom is neglected so that $e^{i\vec{k}\vec{r}} \approx 1$, and the usual dipole selection rules apply:

$\Delta l = \pm 1$ (e.g. $s \to p$ transitions dipole allowed

                        $s \to d$ transitions dipole-forbidden)

$\Delta m = 0, \pm 1$ (important for X-ray magnetic circular dichroism, discussed later)

In a solid, the Coulomb potential seen by the electrons is not spherically symmetric, and the selection rules for hydrogen-like atoms do not apply rigidly. The violation of these selection rules is more pronounced for less symmetric crystals. The strength of "pre-edge" features in X-ray absorption can be used to identify the local chemical environment of atoms, even in amorphous solids that do not yield sharp X-ray diffraction patterns.

XANES at V K-edge
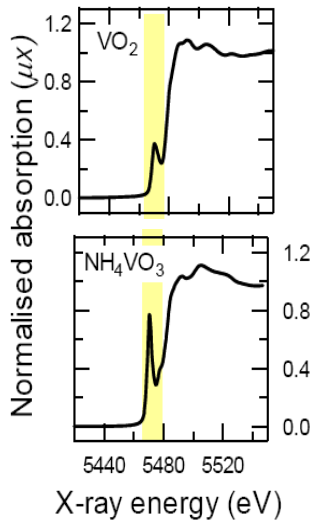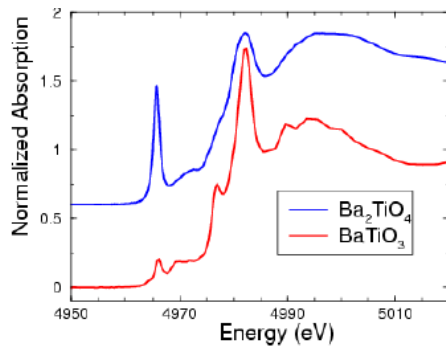

nearly octahedral coordination

Centrosymmetry, no pd mixing,
only quadrupole transitions

nearly tetrahedral coordination

Strong pd-mixing, dipole transitions
contribute to pre-edge structure

http://prins00.ethz.ch/Teaching/xanespdf.pdf

XANES at Ti K-edge

tetrahedral

octahedral

http://leonardo.phys.washington.edu/~ravel/course/basics/AXAS/axas.pdf

② *Transitions into continuum*

$$|f\rangle = |f\rangle_{photon}|f\rangle_{electron} = |0\rangle \frac{1}{\sqrt{V}} e^{i\vec{q}\cdot\vec{r}}$$

with $\dfrac{\hbar}{i}\vec{\nabla}e^{i\vec{q}\cdot\vec{r}} = \hbar\vec{q}$ (photoelectron momentum)
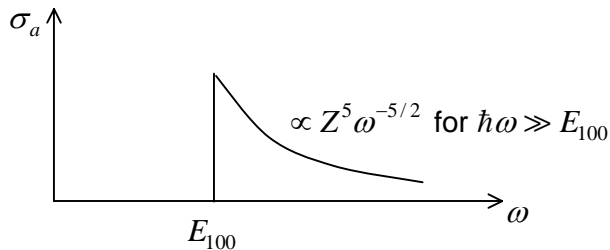
$$M_{fi} = \frac{e\hbar}{mV}\sqrt{\frac{\hbar}{2\epsilon_0\omega}}\int d\vec{r}\, e^{-i\vec{q}\cdot\vec{r}}\,(\hat{\varepsilon}\cdot\vec{q})e^{i\vec{k}\cdot\vec{r}}\Psi_{100}(\vec{r})$$

$$= \frac{e\hbar}{mV}\sqrt{\frac{\hbar}{2\epsilon_0\omega}}(\hat{\varepsilon}\cdot\vec{q})\underbrace{\frac{Z^{5/2}}{\left[\left(\dfrac{Qa_B}{2}\right)^2 + Z^2\right]^2}}_{\substack{\text{Fourier transform of }\Psi_{100} \\ \text{with }\vec{Q}\equiv\vec{k}-\vec{q}}}$$

The density of the final states is $\rho\left(E_f\right) = \dfrac{V}{4\pi^3}\dfrac{d\vec{q}}{dE_f}$ so that evaluating the absorption cross section involves a complicated angular integral over all directions of the photoelectron momentum. See textbook for a complete evaluation.

Qualitative features:

$\propto Z^5\omega^{-5/2}$ for $\hbar\omega \gg E_{100}$

A more accurate calculation yields a slightly modified expression: $\sigma_a \propto Z^4\omega^{-3}$.

This explains the strong energy and element dependence of σ_a noted above.

This dependence can be exploited for a rough identification of heavy and light elements in "dual energy" X-ray radiography. If only one energy is used, a thick object made out of light elements cannot be distinguished from a thin object made of heavy materials. If two radiographs are taken at energies where photoelectric absorption and the Compton effect dominate, respectively, one can tell these two situations apart, because the attenuation due to the Compton effect only depends linearly on Z.

Dual energy x-ray radiography

http://www.ndt.net/article/v07n02/ewert/ewert.htm
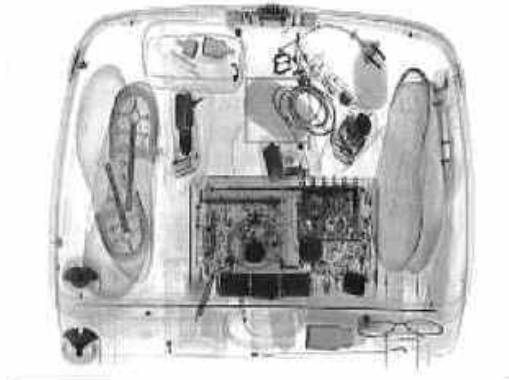
Finally, a quantitative description of the EXAFS oscillations can be obtained by taking into account that the final state of the photoelectron $|f_0 + \Delta f\rangle$ differs from a free-electron plane wave state $|f_0\rangle$ due to scattering from the surrounding atoms in the material.

$$\left|M_{fi}\right|^2 = \left|\langle f_0 + \Delta f |H_{int}|i\rangle\right|^2$$

$$\approx \underbrace{\left|\langle f_0 |H_{int}|i\rangle\right|^2}_{\sigma_a} + \underbrace{\langle \Delta f |H_{int}|i\rangle \langle f_0 |H_{int}|i\rangle}_{\delta\sigma_a} + \ldots$$
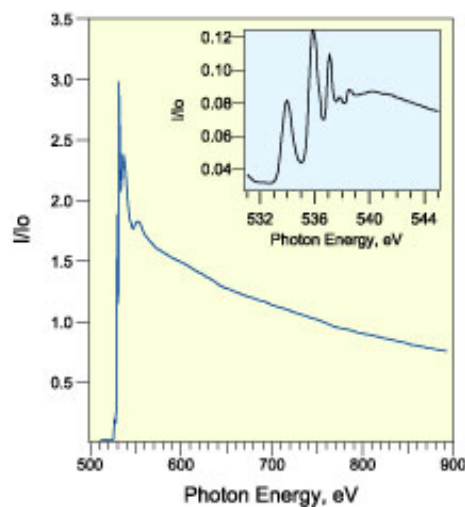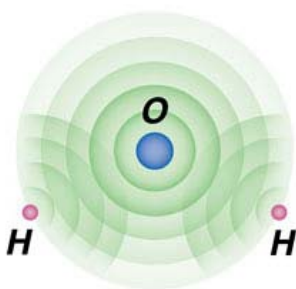
Since $|i\rangle$ is a tightly localized core electron wave function, the integral $\langle \Delta f |H_{int}|i\rangle$ is dominated by the component of the photoelectron wave function **back-scattered** to the original atom at $\vec{r} = 0$. The following heuristic formula is commonly used to analyse EXAFS spectra:

$$\delta\sigma_a \propto \sum_j N_j A_j(\vec{q}) \frac{\sin\left(2\vec{q}\cdot\vec{R}_j + \varphi_j\right)}{R_j^2} e^{-2q^2\sigma_j^2}$$

A photoelectron with wave vector $\vec{q}$ backscattered from an atom at position $\vec{R}_j$ suffers a phase shift $2\vec{q}\cdot\vec{R}_j$ plus a phase shift φ_j contributed by the scattering process. The number of equivalent atoms is denoted by N_j and their scattering amplitude by A_j. In analogy to the form factor for X-ray scattering, this amplitude is reduced by the Debye-Waller factor $e^{-2q^2\sigma_j^2}$ due to thermal vibrations of the atom. In addition, a damping factor $e^{-2R_j/\lambda}$ due to inelastic scattering is added. This expression is evaluated numerically using empirical values for the parameters.

Example:

EXAFS of water vapor at Oxygen K-edge