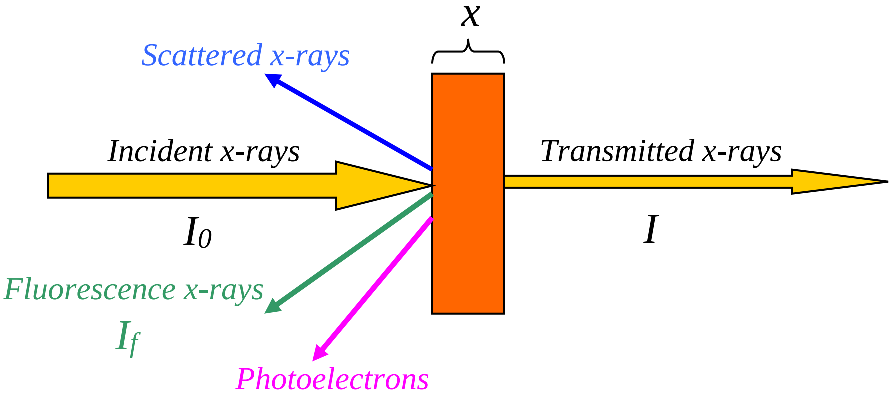
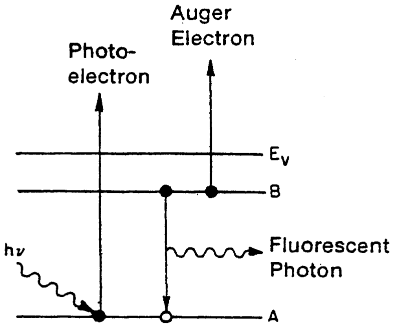
X-ray Absorption Spectroscopy (XAS)

When the x-rays hit a sample, the oscillating electric field of the electromagnetic radiation interacts with the electrons bound in an atom. Either the radiation will be scattered by these electrons, or absorbed and excite the electrons.

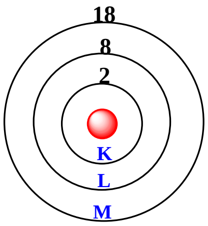




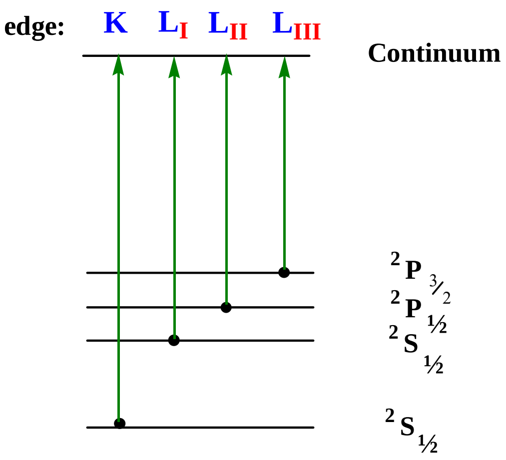
A narrow parallel monochromatic x-ray beam of intensity $\mathbf{I_0}$ passing through a sample of thickness **x** will get a reduced intensity **I** according to the expression:

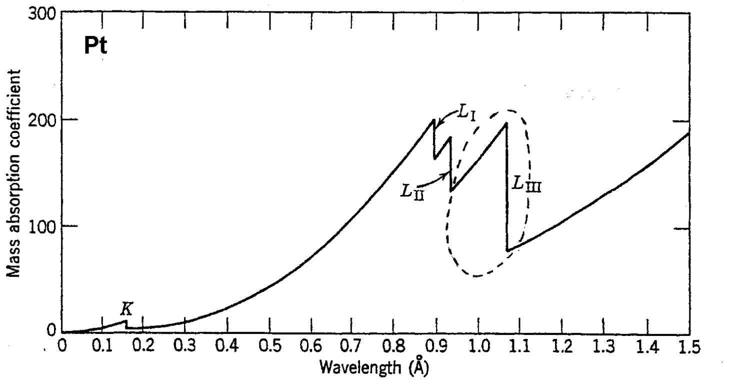
$$\ln (I_0 / I) = \mu x \qquad (1)$$

where μ is the *linear absorption coefficient*, which depends on the types of atoms and the density ρ of the material. At certain energies where the absorption increases drastically, and gives rise to an *absorption edge*. Each such *edge* occurs when the energy of the incident photons is just sufficient to cause excitation of a core electron of the absorbing atom to a continuum state, *i.e.* to produce a *photoelectron.* Thus, the energies of the absorbed radiation at these edges correspond to the binding energies of electrons in the K, L, M, etc, shells of the absorbing elements. The absorption edges are labelled in the order of increasing energy, K, L_I, L_{II}, L_{III}, M_I,…., corresponding to the excitation of an electron from the 1s ($^2S_{1/2}$), 2s ($^2S_{1/2}$), 2p ($^2P_{1/2}$), 2p ($^2P_{3/2}$), 3s ($^2S_{1/2}$), … orbitals (states), respectively.

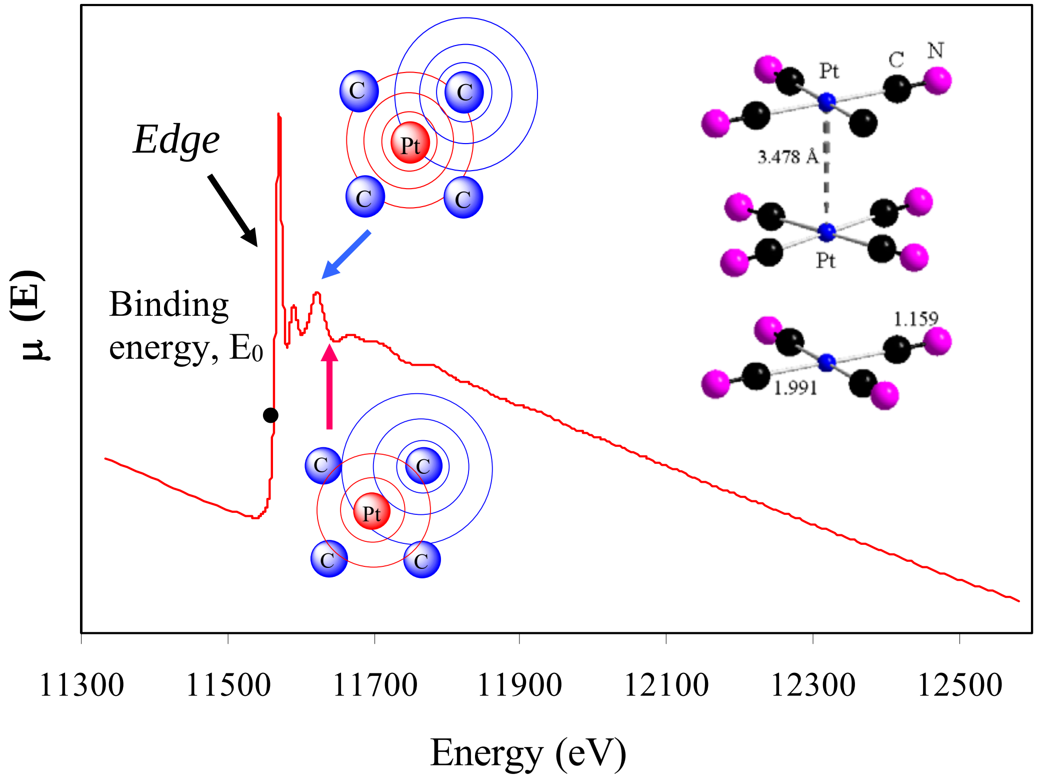


Bohr Atomic Model



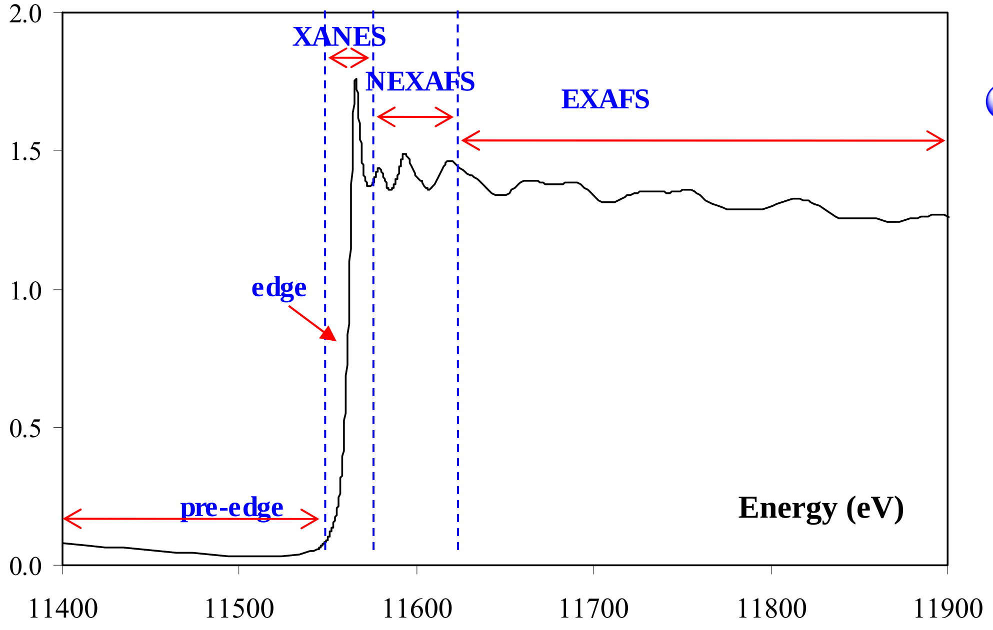


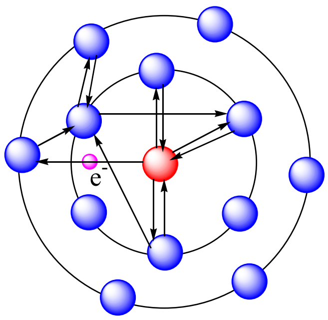
When the photoelectron leaves the absorbing atom, its wave is backscattered by the neighbouring atoms. The figure below shows the sudden increase in the x-ray absorption of the platinum Pt L_{III} edge in $K_2[Pt(CN)_4]$ with increasing photon energy. The maxima and minima after the edge correspond to the constructive and destructive interference between the outgoing photoelectron wave and backscattered wave.



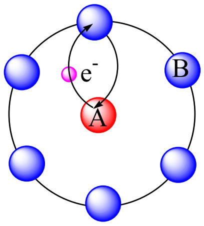
An x-ray absorption spectrum is generally divided into 4 sections: 1) *pre-edge* ($E < E_0$); 2) x-ray absorption near edge structure (*XANES*), where the energy of the incident x-ray beam is $E = E_0 \pm 10$ eV; 3) near edge x-ray absorption fine structure (*NEXAFS*), in the region between 10 eV up to 50 eV above the edge; and 4) extended x-ray absorption fine structure (*EXAFS*), which starts approximately from 50 eV and continues up to 1000 eV above the edge.

The minor features in the pre-edge region are usually due to the electron transitions from the core level to the higher unfilled or half-filled orbitals (e.g, $s \rightarrow p$, or $p \rightarrow d$). In the XANES region, transitions of core electrons to non-bound levels with close energy occur. Because of the high probability of such transition, a sudden raise of absorption is observed. In NEXAFS, the ejected photoelectrons have low kinetic energy (E-E_0 is small) and experience strong *multiple scattering* by the first and even higher coordinating shells. In the EXAFS region, the photoelectrons have high kinetic energy (E-E_0 is large), and *single scattering* by the nearest neighbouring atoms normally dominates.





Multiple scattering



Single scattering