

# ***FUNDAMENTALS OF X-RAY ABSORPTION AND DICHROISM: THE MULTIPLET APPROACH***

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X-ray Absorption Spectroscopy (XAS) using synchrotron radiation is a well-established technique providing information on the electronic, structural and magnetic properties of matter. In X-ray absorption, a photon is absorbed by the atom, giving rise to the transition of an electron from a core state to an empty state above the Fermi level. The absorption cross-section depends on the energy and on the measured element. To excite an electron in a given core level, the photon energy has to be equal or higher than the energy of this core level. This gives rise to the opening of a new absorption channel when the photon energy is scanned from below to above this core-level energy. The energies of the absorption edges therefore correspond to the core-level energies, which are characteristic for each element, making X-ray absorption an element-selective technique.

In general, two regions can be discerned in X-ray absorption spectra: the near-edge and EXAFS (Extended X-ray Absorption Fine Structure) regions. The spectral shape in the near-edge region is determined by electron correlation and density of states (or multiple scattering) effects and gives mainly information about the electronic properties of the absorbing atom. The EXAFS region is dominated by single scattering events of the outgoing electron on the neighbouring atoms, giving information about the local atomic structure around the absorbing site.

Several books and reviews have been published about XANES (X-ray Absorption Near-Edge Spectroscopy) and EXAFS spectroscopy. In this chapter we will treat the theoretical basis of XANES, mainly for systems where electron correlations play an important role (localized electron systems). Multiple scattering effects are treated in the chapter of P. Saintavrit, V. Briois and D. Cabaret, while EXAFS spectroscopy has been described by B. Lengeler.

This chapter will start with an introduction to the theoretical basis of X-ray absorption spectra. The main absorption edges (1s, 2p and 3p edges of transition metals, 3d edges of rare earths) will then be treated in more detail. Emphasis will be given to transitions to relatively localized states, where multiplet effects play an important role.

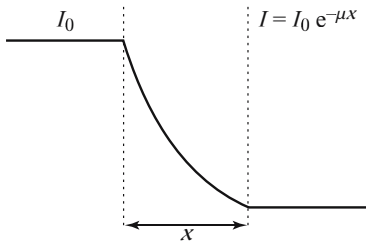
We will also briefly discuss polarization dependent XAS or X-ray dichroism. Dichroism with circularly polarized X-rays (X-ray Magnetic Circular Dichroism or XMCD) has become a powerful tool for the study of magnetic materials, capable to provide element specific information about spin and orbital magnetic moments.

## 1. INTRODUCTION

X-ray absorption spectroscopy has become an important tool for the characterization of materials as well as for fundamental studies of atoms, molecules, adsorbates, surfaces, liquids and solids. The particular assets of XAS spectroscopy are its element specificity and the possibility to obtain detailed information without the presence of any long range ordering. Below it will be shown that the X-ray absorption spectrum in many cases is closely related to the empty density of states of a system. As such XAS is able to provide a detailed picture of the local electronic structure of the element studied.

### 1.1. INTERACTION OF X-RAYS WITH MATTER

In XAS the absorption of X-rays by a sample, as described by Lambert-Beer's law, is measured. The intensity of the transmitted beam at a certain energy  $I(\omega)$  is related to the intensity of the beam before the sample  $I_0(\omega)$  divided by an exponential containing the length of the sample  $x$  times the absorption cross-section  $\mu(\omega)$



$$I(\omega) = I_0(\omega) e^{-\mu(\omega)x} \quad \{1\}$$

$$\mu(\omega) = \frac{1}{x} \ln \frac{I_0}{I} \quad \{2\}$$

**Figure 1** - Transmission through a uniform sample.