

MULTIPLE SCATTERING THEORY APPLIED TO X-RAY ABSORPTION NEAR-EDGE STRUCTURE

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1. INTRODUCTION

Multiple scattering theory (MST) is one of the theories that are used to calculate X-ray absorption spectra. This theory stems from the work by Korringa (1947) [1] who first developed the multiple scattering equations in 1947. The set of equations can be either solved in a real space or reciprocal space calculations. As far as X-ray absorption is concerned, MST has almost always been applied to real space calculations. It allowed to compute the discrete energy levels of a collection of atoms, a cluster, below the zero energy. It was also applied to compute the energy levels above the zero energy belonging to the continuum. The method was fully developed by K.H. Johnson (1973) [2] and applied by Dill and Dehmer [3] to the determination of photoionization differential cross-sections with an application to the nitrogen *K* edge in N₂.

In its usual form, the MST is used to compute the final state wave function of a photoelectron in an inner shell absorption process. Photoabsorption for the inner shell is governed by the matrix element between an initial state $|i\rangle$ and a final state $|f\rangle$ coupled by an interaction Hamiltonian describing the interaction between matter and X-rays. The initial state is strongly localized on the absorbing atom so that photoabsorption probes the value of the final state wavefunction $|f\rangle$ on the absorbing atom. The energy of the final state wavefunction is the kinetic energy of the photoelectron, so that $|f\rangle$ is well above the Fermi energy and belongs to the continuum of the Hamiltonian describing the absorbing sample. The value of the

wavefunction $|f\rangle$ on the absorbing atom depends on the nature and the position of the atoms neighbouring the absorbing atom. This point is not obvious and asks for explanation. For very large kinetic energy of the photoelectron, the potential of the cluster can be neglected in a first approximation and the solutions of the Schrödinger equation are plane waves or linear combinations of plane waves. In any case, these are strongly delocalized solutions. In a second step, if the potential of the cluster is introduced as a perturbation one then expects that the plane wave functions will be modified by the potentials of all the atoms in the cluster, even for those that are far from the absorbing atom. In summary, MST is developed to compute the value of the final state wave function on the absorbing atom and this value depends on the potentials of all the atoms surrounding the absorbing atom.

In order to fix the terminology, we recall that the K edge corresponds to transitions from a $1s$ inner shell to empty levels. Similarly L_I , M_I and N_I edges are respectively transition from $2s$, $3s$ or $4s$ inner shell levels. L_{II-III} are transitions from the $2p$ level and similar denominations for M_{II-III} ($3p$ inner shell) and N_{II-III} ($4p$ inner shell). The two labels "II-III" are there to describe the splitting of the experimental edges due to the spin-orbit coupling acting on the hole of the inner shell. L_{II} corresponds to transitions where the orbital momentum of the p hole, $l = 1$, and spin momentum, $s = 1/2$, are coupled to give $j = l - s = 1/2$ while L_{III} edge is for the coupling $j = l + s = 3/2$. M_{IV-V} edges are spin-orbit split transitions originating from the $3d$ level with M_{IV} corresponding to a coupling $j = l - s = 3/2$ and M_V to a coupling $j = l + s = 5/2$ (and similar definitions for N_{IV-V} edges that concern $4d$ inner shell levels).

In what follows we shall be considering that matter and X-rays interaction is given in the electric dipole approximation. This is the first term in the development of the complete photon field. It is usually enough for K edges of most elements although higher order terms can be necessary for elements heavier than silver^[4] or in very special cases where electric dipole cross-section is zero (for instance X-ray natural circular dichroism in chiral systems). At L_{II-III} edges, the electric dipole Hamiltonian is enough for most cases. A rule of thumb to size the influence of the electric quadrupole term is to compare the wavelength λ of the X-rays with the spatial extension of the inner shell: When λ is smaller than the spatial extension of the inner shell the electric quadrupole term cannot be neglected. In the electric dipole approximation, the selection rules state that the variation of orbital momentum between the initial state and the final state is either $+1$ or -1 . K , L_I and M_I edges probe the empty levels with p symmetry seen from the absorbing atom. L_{II-III} , M_{II-III} , and N_{II-III} probe the empty levels with d and s symmetry. M_{IV-V} and N_{IV-V} edges probe empty levels with f and p symmetry.