# Long Range Order and Short Range Order Theories of X-Ray Absorption Fine Structure

Roughly 70 years have elapsed since the phenomenon of EXAFS was first observed, and it has taken nearly that long to realize that accurate, detailed, structural information could be extracted from it and to develop a quantitative theory. Early progress was impeded by experimental limitations of the then available x-ray sources. Moreover, the theoretical interpretation was also not clear cut at that time. This is not surprising, since a full treatment turns out to depend on many complicated details of atomic and molecular structure, high-energy electron atom scattering, many-electron processes, vibrational structure, and disorder. Indeed, much of this physics has only been unraveled within the past 30 years, and a fully quantitative theory was not developed until the present decade. Remarkably, many of the developments needed to explain EXAFS are complementary to advances in our understanding of ground-state electronic structure, e.g., the development of the density-functional formalism (Kohn and Sham, 1965) for band-structure calculations or low-energy excited states.

From general principles of quantum-mechanical transition rates, it was expected that x-ray absorption should be governed by the Fermi ''golden rule'' in terms of a squared transition matrix element times a density of states for available energy levels. Kronig (1931) originally interpreted the XAFS oscillations in crystals as a density-of-states effect, due to the strong diffraction of electrons by the crystal lattice, the so-called long-range order theory. However, the very fine structure present in the density of states due to long-range Bragg scattering, e.g., the sharp van Hove–type peaks observed in band structure calculations, is generally much too detailed to explain the observed EXAFS, and attempts to match EXAFS peaks with predictions of long-range-order theories proved unsatisfactory. Shortly thereafter, Kronig presented an alternative theory for small molecules, in which the oscillatory structure in EXAFS was attributed to the influence of neighbouring atoms on the transition matrix element in the golden rule, i.e., a short range- order effect (Kronig, 1932). This type of theory is most often used today to explain the origin of XAFS, although, as we shall see later, both long- and short range- order theories can be reconciled when appropriate broadening is introduced.

The short-range-order theory reflects the quantum mechanical wavelike nature of the final, excited, photoelectron state. That is, the dominant wiggles in the XAFS spectrum are

interpreted as a quantum interference phenomenon. The outgoing photoelectron can be viewed as a quantum wave that spreads out over the solid, much as a rock thrown in a pond creates an expanding spherical wave in water. In the same way that water waves reflect off of any obstacles in the pond and, in turn, reflect other waves back toward the original point of the splash, so will other atoms reflect the electron wave back towards the original atom (see the Fig.).
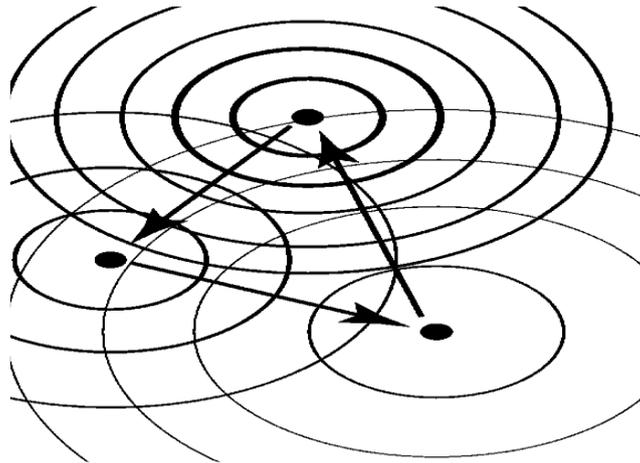
The amplitude of all the reflected electron waves at the absorbing atom add either constructively or destructively to the outgoing photoelectron wave and hence modulate the matrix element between the initial and final states that controls the strength of the transition. Since this interference pattern changes with the energy of the photoelectron (note that the de Broglie wavelength of the electron wave varies inversely with the wave vector k or momentum of the electron), the matrix element, and consequently the absorption, will exhibit similar oscillations. The modern resolution to the controversy between the short- and long-range-order approaches lies in the energy-dependent competition between scattering strength and inelastic losses. A crucial element is the recognition that a high-energy, excited photoelectron state is not infinitely long lived, but must decay as a function of time and distance and hence cannot probe long-range effects. This decay is due primarily to inelastic losses (i.e., ''extrinsic losses'') as it traverses the material, either by interacting with and exciting other electrons in the solid, or by creating collective excitations (e.g., losing energy to plasmon production). In addition, the intrinsic lifetime of the core-hole state (i.e., ''intrinsic losses'') must be considered. In phenomenological terms, the original outgoing wave of the excited photoelectron dies away as it moves further away from the absorbing atom. Ultimately it becomes too weak to significantly reflect any waves off of distant atoms. The returning reflected waves also suffer this same type of extinction. The net effect is that

XAFS can only measure the local atomic structure over a range limited by the net lifetime (or effective mean free path) of the excited photoelectron. This range is typically on the order of tens of angstroms or an inverse lifetime of a few eV and roughly follows a universal dependence. The short-range-order theory focuses on this short-range interference between several important scattering paths. The long-range-order theory, on the other hand, emphasizes the density of states of the extended, excited state, energy levels of the entire material, which can be important at low energies or for strong scattering. Indeed, such an approach is often needed for descriptions of ground-state electronic structure, for example, by band-structure codes. However, the results of this type of approach with the inelastic losses and lifetime considerations in effect washes out the fine structure in the spectra due to the long-range nature of the energy states, thereby recovering the results of short-range-order theory at sufficiently high energies. As noted above, the core hole that is left behind by the excited electron also has a finite lifetime, since higher-lying atomic electrons can make transitions to fill this core hole (either directly, by falling into the orbital and emitting photons as radiative transitions, or indirectly in two-electron non-radiative Auger transitions). Through the uncertainty principle, any state with a finite lifetime does not have a sharp (or delta-function-like) energy level, but is better thought of as having a finite width, e.g., a Lorentzian line shape. In practice, these intrinsic losses lead to an additional broadening of the spectrum and dominate the effective mean free path at threshold. Core widths can be as large as several eV for the deeper core states of heavy atoms, but are relatively small (of the order of 0.1 eV) for light atoms and shallow transitions, compared to the effective widths due to extrinsic losses (typically about 5 eV). Indeed, residual long-range effects often persist, especially in materials with long lifetimes and strong scattering.

References:

1. The historical development of X-ray Absorption Fine Spectroscopy and of its applications to Materials Science by Annibale Mottana and Augusto Marcelli (Springer).
2. X-Ray Absorption Fine Structure (XAFS) Spectroscopy – A Review by ABHIJEET GAUR, B D SHRIVASTAVA and H L NIGAM, Proc Indian Natn Sci Acad 79 No. 4 December 2013, Spl. Issue, Part B, pp. 921-966.