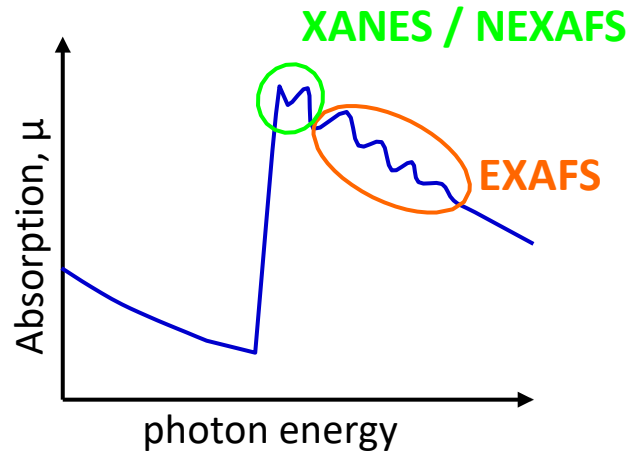**Extended X-ray Absorption Fine Structure**

For photon energies higher than ∼30 eV above the edge, the photoelectron is promoted to a free or continuum state. EXAFS is thus independent of chemical bonding and depends on the atomic arrangement around the absorber. It contains information about the coordination number, interatomic distances and structural and thermal disorder around a particular atomic species. EXAFS does not require long-range order and is applicable to a wide range of ordered and disordered materials therefore providing a powerful tool for structural analysis.

The EXAFS is expressed in terms of the fine structure contribution

$$\chi(E) = [\mu(E) - \mu_0(E)] / \mu_0(E) \sim [\mu(E) - \mu_0(E)] / \Delta\mu_0 \tag{1}$$

where the energy-dependent denominator is approximated by a constant typically chosen as the height of the absorption edge, $\Delta\mu_0 = \mu_0(E_0)$ with E_0 being the energy of the absorption threshold. Instead of using $\chi(E)$, the fine structure is usually written as a function of the photoelectron wave number $k = \sqrt{2m_e(E - E_0)/\hbar^2}$, where m_e stands for the electron mass and $\hbar$ denotes Planck's constant divided by 2π. Using the multiple scattering path expansion, the fine structure contribution can be expressed as a sum over the scattering contributions arising from the various different paths

$$\chi(k) = \sum_j S_0^2 N_j \frac{|f_j(k)|}{kR_j^2} e^{-2R_j/\lambda(k)} e^{-2\sigma_j^2 k^2} \times \sin\left[2kR_j + 2\delta_c(k) + \delta_j(k)\right]$$

(2)

Paths with the same kinds of scattering atoms and a similar path length have been grouped under the index j. Equation (2) thus directly relates the EXAFS signal to the structural parameters N_j, R_j, and σ_j^2 which represent the number of such similar paths, the mean path length divided by two and the variation of all path lengths with index j, respectively. $f_j(k) = |f_j(k)|e^{i\delta_j(k)}$ represents the complex scattering amplitude while $\delta_c(k)$ stands for the phase shift experienced by the photoelectron wave in the potential of the absorbing atom. $\lambda(k)$ and S_2^0 denote the energy-dependent mean free path of the electron and the amplitude reduction factor, respectively. Except for the factor S_2^0, (2) was first derived by Sayers, Stern, and Lytle for single scattering paths using the plane-wave approximation. It assumes that the distance between the absorber-backscatter pair is sufficiently large to treat the outgoing spherical wave as a plane wave once it reaches the backscattering atom. For single scattering events, all paths involving the same kind of scattering atom in the same coordination shell around the absorber are grouped together. The structural parameters N_j, R_j, and σ_j^2 then represent the coordination number, the mean value, and the variance of the corresponding absorber-scatterer distance distribution, respectively. In case of the first nearest neighbour shell, absorbing and scattering atoms are usually connected by a real physical bond, and R_j and σ_j^2 signify the mean value and variance of the bond length distribution. Equation (2) is known as the 'standard EXAFS equation' and has founded the application of XAS as a tool for structural analysis.

For an accurate calculation of the fine structure contribution, however, multiple scattering paths, curved-wave effects and many-body interactions must be taken into account. Nevertheless, $\chi(k)$ can still be expressed in the same form as the original EXAFS equation. This provides a convenient parameterization of the absorber environment in terms of structural parameters for single and multiple scattering paths.

The key features of the EXAFS equation are as follows:

(i) As described in Sect.1.1.2, the interference pattern depends on the photoelectron energy or wave number and on the distance between the absorbing and scattering atoms. This is given by the *sin[2kR_j]* term which causes the oscillatory nature of the fine structure contribution.

(ii) The strength of the scattering and thus the magnitude of the EXAFS depend on the number and type of the scattering atoms, represented by the coordination scattering amplitudes are also characterized by a weak dependence on r.

(iii) The potential of the absorbing or scattering atom leads to a phase shift of the number or degeneracy of paths N_j and the modulus of the scattering amplitude $|f_j(k)|$, respectively. Modern XAS theory replaces the original plane-wave scattering amplitude by effective curved-wave scattering amplitude for either single or multiple scattering events. Apart from the dependence on k, the effective photoelectron wave represented by $\delta_c(k)$ and $\delta_j(k)$, respectively. The absorber potential acts twice on the photoelectron wave, once on the way out and once on the way back. The resulting term $2\delta_c(k)+\delta_j(k)$ appears in the sine function of (2).

(iv) The atoms in a particular coordination shell do not have exactly the same distance from the absorber. Differences are caused either by thermal vibrations (thermal disorder) or by structural variations in the interatomic distances (static disorder) and smear out the oscillations with increasing k. The phase difference in scattered waves due to a given difference in R_j increases with increasing *k*. This yields increased damping of the EXAFS at high wave numbers. In systems where the distance distributions exhibitonly small asymmetry, Gaussian distributions with variance σ_j can be assumed. The term $e-2\sigma_j^2k^2$ in (2) then accounts for the k-dependent damping of the EXAFS oscillations. In analogy to X-ray diffraction, σ_j^2 is often called the EXAFS Debye-Waller factor.

(v) The range that is probed by EXAFS is usually of the order of ten angstroms and is limited by the finite lifetime of the core hole and the finite mean free path of the photoelectron. The core-hole is eventually filled with an electron from a higher shell thereby emitting a fluorescence X-ray or an Auger electron while the photoelectron undergoes inelastic interactions with the surrounding material such as in elastic scattering and electron or Plasmon excitation (extrinsic losses). The term $e^{-2R_j/\lambda(k)}$ in (2) accounts for the increasing decay of the photoelectron wave with increasing distance Rj. The mean free path is approximately given by λ(k)

$\sim k/(|Im\Sigma|+\Gamma/2)$ and thus comprises the finite core-hole lifetime Γ and extrinsic losses calculated in terms of the complex self energy Σ. The damping of the fine structure contribution by both $\lambda(k)$ and σ_j^2 makes EXAFS a local probe and ensures the convergence of the multiple scattering path expansion in this regime.

(vi)   The one-electron approximation assumes that only a single electron participates in the absorption process. In reality, however, this is a many-body process and relaxation of the system in response to the sudden creation of the core-hole reduces the fine structure component. The corresponding amplitude reduction factor S_2^0 is, in principle, weakly energy dependent, particularly close to the absorption threshold. In the EXAFS region it can be taken as a constant to good approximation.