X-Ray Absorption Spectroscopies XANES and EXAFS

An X-ray absorption spectroscopist is usually interested in the energy range of 300 eV-30 keV. This is in stark contrast to optical spectroscopies where valence electron states are probed. In XAS (X-ray absorption spectroscopy) the relevant parameter of the photon is its energy and its “resolution”.

After the absorption event, the photoelectron is emitted. This plays a key role in a microscopic understanding of the spectroscopy. It may be considered equally well as an energetic particle of energy $E$ or as a wave of momentum $k$ given by

$$E = \frac{\hbar k^2}{2m_e} \tag{1}$$

If the photon energy ranges from 300 eV up to 30 keV, the photoelectron energy starts from near zero up to 700-1000 eV typically.

One may think of only two fundamental channels for the photon-matter interaction. First the most likely event is absorption, where the energy of the photon is lost within the target. This is a one photon IN and zero photon OUT channel.

Since, in the 300eV - 30keV range, this photoelectron is more probable than the other one by two or three orders of magnitude, there is a tendency to identify the measurement of the intensity of the transmitted beam $I$ for an incident intensity $I_0$ (i.e. the number of photons that do not interact) with the exact evaluation of the linear absorption coefficient, $\mu$, through

$$\mu t = \ln \left( \frac{I_0}{I} \right)$$

where $t$ is the thickness of the sample.

In fact this measurement is the total cross section which, in addition to the photoelectric cross section, includes the cross sections for elastic scattering (Thomson cross section for free electrons) and inelastic scattering (Compton). These scattering cross sections refer to the second process where there is one photon IN and one photon OUT. A log plot of cross section versus log of the photon energy is displayed for the copper atom.

It is useful to distinguish between photoemission and photoabsorption according to the use made of the photoelectron. When the photoelectron escapes into the vacuum before being captured by a detector, new information is introduced. By measuring the kinetic energy and momentum of the photoelectron one can
infer the band structure of the solid. These angle resolved photoemission studies require some additional hypotheses before the results are turned into a band structure picture. There are surface-sensitive effects and certain assumptions required to derive the momentum within the solid from measurements of the electron characteristics out of the solid. Apart from this specific aspect of absorption where attention is focused on the emergent photoelectron, one has to consider and discuss the two main decay channels following the creation of the electronic vacancy in the core level of the photoexcited atom.

Only interactions with electrons are important. Although the X-ray energy can be regarded as low for nuclei, it is very high for bound electrons (with the possible exception of one shell). Therefore the refractive index $n$ of the matter in the X-ray range is very close to 1, but slightly smaller.

$$n = 1 - \delta + \nu \beta$$

with $\delta$ and $\beta$ of the order of $10^{-5}$. $\beta$ is related to the linear absorption coefficient, $\mu$, and the wavelength of the X-ray, $\lambda$, by the expression

$$\beta = \frac{\mu \lambda}{4\pi}.$$

If we assume the bound electrons to be harmonic oscillators, the response to an excitation with the frequency of the X-ray photons creates dipoles whose magnitudes are proportional to,

$$R \propto \frac{1}{-\omega^2 + \omega_0^2 + i(\beta/2)\omega}$$

where $\hbar \omega$ is the energy of the exciting photon and $\hbar \omega_0$ is the energy of the resonator (bound electrons). [cf. equation (4) from the September 9, 2004 lecture (lecture 4 on the web site for 09-801).] There is such a great difference between $\omega_0$ (small for most of the electrons of the atom) and $\omega$ (large) that all these terms have a small but negative contribution which makes $n$ slightly less than 1. In contrast to the valence electrons, the core electrons do not see a local field since there is almost no dipole momentum created. The fact that

$$n - 1 = \delta + \nu \beta$$

is of the order of $10^{-5}$ reflects the small interaction between X-ray photons and matter. A significant amount of matter is needed in a sample probed by X-rays, but less than in a sample designed for a neutron study and more than for a sample to be probed by electrons.
All these cross sections, constructed from the response of all the electrons in each atom are Z-dependent. They are illustrated for you in plots of log \( \sigma \) versus log \( E \) for the elements Li\((Z = 3)\), Ge\((Z = 32)\) and Gd\((Z = 64)\). The cross sections are those of individual atoms. Interferences can augment or amplify the electric field of the wavelets scattered by a periodically packed collection of atoms. In this case the Bragg peaks can contribute to the total cross section more than the photoelectric effect. This illustrates the power of interferences, which are able to transform a weak individual phenomenon into a set of intense peaks full of valuable structural information. If, on the other hand, the aim of the experiment is to measure the photoelectric cross section, Bragg peaks often spoil the data collected, e.g. for a single crystal sample.

These extreme differences in cross sections are reflected by the time scales for different experiments. For two different synchrotron sources with different fluxes a table below displays approximate time scales. DCI(LURE) in Orsay is an older source and has a lower flux than ESRF in Grenoble.

<table>
<thead>
<tr>
<th></th>
<th>XAS</th>
<th>Elastic Diffraction</th>
<th>Compton Scattering</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCI</td>
<td>&lt; 1s to 600s</td>
<td>hours to day</td>
<td>week</td>
</tr>
<tr>
<td>ESRF</td>
<td>&lt; 1ms to 60s</td>
<td>&lt; 1 hour</td>
<td>&lt; 1 day</td>
</tr>
</tbody>
</table>

Once the absorption of the photon has occurred, the excited atom is left with an electronic vacancy, \( i.e. \) a core hole. The classical model decouples the relaxation of this excitation from the primary process. This approach can be justified experimentally since both decay channels, fluorescence yield and Auger yield, carry information on the atom itself, but keep no memory of the photon that created the core hole. Both yields hardly depend on the energy or the polarization state of the impinging photon. In principle the decay channels should take into account the kinetic energy of the photoelectron and its polarization, but this effect is small. The two main decay channels are essentially an unambiguous identification of the excited atom as are the energy positions of the absorption threshold.

The electronic core levels of an atom in a solid keep their atomic features because of the nearly zero overlap of their wavefunctions between atoms. If the excitation involves the 1s shell, the fluorescence channel is given by a radiative transition of an electron with p symmetry. This symmetry argument comes from the dipole selection rule for a transition from one state to another in an atom. The most probable transition is from the 2p electrons filling the 1s core hole. It generates the \( K_{\alpha 1} \) and \( K_{\alpha 2} \) lines. Other allowed transitions from full p states up to valence electrons are gathered into the generic term \( K_{\beta} \), but for standard X-ray
tubes the K\textsubscript{2} line(s) is(are) due to a s—p transition from the M shell of the atom. The K\textsubscript{α1} emission line intensity is about twice that of the K\textsubscript{α2} since the 2p\textsuperscript{3/2} state is four-fold degenerate while that of 2p\textsuperscript{1/2} is two-fold degenerate. Once the 1s—2p transition is complete, the excited atom is left with an electronic vacancy in the 2p shell. The ensuing cascade, which is part of the relaxation, is virtually decoupled from the initial step of a 2p to 1s transition. The assumption is valid since each step in the full relaxation process involves very different energies. The energy difference between the K\textsubscript{α2} and K\textsubscript{α1} is equal to the difference between the L\textsubscript{2} and L\textsubscript{3} edges in the primary absorption process. The difference for copper is close to 20 eV. It is smaller for elements with Z less than 29 and greater for elements with Z higher than 29. The fluorescence lines (such as K\textsubscript{α1} and K\textsubscript{α2}) are element specific. In the early days of X-rays, J. Perrin recognized these lines as a powerful means for identifying elements in solids. Indeed J. Moseley (circa 1913) found all the ingredients in the atomic Bohr model for predicting fluorescence lines. Moseley was the first to identify rare earth elements, one by one, which was not possible by chemical methods since the filling of the f band plays almost no role in the chemistry of these elements. Quantitative use of fluorescence is presently one key method of trace analysis found in synchrotron radiation laboratories; it offers the additional possibility of selective excitation.

When a 2p electron fills the 1s corehole, it has to release energy (∼ 8000 eV for Cu). Besides fluorescence, a second channel involves a second electron in the process to carry the energy of relaxation out of the atom. This process was discovered by Auger in his use of a bubble chamber. Auger sometimes found more than one trace, which indicated that in addition to the photoelectron leaving the atom, a second electron was involved. This electron has been termed an Auger electron. If the relaxation involves transferring two electrons from the L shell to fill the corehole of the K shell, the process is called KLL. If two valance electrons are involved in filling the corehole, it is termed KVV. In this case the Auger electron leaves the atom with a large kinetic energy. Since the mean free path of electrons is short, the electrons are thermalized in subsequent cascades. The result is a spectrum of photoemitted electrons spread over a wide range of kinetic energies. There are many electrons with a very small kinetic energy and a progressive decay of the electron flux with increasing kinetic energy. The fastest electrons are valence electrons ejected from the surface of the sample with the full energy of the absorbed photon. There are no pure Auger lines since many secondary electrons come out of the sample with the same energy as the Auger electrons. The latter appear as small peaks above background. For shallow excitations of heavy elements one may encounter a situation where the corehole and one of the two electrons involved in the relaxation belongs to the same shell. In this case the
terminology is modified to speak of the Coster-Krönig effect (L-LM or L-ML). It is also possible that the three particles (the hole and the two electrons) belong to the same shell - this is called the super Coster-Krönig effect. From energy arguments it is reasonable to find a faster decay process if these two last channels are effective. A large transition probability is equivalent to a short lifetime or a large energy width of the core hole.

The core hole width is related to the probability of the decay channels. This width, however, reflects the uncertainty in the binding energy of the core electron in the primary process which is measured by photoelectric absorption. The framework of classical physics with a separated sequence of events leads to a confusing concept that seems to contradict a causality principle, namely the core electron must know the probabilities of the subsequent events. This view should not be an obstacle if we consider the matter as a quantum system. The relation between the lifetime, \( \tau_i \) of the excited state and the corehole energy width \( \Delta E_i \) is

\[
\Delta E_i = 2\Gamma_i = \hbar / \tau_i.
\]

Since two channels are operative we need to split the width into its fluorescent component, \( 2\Gamma_i F \) and \( 2\Gamma_i A \) for the Auger channel. The deeper the excited shell, the larger is the probability of corehole filling. This is true for the two main components but their \( Z \) dependences are different. For a K shell excitation of low \( Z \) elements it is the Auger process that is more effective up to Gallium. For shallower excitations the cross-over is at higher atomic number, \( Z \).

The absorption of an X-ray by a core electron in a many electron atom follows the selection rule for an allowed transition dipole moment for the stronger absorption bands in atomic spectroscopy. Thus an excited 1s core electron is sent to an empty p state of the atom. (Likewise, a 2p core electron would be sent to an empty d state or an empty s state.) The intensity of the transition, depends on the oscillator strength, which is reflected by the radial overlap of the initial and final state. The K-edge spectrum of atomic Neon is illustrated here. The first transitions to 3p, 4p, 5p can be easily distinguished before the continuum sets in, which results from the overlap of the different np components.

Both structural and electronic properties may be delineated by XAS. It is site selective. Successive tuning of the X-ray photon energy to a specific threshold of each element allows independent site-by-site collection of the data. Selection rules for transitions make it possible to obtain information on selected empty states. For example, the empty 3d states of copper in high \( T_c \) materials may be assessed from \( L_{III} \) spectroscopy of Cu by tuning the photon energy to about 930 eV. The dipolar interaction for the electronic transition gives a sensitivity to anisotropy or angular resolution for non cubic single crystals. By tilting a crystal of the square
planar cuprate ion in order to get in-plane polarization makes it possible to probe
the in-plane empty orbitals. Tilting the square planar unit perpendicular to the
polarization puts the c axis along the electric field, so the information derived
is c-oriented. The core hole relaxation may be used to discriminate between
valances of the same atom. Copper is again posed as an illustration. Monovalent
copper, Cu(I), contains 10 d electrons but divalent Cu(II) contains only nine. The
Coulomb interactions of the corehole created in the 1s shell and each ion differ in
magnitude because of the different filling of the 3d band. Cu(I) gains more energy.
The rising part of the K-edge of Cu(I) takes place at a lower energy than that
of Cu(II). Two other phenomena could also account for this observation. More
or less distant neighbors shift the threshold to less or more to the high energy
side, as might be expected from σ* molecular orbitals compared to π* orbitals.
Secondly, because of the immediate charge screening of the core hole, charge
transfer from the ligand to the excited ion may take place: XAS spectroscopy
sees a final state with a greater d filling than in the ground state. Angle-resolved
XAS data form the single crystal shows that the transitions (M, N in figure(b))
to 4p_{x,y} antibonding orbitals are clearly distinguishable from the transitions (B,
E in figure(b)) to 4p_z antibonding (La_{2}CuO_{4}) orbitals. The spectrum at 54°
is the magic angle that mimics the crystalline powder spectrum. The non-bonding
orbitals in Nd_{2}CuO_{4} appear in the initial rise of the absorption cross-section (B,
E in figure(a)). The A feature in the absorption spectrum for Cu_{2}O is due to the
2 non-bonding 4p orbitals of the linear unit which is present in Cu_{2}O.

The great advantage of core level spectroscopy compared to visible light spec-
troscopy comes from the simple initial state which has essentially atomic char-
acter. In the framework of one electron theory, which with minor corrections,
is adequate for introducing the formalism for EXAFS. The only difficulty comes
from the calculation of the final state of the photoelectric transition.

Two different ways of calculating the final state in the EXAFS regime have
been developed. (1) The band structure approach requires a system with pe-
riodicity in three dimensions and is thus restricted to ordered solids. (2) The
scattering formalism takes the wavefunction |f> to be a solution of the excited
potential and improves it systematically by including single backscattering from
neighboring atoms, and spatial variation of the scattered wavelets. In addition,
any multiple scattering events need to be accounted for in the low energy range,
XANES. Unlike the band structure approach, the scattering formalism is of gen-
eral applicability; it covers disordered condensed matter, clusters and molecules
as well.

Of particular importance is the fact that, except in unusual circumstances,
multiple scattering does not contribute much in the high energy range of the
spectrum $\geq 50-100$ eV. A practical way of separating XANES from the EXAFS domain is to compare the wavelength of the photoelectron to the distance between the absorber and the backscatterer. A short wavelength means EXAFS whereas long wavelengths imply multiple scattering.

The following theoretical discussion is limited to the EXAFS formalism used by the experimentalist. The formalism is based on the idea that the photon merely helps to create the photoelectron. The latter is a low energy charged particle that is scattered during its propagation by any abrupt change of the potential energy such as the atomic potential of its neighbors. The outgoing photoelectronic wave interferes with the backscattered wavelets to build the EXAFS oscillations. In fact EXAFS is a low energy electron diffraction experiment, where the photoelectron comes from a chosen type of atom.

A useful way to clarify the physical nature of EXAFS is to study an AB diatomic molecule by constructing the final state step by step. The molecule is just taken to be a pair of atomic potentials with a flat region in between. (This is known as the muffin tin approximation in solid state band structure calculations.) Let us suppose that the photon energy is tuned to excite the 1s level of atom A - i.e. its energy is slightly above ($\approx 100$ up to 1000 eV) the 1s binding energy.

1-The emitted photoelectron reaches vacant orbitals of p symmetry. It is fast enough to be considered a free electron and its wavefunction can be viewed as a quasi plane wave when it reaches the potential of atom B. The specific phase shift of this wave at the position of B is the sum of the optical path $k \cdot r_B$ and the phase shift caused by passing through the potential of the emitter. For an isolated atom A, the final one-electron state is an outgoing wave $|f_0\rangle$.

$$|f_0\rangle \propto \frac{\exp[i(k \cdot r_B + \delta_A)]}{2kr_B}$$

2-For an AB molecule, $|f\rangle$ is slightly different from $|f_0\rangle$.

$$|f\rangle = |f_0\rangle + |\delta f\rangle = |f_0\rangle (1 + \chi)$$

since the photoelectron is scattered by the potential of atom B in all directions with a complex amplitude $f(\theta, k)$ that depends on direction and kinetic energy

$$E = \frac{\hbar k^2}{2m_e}.$$ 

What must be considered is the backscattered wavelet ($\theta = \pi$) which returns to the emitter and interferes with the outgoing wave. Measured at the emitter site itself, the amplitude of the wave function for the final state contains information
on the distance AB and on the chemical nature of the neighbor B.

\[ |f| \propto \frac{\exp[i(\mathbf{k} \cdot \mathbf{r}_B + \delta'_A)]}{2kr_B} \left[ 1 + f_B(\pi, k) \left( \frac{\exp[i(\mathbf{k} \cdot \mathbf{r}_B + \delta'_A)]}{r_B} \right) \right]. \]

The backscattered amplitude is,

\[ f_B(\pi, k) = \frac{1}{2ik} \sum_l (2l + 1) \left( e^{2i\delta_l} - 1 \right) P_l(-1). \]

The momentum \( k \) is given by the kinetic energy of the photoelectron, which is roughly the difference between the energy of the photon and the binding energy of the photoexcited core electron. The position of the backscattering atom is \( \mathbf{r}_B \). \( f_B(\pi, k) \), the backscattering from atom B, is a complex number. Both its amplitude and argument allow the backscattering atom to be chemically identified. \( \delta'_A \) is the phase change that the photoelectron undergoes on each trip forth and back. The prime indicates that the potential is not strictly atomic, since the newly created corehole perturbs the electronic distribution - i.e., the wavefunction of all the remaining electrons of the atoms. \( \delta'_A \) should carry an extra subscript, \( \delta'_{IA} \), in the case of K-edges in order to specify the p symmetry of the photoelectron according to the selection rules. \( \delta_l \) appears in the calculations of differential cross-sections of a point charge scattered by the atomic potential with the usual Legendre polynomial \( P_l(\cos \theta) \).

The mathematics becomes very easy. The normalized energy dependent oscillations of the absorption cross-section, \( (\mu - \mu_0)/\mu_0 \) is the EXAFS signal of this AB molecule probed from the A side.

\[ \chi(k) = \frac{\mu - \mu_0}{\mu_0} = -\frac{|f_B(\pi, k)|}{kr_Br_B} \sin(2kr_B + n\phi) \]

and

\[ \phi = 2\delta'_{IA} + \theta_B \]

where \( \theta_B \) is the argument of the backscattering amplitude.

EXAFS data extend over a large domain of momentum. Compared to neutron and X-ray diffraction techniques this is an asset. The fact that the low energy part of the spectrum does not involve the same mathematical analysis restricts the power of this technique in determining long distances accurately. This limitation becomes an advantage if the aim is to determine close coordination, i.e., the distances, the number and the chemical nature of the immediate neighbors. The EXAFS modulations \( \chi(E) \) are extracted from the X-ray absorption cross-section via the relation

\[ \sigma(E) = \sigma_0(E)[1 + \chi(E)] \]
where \( \sigma(E) \) is the total cross section of the sample and \( E \) is the kinetic energy of the photoelectron. \( \sigma_0(E) \) is the free atom-like cross section but this quantity is never actually measured. It should be what was denoted as \( \mu_0 \), the real atomic absorption coefficient. An accurate determination implies measuring an atom in the gas phase \( \text{e.g.} \) Ne XAS which usually does not exist at the temperature of the measurement. In practice the experimentalist derives \( \sigma_0(E) \) as a smooth background going gently through the oscillations.

\( E \) is related to the energy of the impinging photon through

\[
E = h\nu - E_0
\]

where \( E_0 \) is the origin for the kinetic energy of the photoelectron. \( E_0 \) is close to the threshold energy, but does not have to coincide with this value. For a free electron metal \( E_0 \) should be close to the bottom of the conduction band. In the framework of the plane wave approximation, multiple scattering effects and multiple electronic-absorption processes are neglected. The final state is merely a superposition of the outgoing spherical wave and the wavelets backscattered by the neighbors, which contain interferences that are constructive or destructive according to the optical path. Refinements of the model should consider possible anisotropy of the potential to account for the ligand field. But in most practical cases it is not a significant point and lies beyond the accuracy of the method in realistic situations.

The commonly used practical model is:

\[
\chi(k) = -\frac{1}{k} \sum_j 3 \cos^2 (R_j \cdot \epsilon) \frac{\mid f(\pi, k) \mid}{R_j^2} \sin(\Phi_j) \exp(-2\sigma^2 k^2) \exp \left( -\frac{2R_j}{\Lambda(k)} \right)
\]

\[
\Phi_j = 2kR_j + \delta_l + \theta_j
\]

\[
\theta_j = \text{arg}(f_j(\pi, k))
\]

\( j \) labels any neighbor at \( R_j \) that contributes to the EXAFS signal. The first exponential, \( \exp(-2\sigma^2 k^2) \), is like a Debye-Waller damping factor which accounts for thermal vibration in the harmonic approximation. In contrast to Debye-Waller factors derived from neutron and X-ray diffraction experiments, only the change of the distance \( R_j \) contributes so that the mean square amplitude of vibration, \( \sigma^2 \) is characteristic of an internal vibration. Acoustic modes (long wavelengths) do not contribute. The Debye formula for the scattering amplitude from a crystal shows clearly that long distances generate the diffraction pattern. It is just the opposite for EXAFS where no contributions comes from long distances. Only those pairs separated by the shortest distances and having a specific atom at the origin generate EXAFS. The last exponential, \( \exp(-2R_j/\Lambda(k)) \), accounts for
inelastic processes. These limit the coherency of the photoelectron to a mean free path \( \Lambda \) which is energy dependent and therefore \( k \) dependent. It is the same mean free path as that encountered in photoemission. In general, it has a minimum of about 5 Å around 50 eV and increases above this energy more or less as \( k \) becomes larger.

The polarization dependent contribution of atom \( j \) to \( \chi \) is

\[
3 \cos^2(R_j \cdot \epsilon).
\]

Since synchrotron radiation is polarized, linearly in the case of classical EXAFS data collection, the dot product of the dipole Hamiltonian generates the square of the cosine of the angle between \( R_j \) and the electric field, \( \epsilon \). The amplitude of the outgoing wave is proportional to \( \cos[R_j \cdot \epsilon/R_j] \). If the probed atom is in a site of cubic symmetry, then the sum over \( 3 \cos^2(R_j \cdot \epsilon) \) is replaced by a sum over \( N_j \) where the subscript \( j \) now labels the successive neighboring shells instead of the individual atoms. In order to keep the practical shell description for local ordering, an effective number

\[
N'_j = \sum_i 3 \cos^2(R_i \cdot \epsilon)
\]

of atoms is often used, with the subscript \( i \) running over all the atoms within the shell \( j \). If the system is cubic, \( N'_j \) is exactly the number of neighbors in the crystallographic structure.

Surfaces are obviously an anisotropic system. In this case polarization dependent spectroscopy is a very powerful tool and enables one to determine which site is involved in adsorbate-surface interactions. The polarization dependence is even more attractive in the XANES regime where the large electron mean free path at low energy allows for significant contributions from multiple scattering events or longer paths of single backscattering. In the domain that is close to the absorption edge, it is worthwhile to think in terms of band structure, and XAS then probes the empty orbitals. For example, by looking at the angular dependence of the \( \pi^* \) and \( \sigma^* \) resonances at the oxygen K-edge using XAS, the CO molecule has been shown to sit perpendicular to the Cu (100) surface. The intensity of the \( \pi^* \) is maximum when the electric field is parallel to the surface whereas the intensity of the \( \sigma^* \) is minimal. The reverse is observed when the sample is turned by 90°.

The phase shifts and backscattering amplitudes, which are needed for ab-initio fitting routines, are very difficult to get correctly from theoretical calculations alone. What is done in practice is to measure them in a model compound for which the structure is well known and chemically close to the unknown sample.
under investigation. The simplicity and consistency of this approach alleviates three major sources of error in the naive model. The use of model compounds with similar bond lengths, and therefore phase shifts and amplitudes cancels the bad effects of the plane wave approximation. The origin for the kinetic energy, \( E_0 \) of the photoelectron can be well determined by locating \( E_0 \) right at the edge of the model compound which reduces the error in the phase shifts. If the ligand field of the model compound is close to the investigated sample, the chemical effects including the local anisotropy, are included in the phase shifts and background scattering amplitudes that are extracted and transferred from the model compound. In short the use of EXAFS data from a model compound is essential if reliable structural parameters are to be determined. Roughly 80% of \( \Phi \) is due to the optical pathlength, \( kR_j \), 15% due to the absorber contribution, \( \delta_l \), and only 5% for the backscatterer phase of \( \theta_j \).
MEAN FREE PATH

\[ A \approx k / \Gamma \]

Amplitude of back scattering by the neighbours