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OTHER EXAFS-LIKE PHENOMENA

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Abstract: A description and comparison of various EXAFS-like phenomena are presented based on theoretical and practical considerations. Most of the phenomena are similar but not exactly the same as EXAFS. This does not limit their usefulness for structure determination but requires separate experimental calibration and theoretical calculations.

Introduction

After the discovery that EXAFS has structural information that can be directly obtained from the measured data, several other experimental phenomena were shown to also have EXAFS-like character. In this review I shall describe these other phenomena and discuss their relation to EXAFS.

First, the basic character of EXAFS-like behavior will be described and distinguished from photoelectron or electron diffraction. This distinction was first made by Patrick Lee. He showed that the number of EXAFS photoelectrons detected at a particular angle relative to a bond direction will have much larger and different oscillations with energy than the EXAFS effect. These oscillations are dominated by diffraction effects. Only by averaging the photoelectrons over all $4\pi$ solid angles do the oscillations reduce to EXAFS.

To understand this phenomenon, consider the diffraction of any wave phenomenon, in particular electrons, from a periodic array of atoms, i.e., from a crystal. The electrons are incident at all angles on a polycrystalline sample, and their scattered intensity is detected at a fixed angle. As the energy of the electrons, and thus their wavelengths, is varied, the scattered intensity will display Bragg peaks which give large changes when such a peak coincides with the detected direction. It is well known that averaging the diffracted intensity over $4\pi$ gives a total diffracted intensity which is independent of long-range order and eliminates the large fluctuations caused by the Bragg peaks. Thus, an EXAFS-like phenomenon must be one that does not angularly resolve the final photoelectron state $|f\rangle$. In this manner the distinction is made between angularly resolved photoelectron diffraction effects and EXAFS-like effects which remain in the state $|f\rangle$ after angular averaging.

Experimentally, EXAFS is usually done at a synchrotron radiation facility, although some laboratory EXAFS facilities have been built. The motivation for developing other EXAFS-like phenomena is to be able to perform such measurements in the laboratory, thus avoiding the experience at a synchrotron source. Because of this, the other EXAFS-like techniques utilize electron beams in place of X rays to excite the phenomenon.
Qualitative Description

Six different EXAFS-like phenomena have been described in the literature. These are EXAFS: (S)EELFS (Surface) Extended Energy Fine Structure], EXELFS (Extended Electron Loss Fine Structure); EAPFS (Extended Appearance Potential Fine Structure); EXBIFS (Extended X-ray Bremstrahlung Isochromat Fine Structure); and EXFAS (Extended Fine Structure in Auger Spectra). These can be described by the energy diagrams shown in Fig. 1.

Fig. 1. Energy-level diagrams for various EXAFS-like phenomena as described in text.

In EXAFS \((a)\) (Fig. 1a) an x-ray photon excites a core electron into an escaping photoelectron state \(|f\rangle\). The photoelectron has an energy \(E_{\text{photo}} = \hbar \omega - E_c\), where \(\hbar \omega\) is the x-ray photon energy and \(E_c\) is the binding energy of the core state below the chemical potential or Fermi level \(\mu\). In EXELFS \((b)\) and (S)EELFS \((c)\) an incoming electron of energy \(E_i\) excites a core electron into the state \(|f\rangle\) with energy \(E_c\) (Fig. 1b). The incoming electron is scattered into state \(E_s\) after losing an energy \(E_i = E_s - E_e = E_e - E_c\). In the case of EXELFS, \(E_i >> E_e\), while in (S)EELFS \(E_i\) is only a few times greater than \(E_e\). In EAPFS \((d)\) the diagram in Fig. 1c is the same as in Fig. 1b except that now \(E_s \approx E_c\) and thus both \(E_s\) and \(E_e\) are in states \(|f\rangle\) of low enough energy that each contains EXAFS effects. For EXBIFS \((e)\) the incoming electron of energy \(E_i\) of Fig. 1d is scattered by the atom, but instead of exciting a core electron, an x-ray photon of energy \(\hbar \omega\) is excited, with the scattered electron dropping to an energy \(E_s\) after losing an energy \(E_i = E_s - E_e = \hbar \omega\). Note that EXBIFS is just the inverse photoelectric effect, which can be seen by reversing the time sequence of events.

Finally, the EXFAS phenomenon \((f)\) is related to an Auger process between a core level and two valence electrons. A core electron is excited by bombarding electrons (Fig. 1e). The resulting

† The S is in parentheses because the technique probes a depth of tens of angstroms below the surface. Depending on how it is employed, this may or may not impart a surface sensitivity to the technique.
core hole can be filled by the Auger process shown in Fig. 1f, where a valence electron drops into the core hole imparting the released energy to another valence electron. The EXFAS process is explained as an excited electron in the state $|f\rangle$ dropping into the core hole, imparting the released energy to another valence electron.

What is not clear at the moment is how the state $|f\rangle$ becomes filled in this case. It has been suggested [9] that the excited core electron populates $|f\rangle$. Further investigation of this phenomenon is required before its origin can be clarified, and for that reason I shall not discuss further the EXFAS process.

It is instructive to also describe the various EXAFS-like phenomena by scattering diagrams as shown in Fig. 2.

![Scattering diagrams for various EXAFS-like phenomena](image)

Fig. 2. Scattering diagrams for various EXAFS-like phenomena as described in the text.

In EXAFS (Fig. 2a) an incoming photon is absorbed, knocking a photoelectron from a core state into the state $|f\rangle$ with $E_e$ and exciting a core hole in the atom. The number of absorbed photons is measured as the energy of the photon is varied (indicated by the symbol $\sim$). For both EXELFS and (S)EELFS (Fig. 2b) an incoming electron of fixed energy $E_i$ interacts with an atom exciting a core electron into the state $|f\rangle$ with energy $E_e$, again leaving an excited core hole behind. The incoming electron is scattered by this process into the state with energy $E_s$. The energy $E_s$ is detected and varies according to the value of $E_e$. In EAPFS (Fig. 2c) the energy $E_i$ of the incoming electron is varied so that it can excite a core electron into the state $|f\rangle$ with energy $E_e$ and itself is scattered into another state $|f\rangle$ of energy $E_s$, leaving a core hole behind. In this case the total number of electrons $E_s$ and $E_e$ is detected as the energy $E_i$ is varied. In EXBIFS (Fig. 2d) the energy $E_i$ of the incoming electron is varied as the number of excited photons is detected at a fixed energy $h\omega$. The scattered electron ends up with the energy $E_s$. When $E_i \geq h\omega$, the electron scatters in the state $|f\rangle$ with variable energy $E_s = E_i - h\omega$. From Fig. 2d the designation of EXBIFS as an inverse photoelectric effect is clear by reversing all arrows. In this case the photon excites the electron $E_s$ in state $|f\rangle$ into the excited state of energy $E_i$.

**Theoretical Comparison**

**A. EXAFS**

The probability of an EXAFS process to occur has to be treated quantum mechanically and is proportional to the square of a matrix element $M$, where

$$M = \langle i | H' \exp i\vec{q} \cdot \vec{r} | f \rangle.$$
Here \( \langle i \rangle \) is the conjugate of the initial state \( |i\rangle \), the perturbing field of the x-ray photon is \( H' \) \( = \) \( r \cdot r' \), and \( |f\rangle \) is the final photoelectron state with energy \( E_e \). \( E_e \) can range up to \( \sim 1000 \) eV, still producing appreciable EXAFS signal: \( q = \omega / c = 2\pi / \lambda \), where \( \omega \) is the radial frequency of the photon, \( c \) is the velocity of light, and \( \lambda \) is the photon wavelength. The state \( |f\rangle \) contains the EXAFS signal. As is well known [4], the EXAFS signal is caused by an interference of its outgoing part by the backscattered portion of \( |f\rangle \) produced by the atoms surrounding the excited one. The state \( |i\rangle \) has a spatial extent \( a \) which is small compared with \( \lambda \), so that \( qa \ll 1 \) and the dipole approximation can be used.

I distinguish two cases. In one case, \( |i\rangle \) is a deep core state defined by its energy \( E_c >> E_e \). The matrix element \( M \) is nonzero only over the spatial extent of \( |i\rangle \). In this region the Schrödinger equation for \( |f\rangle \), namely

\[
\left( \frac{p^2}{2m} + V(r) - E \right) |f\rangle = 0 ,
\]

can be approximated by setting \( V(r) - E_c \approx V(r) \), since the atomic potential \( V(r) \) is of the order of \( E_c \) and is thus much greater than \( E_e \). Thus, \( |f\rangle \) satisfies the same equation as \( |i\rangle \) does. In this region \( |f\rangle \equiv A|i\rangle \), where \( A \) is a constant in space. However, \( A \) is a function of \( E_e \) because of the interference effect caused by the surrounding atoms. The matrix element \( M \), and thus the EXAFS, obtains its full oscillatory energy dependence only from \( A(E_e) \), which is its value at the center of the atom.

In the shallow core state case, \( E_e \approx E_c \approx V(r) \), so that \( E_e \) cannot be neglected relative \( V(r) \) meaning that \( |f\rangle \) is no longer a constant times \( |i\rangle \) in the region where they both overlap. Thus,

\[
|f\rangle = A(r, E_e)|i\rangle ;
\]

i.e., \( A \) is now a function of both \( r \) and \( E_e \). The matrix element now is different from the deep core case. However, this difference cancels out when the EXAFS is normalized by dividing by the atomic absorption at the same energy because the atomic absorption has the same \( r \) dependence.

The story does not end here, because in practice the EXAFS is usually not normalized by the atomic absorption at the same energy. It is usually normalized by the edge step. The difference between a deep core and a shallow core will not cancel in that case. The effect is to make the EXAFS amplitude decrease with \( E_e \) more rapidly for the shallow core than for the deep core. Thus, for example, the EXAFS amplitude normalized by the edge step could be different for the \( K \), \( L \), and \( M \) edges of the same material even when \( |f\rangle \) has the same symmetry, i.e., \( M_{23} \neq L_{23} \). In addition, shallow core holes are more susceptible to interactions with other electron states which are closer in energy. Thus, the EXAFS may not be transferrable between deep and shallow core states, as noted in Ref. 11.

B. EXELFS

Referring to Figs. 1b and 2b for EXELFS, \( E_i >> E_e \) and therefore \( E_i >> V(r) \). For example, \( E \approx 100 \) keV and \( E_e \), \( V(r) \approx 1 \) keV. EXELFS is most useful for low \( Z \) atoms [5,11], where \( V(r) \approx 1 \) keV because its cross section for exciting EXAFS drops rapidly with \( E_e \). In this case the initial state \( |I\rangle = |i\rangle \exp(ik \cdot r') \), namely the initially filled core state and the incoming electron which is not appreciably perturbed by the \( V(r) \) of the atom. The scattered electron still is not appreciably perturbed by the atom and the final state consists of \( |F\rangle = |f\rangle \exp(ik' \cdot r') \). The matrix element \( M = \langle F|u(\Delta r)|I\rangle \), where \( u(\Delta r) \) is the interaction energy between the incoming electron and the core electron, which is some function of the distance \( \Delta r = \vec{r} - \vec{r}' \) between the two. By a change of variables,

\[
M = \left( \int \exp(iq \cdot \Delta r)u(\Delta r)d^3\Delta r \right) \langle f| \exp(iq \cdot \vec{r}|i\rangle ) ,
\]

where \( q = k - k' \). The first factor is smoothly varying with \( E_e \) and the second factor is essentially the same term as appears in EXAFS. By using appropriate apertures in detecting the scattered electrons, namely detecting only small angles of scattering, \( q = \ll 1 \), and the dipole approximation
is obtained, as in EXAFS. EXELFS in the dipole case contains the same information as EXAFS, but, in addition, by increasing the aperture, higher order multipole excitations can be introduced. Thus, it contains more information than EXAFS.

C. (S)EELFS

The scattering configuration in (S)EELFS is the same as in EXELFS except that now $E_i \approx E_e \approx V(r)$. For example, typical values are $E_i \approx 2 \text{ keV}$, $E_e \approx V(r) \approx 1 \text{ keV}$. In this case the incoming and outscattered electrons are perturbed when they enter the vicinity of the atom. The initial state then becomes

$$|I\rangle = |i\rangle \psi(r') \exp(ik' \cdot r')$$

and the final state

$$|F\rangle = |f\rangle \psi'(r') \exp(ik' \cdot r')$$

where the factors $\psi$ and $\psi'$ are the perturbations introduced by the atomic potential. The matrix element $M$ has an EXAFS-like factor:

$$M \propto \langle f | \exp(ik \cdot \bar{r}) f(q, \bar{r}) | i \rangle,$$

where $f(q, \bar{r})$ is introduced by the $\psi(r')$ and $\psi'(r')$ factors. In addition, because the energies of the scattered electron and the excited electron are not too different, exchange effects are important and $M$ has another term with opposite sign where the scattered and excited electrons are interchanged.

Experimentally, one cannot control $q'$ as was the case in EXELFS. Thus, some mixture of multipole excitations are present in the matrix element together with exchange effects and one expects some difference from EXAFS. To assess how important these differences are requires experiments and theoretical calculations. Experiments indicate that (S)EELFS is surprisingly close to EXAFS in at least some cases [10]. Theoretical calculations have also been made [12] which indicate that there are, as expected, some differences between EXAFS and (S)EELFS.

The (S)EELFS experiments are usually performed using a thick sample in a configuration where the electrons must scatter a large angle in order to escape the sample and be detected. It requires quite detailed calculations to assess the contribution of multiple inelastic scattering of such electrons and its perturbations on the (S)EELFS spectrum, which theoretically is assumed to be only a single scattering event. Recent experiments [13,14] to assess the importance of multiple inelastic scatterings measured the (S)EELFS while changing the incident electron energy with the expectation that the probability of multiple inelastic scattering would change significantly. No large change in (S)EELFS spectrum was found, and it was concluded that multiple scatterings are not important. However, before such a conclusion can be trusted, an estimate of the change of multiple scattering probability with the range of energies employed in the experiment should be made to confirm that it was significant. Clearly, further experiments and calculations are necessary to clarify the situation.

It should be emphasized that though (S)EELFS is not the same as EXAFS this does not diminish its structure-determining capabilities. What it does mean is that to obtain accurate structures requires a calibration and theory specific to the effect and not based on EXAFS.

D. EXBIFS

For EXBIFS two cases need to be distinguished, where the incoming electron is a high-energy or a low-energy one in the sense whether $E_i \gg V(r)$ or not. For simplicity we consider the high-energy case because that is easier. The low-energy case is qualitatively similar, as discussed for EXELFS, though somewhat different quantitatively. The initial state consists of an incoming high-energy electron (Figs. 1d and 2d):

$$|I\rangle = |\hat{k}\rangle = \exp i\hat{k} \cdot \bar{r}.$$
while the final state is an electron in the EXAFS state $f'$, where the prime indicates that the state is in the presence of no core hole:

$$|F_i' = |f'\rangle .$$

The appropriate matrix element is

$$M = \langle f'|H'\exp(iq'r)|\hat{k}\rangle ,$$

which has EXAFS-like information. Here $q' = \frac{\omega'}{c}$ is the wave number of the photon and $H'$ is the same perturbation of the electromagnetic field that appears in the EXAFS effect, which has the matrix element

$$M = \langle f|H'\exp(i\vec{q}r)|\hat{r}\rangle .$$

Note the difference between the EXBIFS and EXAFS matrix elements is in the initial state plus the final states differs because one is with a core hole and the other is without. In EXAFS the initial state is localized near the center of the atom validating the dipole approximation. Such is not the case for EXBIFS, and the dipole approximation is not valid.

EXBIFS probes an EXAFS-like phenomenon but is not the same as EXAFS. As is the case with (S)EELFS, this does not diminish its structure determination capability but does require its own calibration and theoretical calculations.

Recent experiments [9] have shown the EXAFS-like quality of EXBIFS, but there are, as expected, distinct differences between the amplitude and phases of EXAFS and EXBIFS.

E. EAPFS

As noted in Figs. 1 and 2, the diagram of EAPFS is the same as (S)EELFS except that one varies the incoming electron energy and detects all of the scattered and excited electrons which are in the EXAFS states $|f\rangle'$ and $|f\rangle$, respectively. In this case the scattered electron state $|f\rangle'$ also has a low enough energy to contain significant EXAFS information. Exchange effects are even greater in this case than in (S)EELFS, but the aspect that appears at first glance most discouraging is that the energies $E_s$ and $E_e$ of $|f\rangle'$ and $|f\rangle$ are not unique. For a given incident electron energy $E_i$, these energies spread over the region limited by the condition of $E'_s + E_e = E_i - E_e$. One might think that the EXAFS information would integrate out as would happen in an EXAFS experiment with poor energy resolution.

However, if there is a high density of states at the chemical potential $\mu$, then differentiation of the signal with respect to energy produces a spike which fixes one state at $\mu$, uniquely sets the energy of the other state, and avoids smearing out the EXAFS information [7]. To understand this, the following argument is used [7].

The detected electron current

$$I \propto \rho(E_e)\rho(E_s)$$

Using the condition satisfied by the sum of $E_s$ and $E_e$ given above, this becomes

$$I \propto \rho(E_e)\rho(E_i - E_e - E_e) .$$

Differentiating with respect to $E_i$ gives

$$\frac{dI}{dE_i} \propto \rho(E_e)\frac{d(E_i - E_e - E_e)}{dE_i} .$$

Since the derivative has a large spike at $\mu$ or where $E_i - E_e - E_e = 0$, this produces a large contribution for $E_e = E_i - E_e$, a unique value. This part of the signal will produce an EXAFS-like signal at energy $E_e = E_i - E_e$, while the rest of the signal is smeared out, producing a smooth background.
Again, EAPFS is not identical to EXAFS but is only EXAFS-like and requires its own calibration and calculations. Extensive calculations \(^1\) and experiments \(^2\) have been done on EAPFS and its relationship to EXAFS. The theory indicates that the phase shift in EAPFS is approximately similar to EXAFS and a pseudo-dipole rule applies. However, there should be differences in amplitude, but by use of appropriate standards to calibrate EAPFS it may be able to obtain coordinate numbers. Experiments \(^2\) show that (S)EELFS and EAPFS give similar results for a Ti/Si thin film system and that EAPFS appears to be inherently more surface sensitive than (S)EELFS.

The theoretical discussion of the various EXAFS-like phenomena can be summarized as follows. EXELFS is exactly equivalent to EXAFS with the addition of an experimental control over the multipole contribution. (S)EELFS is only EXAFS-like with the need for adding exchange effects and an experimentally uncontrolled multipole contribution. EXBIFS is only EXAFS-like with an experimentally uncontrolled multipole contribution and no core hole excitation so that it is not atom specific. EAPFS is only EXAFS-like with the need for adding exchange effects and an experimentally uncontrolled multipole contribution. In order for its EXAFS-like contribution to be significant in the differentiated signal, a large density of states is required at the chemical potential (Fermi energy).

**Practical Comparisons**

In addition to the theoretical considerations, there are practical considerations that enter into the determination of the usefulness of a technique. Table I summarizes some of the practical comparisons.

Table 1. Practical comparisons between the various EXAFS-like phenomena.

<table>
<thead>
<tr>
<th></th>
<th>Vacuum Environment Effect Required</th>
<th>Radiation Damage for Given Concentration Statistics Specific Atom Multipole</th>
<th>Convenience Specific Multipole</th>
<th>Spatial Resolution Bulk or Surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>EXAFS</td>
<td>No</td>
<td>Low</td>
<td>Dilute</td>
<td>Yes</td>
</tr>
<tr>
<td>EXAFS</td>
<td>No</td>
<td>Low</td>
<td>Medium</td>
<td>Yes</td>
</tr>
<tr>
<td>EXELFS</td>
<td>Yes</td>
<td>Low (low Z)</td>
<td>Medium</td>
<td>Yes</td>
</tr>
<tr>
<td>(S)EELFS</td>
<td>Yes</td>
<td>High</td>
<td>High</td>
<td>Yes</td>
</tr>
<tr>
<td>EXBIFS</td>
<td>Yes</td>
<td>High</td>
<td>High</td>
<td>No</td>
</tr>
<tr>
<td>EAPFS</td>
<td>Yes</td>
<td>High</td>
<td>High</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Only EXAFS can operate outside a vacuum environment, which is an advantage for some cases such as biological samples. Radiation damage considerations will be important for those samples which are susceptible to such damage. EXELFS has increasing radiation damage as the atomic number \(Z\) of the atom increases. Since EXELFS is usually performed in an electron microscope, it has the spatial resolution of that instrument. In principle, many of the other electron-beam-excited phenomena can also be measured in a suitably modified electron microscope. However, this has not been done on a commercial basis, and so the Table does not credit the technique for the spatial resolution of an electron microscope. It is also possible that a suitable modification of EXBIFS
and EXELFS will give the techniques surface sensitivities, but such modifications have not been made as yet.

Besides the comparisons listed in Table I a very important consideration favoring the other EXAFS-like techniques is the ability to employ laboratory-based commercial equipment. Since this equipment can perform other analyses of the samples it can help characterize them more fully under exactly the same sample conditions of the EXAFS-like techniques. For certain applications these capabilities and convenience may be essential to fully characterize the samples, and one would expect that the other EXAFS-like techniques will become more fully applied in the future. However, I hope that this review has emphasized the need for more detailed experiments, calculations, and calibrations to make the techniques more quantitative. It is not necessary for the techniques to contain exactly the same EXAFS information as EXAFS to be be useful for structure determination as long as they are calibrated separately.

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