XANES AND THE DETERMINATION OF BOND ANGLES

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Abstract - It is argued that conventional weak scattering probes provide no direct information beyond the radial distribution function. In contrast, X-ray Absorption Near Edge Structure is produced by the multiple scattering of low energy electrons and has sensitivity to bond angles and symmetry of the environment

I. WEAK SCATTERING AND PAIR CORRELATIONS

The traditional probe of structure is a wave that is weakly scattered by the material under consideration, such as X-rays or neutrons. Weak scattering has the great virtue of a simple interpretation. For example, a plane wave,

$$\exp(\underline{k}_i \cdot \underline{r}), \tag{1}$$

incident on the solid is scattered to an outgoing wave,

$$A(\underline{q}) \exp(\underline{k}_f \cdot \underline{r}), \tag{2}$$

where
$$A(\underline{q}) = \Sigma f_s(\underline{q}) \exp(i\underline{q} \cdot \underline{R}_s), \tag{3}$$

$$\underline{q} = \underline{k}_i - \underline{k}_f, \tag{4}$$

and $\underline{R}_s$ is the position of the sth atom, with scattering factor f_s; $\underline{k}_i$ and $\underline{k}_f$ are the incident and scattered wave vectors respectively. The experiment observes

$$|A(\underline{q})|^2 = \Sigma f_s f_t^* \exp(i\underline{q} \cdot (\underline{R}_s - \underline{R}_t)), \tag{5}$$

an expression in which the atomic coordinates occur in pairs, and only in pairs. Such an expression can only ever tell us about the pair correlation function in the material but in ordered, crystalline materials this information is usually sufficient to give us the higher order correlation functions by implication [1/2]. In the case of an orientated crystal measurement of $|A|^2$ for a full set

of 3D vectors, $\underline{q}$, provides enough information to fix the higher
order correlations. By contrast, in a liquid there is much less
information available because the scattering is on average isotropic
so that $|A|^2$ is a function only of $|\underline{q}|$. Occasionally this provides
enough information to determine all correlation functions, but in
most instances this is not the case. In this sense disordered
materials differ in a fundamental way from their ordered
counterparts. Their structure is much more subtle, as indicated by
their finite entropy content, and demands new probes to reveal its
details to us.

II. MULTIPLE SCATTERING - A PROBLEM FOR THE THEORIST

When scattering is strong, the probe can be expected to
interact with more than one scattering centre in the solid, and
equation (3) must be generalised to

$$A_{ms}(\underline{k}_f,\underline{k}_i) = \Sigma \ \exp(i\underline{k}_f \cdot \underline{R}_s) \ f_s(\underline{k}_f,\underline{k}_i) \ \exp(i\underline{k}_i \cdot \underline{R}_s) +$$
$$\exp(i\underline{k}_f \cdot \underline{R}_s) \ f_s \ G_{st} \ f_t \ \exp(i\underline{k}_i \cdot \underline{R}_t) +$$
$$\exp(i\underline{k}_f \cdot \underline{R}_s) \ f_s \ G_{su} \ f_u \ G_{ut} \ f_t \ \exp(i\underline{k}_i \cdot \underline{R}_t)$$

(plus higher order terms)   (6)

The new ingredients in this formula are

(i)   the scattering factors, f, are now generally
           complex, reflecting multiple scattering events
           within individual atoms.

(ii)   The scattered amplitude, A_{ms}, is no longer a
           function of $|\underline{k}_f - \underline{k}_i|$ alone, but depends on $\underline{k}_f$ and
           $\underline{k}_i$ independently.

(iii)   Several atomic coordinates appear in a typical
           term through the propagators, G, which represent
           the wave travelling between atoms.

This last point becomes more explicit if we take the case of point
scatterers for which

$$G_{st} = \exp(ik|\underline{R}_s - \underline{R}_t)|)   (7)$$

so that the overall dependence on atomic coordinates of the last
term in equation (6) would be

$$\exp(i\underline{k}_f \cdot \underline{R}_s + ik|\underline{R}_s - \underline{R}_u| + ik|\underline{R}_u - \underline{R}_t| + i\underline{k}_i \cdot \underline{R}_t).   (8)$$

As the wave explores the solid, scattering from successive
atoms, it measures the path length through the phase which it
acquires. We might imagine that in principle we could find all
possible path lengths for multiple scatterings in the medium by
Fourier transforming the scattered intensities. This information
could be interpreted in terms of pair correlations. However the
program is not a practicable one, partly because the propagators, G,
are rarely simple phase factors, and partly because the individual
atomic scattering factors, f, introduce further complications which
are difficult to correct for.

The only practical way of proceeding that has been used to interpret multiple scattering data has been to postulate a trial structure, calculate the implied spectrum, compare with experiment, and then successively refine the structure. The passage from trial structure to calculated spectrum is non-trivial and is one of the limiting factors to interpretation of data which in principle contain the information we require.

One multiple scattering probe that has been much used in structure determination is the low energy electron/3/. Traditionally low energy electron diffraction (LEED) has been used as a surface structure probe. Here the strong scattering interaction is required to give surface sensitivity, and the multiple scattering processes are regarded as something of a nuisance. LEED experiments are now routinely interpreted to give surface structures, and essentially the same theory can be used in another context to give higher order correlation functions.

X-ray absorption near edge structure (XANES, or NEXAFS as some call it) /1/4/ results from the ejection of an electron from an inner core of the absorbing atom. The ability of the electron to escape from the atom determines the absorption cross section and in the near edge region, where the electron has, say, less than 50eV of kinetic energy, multiple scattering is dominant; in contrast to the region of extended X-ray absorption fine structure (EXAFS) /5/6/, more than 50 eV above the edge, in which cross sections are small enough for most multiple scattering processes to be neglected. Here we have a probe which can be tuned to the environment of a particular atom by selecting the appropriate absorption edge. The ejected electron having a finite elastic lifetime explores only the immediate surroundings of that atom before it vanishes in incoherent processes which in turn limits the number of multiple scattering events that we have to interpret.
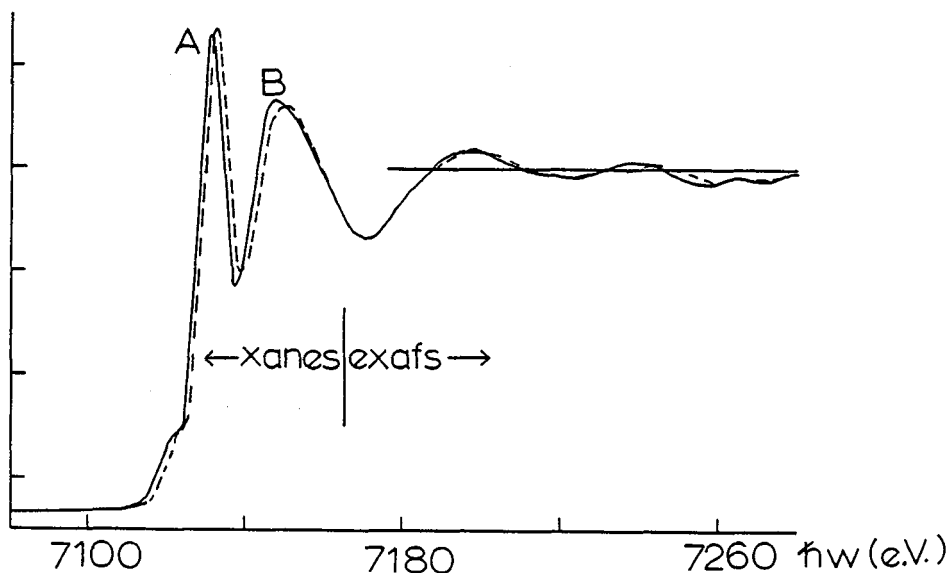
Fig. 1 - The relative absorption coefficient for X-rays in the vicinity of the iron K edge. The division of the spectrum into XANES and EXAFS is somewhat arbitrary.
_____ $K_4Fe(CN)_6 \cdot 3H_2O$ and _ _ _ $K_3Fe(CN)_6$.

Figure 1 shows the X-ray absorption spectrum for an iron K edge in $K_2Fe(CN)_6$ /8/. Clearly the first 50eV of the spectrum is heavily modulated by scattering of the ejected electron and does in fact contain information beyond the radial distribution function.

Despite the complexity of the multiple scattering process some physical insight into how such quantities as bond angles affect spectra is possible. This is particularly true at the limits of the XANES energy range where strong scattering of electrons is largely confined to the forward direction. In this case the single scattering spectrum is strongly perturbed when the central emitting atom and two further atoms lie in a straight line. The central atom gets in the way of signals returning from the furthest atom and a single scattering interpretation of the spectrum under these circumstances leads to erroneous bond lengths. Sometimes the effect is referred to as "shadowing" by the central atom, though a more accurate description is "focussing" because the attractive potential around the atom draws in the electrons and enhances their intensity at the furthest atom.
    At lower energies within 5 or 10eV of threshold another rather different picture is sometimes more appropriate. The states in this energy range can be thought of as antibonding states which reflect the chemistry of the environment. Thus it is not surprising if bond angles (ie three - body correlation functions) have a strong effect on spectra. We can expect sensitivity to such chemically relevant quantities as the symmetry of the environment as well as to saturation of bonds.

III. SOME MULTIPLE SCATTERING CALCULATIONS

We shall not dwell here on details of how the calculations are performed which is described in detail in the literature/1/9/10/. It is possible to describe the scattering of the individual atoms by spherically symmetric one - electron potentials constructed according to one of the standard "muffin - tin" procedure, using the local density formalism. The multiple scattering between atoms is a more difficult quantity to handle as explicit summation of the terms of various orders in equation (6) is not possible, even if the series were to converge. By grouping the terms in a systematic fashion calculations can be made for quite complicated trial geometries, especially if there is any symmetry to be exploited. Even for situations without much symmetry it is now possible to make calculations, thanks to the development of new, fast, perturbation schemes/11/12/13/. The calculations require a large computer such as the Cray, but are probably much less expensive than the experiments they are designed to interpret.
    To verify that experiments can be reproduced by theory when the geometry is known we show in figure 2 some calculations for silver, taken from reference /1/. To describe the data it was necessary to consider a cluster of 43 atoms centred about the absorbing atom. The main features of the spectrum are reproduced, especially the positions of peaks which are especially significant because of the implication that we have got the conditions for constructive interference right, and hence have the right bond lengths and angles in our calculation. The intensities are recognised to be more subtle quantities.
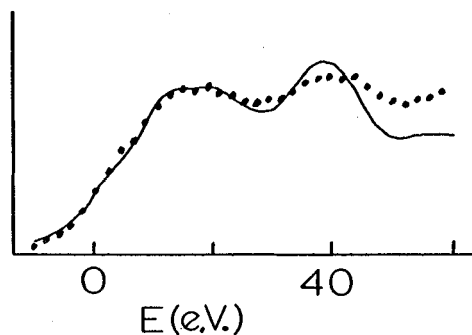
Fig. 2 - K-edge XANES for silver. The calculations (full curve) used a 3-shell, 43 atom, cluster. The experimental (dashed) curve was taken from reference /14/.
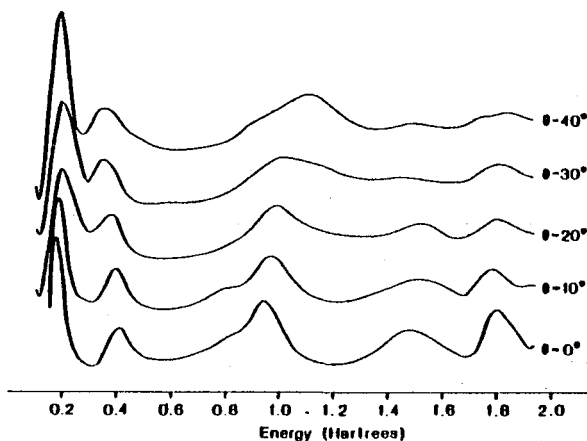

Fig. 3 - K-edge XANES calculation for the transition metal carbonyl compound for various angles of rotation (Θ) of the oxygen shell.

  To test how sensitive data are likely to be to bond angles a hypothetical carbonyl compound was investigated. It comprised a central transition metal octagonally coordinated by six carbonyl groups. In most compounds of this type the metal - carbon and carbon - oxygen bonds lie in the same straight line, but can occasionally be bent. The test calculation examined changes in the spectra for geometries in which the radial distribution about the central atom was preserved. Imagine the z-axis chosen along one of the

metal-carbonyl bonds. In the x-y plane there are two rings: an inner
one consisting of four carbon atoms, and an outer one consisting of
four oxygen atoms. The outer ring can be rotated, preserving the
radial distribution as required, but changing the carbon-oxygen bond
angle. In any weak - scattering theory such rotations would not
change the spectra. Any changes are therefore entirely and
exclusively attributable to the changes in bond angle. Figure 3
shows the results for various angles of rotation and indicates that
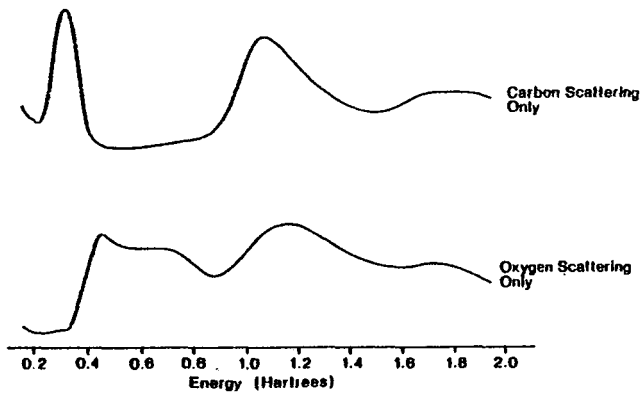there is substantial sensitivity to the angle.

Fig.4 - Calculations as above for $\Theta=0$ but with scattering from only
the carbon, or oxygen shells included.

In figure 4 we show the spectra when only carbon and only oxygen are
present in the system to make the point that the spectrum for the
carbonyl is not simply the sum of these two spectra, as would be the
case in a single scattering theory.
    Finally to illustrate that the calculations can be performed
for systems having considerable complexity, figure 5 shows some
calculations for haemoglobin compared to experiment /15/. The
cluster used in the calculations consisted of the porphyrin group
together with the imidazole group. The porphyrin group was idealised
in that it was taken to be planar and four-fold symmetrical, though
in more recent versions of the theory this idealisation would
probably not be necessary. The agreement with experiment is seen to
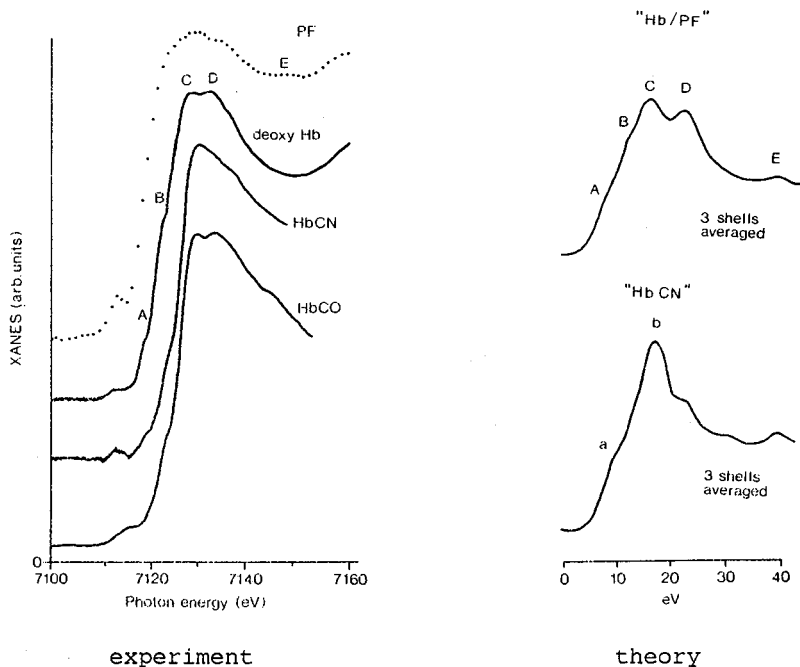be very encouraging.

Fig. 5 - Experimental K-edge XANES for the picket fence compound PF, deoxy Hb, HbCN and HbCO. Theoretical curves for the picket fence compound and for HbCN are also shown.

IV. CONCLUSIONS

Whilst being optimistic about the potential of XANES to provide information beyond the radial distribution function, it should be said that there are limitations to the technique. The chief of these probably lies in the experimental data themselves. They suffer from an inherent limitation to the resolution in energy dictated by the finite lifetime of the core hole being created. Structure in spectra on a scale finer than about 3eV is not observed. Given that the range over which multiple scattering effects are prominent is only about 50eV, it can be seen that the number of independent pieces of information contained in the data is of the order of 10. Thus to imagine that a XANES experiment would find all the bond angles in a complex amorphous system is a hopeless dream. A more realistic aim would be to start from a situation in which something is already known about the system, perhaps from chemical arguments, and to ask the experiments to distinguish between perhaps two or three clearly defined models, either by making use of theoretical calculations predicting their XANES spectra, or by making comparisons with spectra taken for model compounds of known structure. Within these limitations XANES can provide us with information that is available from no other source.

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