

Interpretation of EXAFS Data

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An outline of the theory of X-ray absorption as applied to X-ray absorption spectroscopy is given, concentrating on EXAFS, showing how structural parameters are contained within the theory. A full description of the scattering problem and of inelastic effects is also included, and a description is given of how structural information may be extracted from experimental data. The emphasis is on curve-fitting methods, including those techniques which allow the inclusion of external constraints.

Keywords: X-ray absorption; scattering theory; structure of materials.

1. Introduction

It has long been known that X-ray absorption spectra obtained from condensed samples show an oscillatory structure that can extend for many hundreds of volts above the edge (Kronig, 1931, 1932). This is known as extended X-ray absorption fine structure (EXAFS).

Since the first EXAFS experiment on an X-ray beamline at a synchrotron was reported (Kincaid & Eisenberger, 1975), there has been an impressive development in EXAFS studies. 99% of these are now carried out at synchrotron radiation facilities. This dominance arises from the twin requirements of continuum radiation and high intensity. The EXAFS oscillations are weak, of the order of 1–10% of the absorption coefficient. In a noise-limited experiment we therefore need to collect 10^6 – 10^8 photons at each energy point of the spectrum, with perhaps 200 energy points spaced over a 1 keV energy range making up the spectrum. Even recent developments in computer-controlled laboratory-based systems (Udagawa, 1991), which can run unattended for the long periods required to accumulate good spectra with a rotating-anode source, do not seriously challenge the superiority of electron storage rings for XAS studies.

Modern X-ray absorption spectroscopy (XAS) began with the work of Sayers, Stern & Lytle (1971). They pointed out that a single-scattering short-range order theory could adequately account for the structure beyond about 50 eV from the edge (the EXAFS – close to the edge the structure is strongly affected by multiple-scattering contributions and is known as XANES, X-ray absorption near-edge structure) and described the potential of EXAFS in the determination of local atomic geometries. Their short-range theory of EXAFS explained the observed oscillatory structure in the X-ray absorption coefficient as a final-state electron effect, arising from the interference between the wavefunction of the outgoing photoelectron and that small part of the wave that is scattered back from neighbouring atoms. Thus, conceptually, EXAFS may be regarded as a type of electron

diffraction in which the source of electrons lies within the atom which participated in the X-ray absorption event.

The primary objective in XAS studies is to determine the local atomic environment of the excited atom by analyzing the measured oscillatory structure. The interference which gives rise to the EXAFS reflects directly the total phase and amplitude of the backscattered wave. This is shown in Stern's (1974) original semi-phenomenological expression for the EXAFS function $\chi(k)$ which describes the oscillatory part of the K absorption coefficient:

$$\chi(k) = -A(k) \sum_j (N_j/kR_j^2) |f_j(k, \pi)| \exp(-2\sigma_j^2 k^2) \times \exp(-2R_j/\lambda) \sin(2kR_j + 2\delta_1 + \psi_j). \quad (1)$$

In (1), the EXAFS is defined in terms of sets of identical scattering atoms, usually referred to as *shells*: a typical shell contains N_j identical scattering atoms at a mean distance R_j from the excited atom, each with an electron-scattering factor f_j . The phase of the backscattered wave is largely due to the product of the photoelectron wavevector k and the total distance travelled, $2R_j$. This is the distance out to the scattering atom and back since the major contribution to the absorption matrix element comes from regions of space very close to the nucleus of the excited atom, where the highly localized initial core state exists. The phase also contains contributions from the scattering process, the phase ψ_j of the electron-scattering factor, and from the passage of the photoelectron out and back through the potential of the excited atom, $2\delta_1$ (for a K edge, the photoelectron must have angular momentum $l = 1$). The amplitude of the backscattered wave depends on the number of scattering atoms, N_j , and their scattering strength $|f_j(k, \pi)|$: since the wave must return to the origin, only backscattering is significant in this simple single-scattering expression. There is also a Debye–Waller factor which depends on σ_j^2 , the mean-square variation in R_j . In addition there are two factors which reflect the many-body nature of the X-ray absorption process: an elastic mean free path parameter

λ (only elastically scattered electrons can take part in the interference process) and an amplitude factor $A(k)$, which measures the proportion of absorption events that result in the excitation of just a single photoelectron.

Thus, we see that analysis of the EXAFS can yield information not only on the distance but also on the number and chemical type [through $f_j(k, \pi)$] of the near neighbours of the excited atom. Only near neighbours contribute because of the presence of the mean free path factor $\exp(-2R/\lambda)$: EXAFS spectra typically contain information on atoms less than 5 Å from the excited atom. Also, since the EXAFS is measured on a known absorption edge, for an atom of known atomic number, the technique is chemically specific, giving the environment of a known type of atom. It is therefore particularly useful for the study of systems containing many different types of atom, especially if we are interested in the environment of an atom of low concentration, a situation which occurs in many biological molecules.

In the following sections we shall give an outline of the theory of EXAFS, showing how expression (1) and more accurate expressions for the EXAFS function arise. We shall also consider methods of data analysis and demonstrate how the structural information contained within an EXAFS spectrum is extracted.

2. The theory of XAS

The attenuation of X-rays passing through a medium occurs via three principal processes: scattering, pair production and photoelectric absorption. In the energy range used in XAS studies, 1–40 keV, photoelectric absorption totally dominates the attenuation process.

In photoelectric absorption a single X-ray photon is absorbed by an atom. Because of the presence of the electron–electron interaction this is strictly a many-body process and should be treated as such. However, good results are obtained by the use of a one-electron theory, in which all of the photon energy is given up to one photoelectron, with many-electron effects treated as a secondary process. This is the form of theory we shall employ: many-electron effects are considered in §2.3.

In a one-electron process energy conservation requires that:

$$E_f = \hbar\omega - E_b \quad (2)$$

where $\hbar\omega$ is the energy of the X-ray photon, E_b the (positive) binding energy of the electron in its initial core state and E_f its energy after absorption of the photon. We always assume that the final-state electron is unbound, *i.e.* that it has a continuous distribution of allowed energies.

The absorption of an X-ray photon by an atom is a quantum-mechanical process and may be understood by the use of time-dependent perturbation theory. We thus obtain Fermi's Golden Rule as the expression for the absorption cross section. So long as the X-ray wavelength is much longer than the dimension of the initial state, a situation

which always applies in the XAS regime, we may use the dipole approximation. Within this the X-ray absorption coefficient is given by the equivalent expressions:

$$\begin{aligned} \mu(\omega) &= (4\pi e^2 \omega / c) \sum_f |\langle f | \boldsymbol{\varepsilon} \cdot \mathbf{r} | i \rangle|^2 \delta(E_f - \hbar\omega - E_i) \\ &= (4\pi e^2 \omega / c) |\langle f | \boldsymbol{\varepsilon} \cdot \mathbf{r} | i \rangle|^2 \rho(E_f) \\ &= (4\pi e^2 \omega / c) (-1/\pi) \langle f | \boldsymbol{\varepsilon} \cdot \mathbf{r} G^+(r, r', E_f) \boldsymbol{\varepsilon} \cdot \mathbf{r}' | i \rangle \end{aligned} \quad (3)$$

in Dirac notation, which we shall use for brevity. In the perhaps more familiar integral notation the matrix element is written as

$$\langle f | \boldsymbol{\varepsilon} \cdot \mathbf{r} | i \rangle = \int d^3r \psi_f^* \boldsymbol{\varepsilon} \cdot \mathbf{r} \psi_i. \quad (4)$$

$|i\rangle$, equivalent to $\psi_i(r)$, is the wavefunction of the initial state, $|f\rangle$ that of the final state ($\langle f|$ is the complex conjugate of $|f\rangle$) and $\rho(E_f)$ the density of allowed states at the final-state energy E_f . $\boldsymbol{\varepsilon}$ is the polarization vector of the electric field of the X-ray beam. The sum over final states, which gives rise to the density of states factor and also allows us to introduce the final-state Green's function G^+ , arises because we measure the X-ray absorption, not the photoelectron current, so every energy-conserving final state contributes. In the closely allied technique of photoelectron diffraction, we *do* detect the photoelectron and the final-state sum does not appear. The theory of photoelectron diffraction is very similar to that of EXAFS (Fadley, 1992) except that the Green's function formalism is not used.

The scattering approach to EXAFS shows that the density of final states, $\rho(E_f)$, is that of a free electron of wavevector k and energy $\hbar^2 k^2 / 2m$: in this approach it arises from the normalization of the final-state wavefunction to unit outgoing flux. The wavevector and energy of the photoelectron are linked by

$$\hbar^2 k^2 / 2m = E_f - E = \hbar\omega - E_{\text{edge}} + E_0, \quad (5)$$

in which E is the energy, in the sample, of a free electron of zero wavevector. E therefore corresponds to the effective mean potential seen by the photoelectron. Note that we do *not* measure the energy and momentum of the photoelectron from the absorption edge. The edge occurs at the Fermi energy, or rather at the lowest unoccupied energy level, and has the energy E_{edge} . The offset E_0 is usually called the threshold energy: it is of order 10 eV and is negative.

With the free-electron form for the density of final states $\rho(E_f)$, the only factor which can give rise to the oscillatory structure, the EXAFS signal, is the matrix element. Now the initial-state wavefunction is fixed. It is the final-state wavefunction, or the final-state Green's function, which varies with photon energy, by virtue of (2), and this must be the origin of the structure. Hence our statement that EXAFS is a final-state effect.

In order to be able to extract structural information from the EXAFS signal we must be able to calculate the X-ray absorption coefficient. In practice this means calculating

the final-state wavefunction or Green's function, since the initial state is a deep core state whose wavefunction is known and independent of environment. There are two main approaches to this problem, which we shall refer to in this paper as the XANES and EXAFS approaches. The difference between the two lies in the relative importance of multiple scattering of the photoelectron.

2.1. XANES

XANES is structure which lies close to the absorption edge: the upper energy limit is usually set arbitrarily some 50 eV above the edge. In this region of low photoelectron energy the elastic mean free path is long and the electron-scattering factor $f(k, \pi)$ is generally large. Thus, multiple scattering can be highly important. A detailed report of this has been given by Tyson, Hodgson, Natoli & Benfatto (1992). In some cases the scattering series may not converge, in which situation the final-state wavefunction must be calculated using band-structure or cluster methods.

Band-structure methods have been used for many years to calculate the XANES spectra of crystalline materials, although this terminology is rarely used. An obvious example is the use of soft X-ray absorption spectra to obtain information on the unoccupied density of states, which goes right back to the beginnings of solid-state physics (Mott & Jones, 1936). OPW methods have been the most popular, but all band-structure techniques have been used at some time. All involve Brillouin zone sums. The results of such calculations are angular momentum projections of the final density of states, the selection rule implicit in (3) ensuring that only one or two components contribute. An equivalent calculation, based on molecular orbitals, may be made for molecular systems.

More recently, cluster calculations of the XANES structure have become the norm. The validity of these is based upon the fact that the photoelectron mean free path, although long, is not infinite, if only because of the lifetime of the core hole left upon photoexcitation (see §2.3). Multiple scattering is strong, so the use of a scattering series in these calculations is inefficient and it may not even be convergent. Thus, we solve for the final-state wavefunction, or more usually Green's function, in a finite-size cluster by inversion of a matrix which represents the interaction of the photoelectron with *all* of the atoms in the cluster (Durham, Pendry & Hodges, 1981). The size of the cluster has a major effect on the computing time required and is set at the minimum value needed to give an adequate description of the XANES.

The result of a XANES calculation is the X-ray absorption coefficient $\mu(\omega)$, which may be compared with experiment. In all cases the calculation is so time-consuming computationally and involves so many atomic coordinates that it is not practicable to try to fit the calculated spectrum to experiment. Instead, calculations are made for a few cluster geometries, using interatomic distances derived from EXAFS or other data, and these are used to 'fingerprint' the experiment, to identify the symmetry of the site occupied

by the excited atom. A good example of this method of analysis is the study of the various forms of haemoglobin, completed by Durham *et al.* (1983), in which it is clearly shown that the orientation of the ligands of the iron atom has a strong influence on the near-edge structure. XANES is perhaps the only spectroscopic technique which is sufficiently sensitive to multiple-scattering contributions to provide such information directly.

2.2. EXAFS

The EXAFS region is conventionally taken to start some 50 eV above the edge, although single-scattering calculations may often be taken down to within 10–15 eV of the edge. Observable structure often exists over 1000 eV above the edge. The high-energy photoelectron has a short mean free path and electron scattering is comparatively weak. In this region the scattering series rapidly converges and in many cases only single-scattering processes need be considered. Thus, EXAFS calculations are reasonably simple and computationally rapid. These attributes lead to the possibility of fitting calculated EXAFS spectra to experiment and so obtaining detailed structural information.

If the electron scattering is not too strong then it is convenient to expand the final-state wavefunction in a scattering series. We may then consider this wavefunction as a sum of two terms: the original outgoing wave plus a scattered wave. If the excited atom were isolated then only the first component would exist. In this case the matrix element, and hence the absorption coefficient, shows no fine structure. Such is observed for a monatomic gas such as argon. If the excited atom is now surrounded by other atoms, as in a molecular gas or in any condensed phase, then the outgoing photoelectron will be scattered by these atoms, giving rise to incoming waves which can interfere constructively or destructively with the outgoing wave. This interference gives rise to an oscillatory variation of the matrix element as the photon energy changes since the wavelength of the photoelectron is a function of $\hbar\omega$ according to (5). The significant region of space for this interference is the region where the initial-state wavefunction is large, close to the nucleus of the central atom. Thus, in a scattering formalism we need only consider closed photoelectron paths, those which return the photoelectron to the atom from which it was emitted. This is because the photoelectron itself is not observed in XAS. In the related technique of photoelectron diffraction, where the photoelectron is observed, open paths are significant: here we must include all paths that leave the photoelectron travelling in a particular direction.

The scattering analysis leads us to write the X-ray absorption coefficient in the form

$$\mu(k) = \mu_0(k)[1 + \chi(k)] \quad (6)$$

where k , the photoelectron wavevector, is given by (5). $\mu_0(k)$ is the smoothly varying background which corresponds physically to the absorption coefficient of an isolated atom. $\chi(k)$ is the EXAFS function, which is defined by

this equation: it is this function which was originally investigated by Sayers *et al.* (1971) with the result given as (1). We note that $\mu_0(k)$ is only that part of the absorption coefficient which is due to transitions from the initial state of interest, *i.e.* the contribution of one particular edge.

In order to calculate the EXAFS function $\chi(k)$ we need to calculate the wavefunction of the photoelectron. Since the initial state has a well defined angular momentum it is most convenient to expand the photoelectron wavefunction in terms of eigenfunctions of the angular momentum operator. Thus, we write

$$|f\rangle = \sum_{lm, l'm'} (\mathbf{I} + \mathbf{Z})_{l'm', lm} |lm\rangle \quad (7)$$

where the unit matrix \mathbf{I} gives the outgoing part of the wave and the matrix \mathbf{Z} gives the scattered part. The components of $|f\rangle$ which contribute to the absorption will be strongly limited by the selection rules inherent in (3).

With this form for the final-state wavefunction the EXAFS function defined by (6) is a linear function of the matrix \mathbf{Z} :

$$\chi(k) = (1/\mu_0) \sum_{m_0} \sum_{lm, l'm'} \langle l_0 m_0 | \epsilon \cdot \mathbf{r} | lm \rangle \times 2\text{Re}\{Z_{lm, l'm'} \exp[i(\delta_l + \delta_{l'})]\} \langle l'm' | \epsilon \cdot \mathbf{r} | l_0 m_0 \rangle \quad (8)$$

where l_0 and m_0 are the angular momentum quantum numbers of the initial state, the m_0 sum being over the degenerate sub-levels of total angular momentum l_0 which is fixed by the edge. For a K edge, with excitation from a $1s$ state, we have $l_0 = 0$ so that $m_0 = 0$ only. In (8) the matrix elements contain wavefunctions for isolated atoms only and, with the excited atom phase shift factored out as shown, are real (Gurman, 1983). All of the effects of scattering are contained in the matrix \mathbf{Z} .

Equation (8) is often described as a first-order approximation, implying a neglect of the \mathbf{Z}^2 term and a consequent inaccuracy. However, the optical theorem shows that it is, in fact, exact.

In the case of a polycrystalline or amorphous sample the angle between ϵ and \mathbf{r} is randomly distributed. When we average over this angle only the diagonal matrix elements of \mathbf{Z} survive. The dipole selection rule further limits the final-state angular momentum l to the values $l_0 \pm 1$ if the matrix element is to be non-zero. The transition $l_0 \rightarrow l_0 + 1$ always dominates the absorption (Gurman, 1983) and if we approximate the theory to include just this contribution then we may cancel the free-atom matrix elements in (8). (For K -edge absorption, the only possible transition is $l_0 \rightarrow l_0 + 1$.) Thus, we find

$$\chi(k) = (2/2l + 1) \sum_m \text{Re}[Z_{lm, lm} \exp(2i\delta_l)] \quad l = l_0 + 1 \quad (9)$$

so that we never need to calculate the atomic matrix elements.

We see from (9) that the EXAFS function $\chi(k)$ depends only on the matrix \mathbf{Z} which describes the scattering of

the outgoing photoelectron. Since EXAFS is an interference phenomenon, only elastic scattering events need be considered. Also, since the only part of the final-state wavefunction which is of importance in the matrix element is that very close to the nucleus of the excited atom, the only scattering paths of interest are those which return the photoelectron to the excited atom. Moreover, the elastic mean free path is short so that only a few of these closed scattering paths contribute. Thus, we expand \mathbf{Z} in a series over different paths and orders of scattering. Only low orders contribute and in many cases only single (back)scattering events contribute significantly. For a given order of scattering, \mathbf{Z} may be written as a sum over (a few) closed electron paths. Further, since $\chi(k)$ is a linear function of \mathbf{Z} , the contributions from each path will be independent. Thus, we can build up $\chi(k)$ as a sum over closed electron paths.

The form of the \mathbf{Z} matrix was first given by Lee & Pendry (1975). They noted that the electron propagates between atoms as a free spherical wave: in an angular momentum representation the wavefunctions then have the form of Hankel functions. Lee & Pendry worked through the algebra of the scattering in detail, for all orders of scattering, obtaining an exact expression for \mathbf{Z} . Their expression may be simplified considerably for polycrystalline or amorphous samples, by virtue of the sum over diagonal elements which appears in (9). This gives rise to the Fast Curved Wave theory (Gurman, Binsted & Ross, 1984, 1986). In this theory the single-scattering contribution from a scattering atom at R is given by

$$\chi(k) = (2/2l + 1) \text{Re} \sum_{L_1 L_2} \exp(2i\delta_l) \left[h_{L_1}^{(1)}(kR) \right]^2 T_{L_2}(2l + 1) \times (2L_1 + 1)(2L_2 + 1) [C(1L_1 L_2; 000)]^2 \quad (10)$$

in which C is a Clebsch–Gordan coefficient and T is the usual scattering t matrix which may be written in terms of electron-scattering phase shifts. This exact expression is very rapid to compute.

Higher order scattering terms are also calculated within the FCW theory. However, these take too long to compute to be generally useful in fitting routines although such analyses have been done (Gurman *et al.*, 1986; Strange, Blackburn, Knowles & Hasnain, 1987). Approximate fast schemes which can be used for this purpose have been developed by Gurman (1988), Rehr & Albers (1990) and Filipponi (1991).

In the case of single-crystal samples we do not average over the directions of \mathbf{r} . In this situation, extensively used in surface studies, beam polarization and direction effects become important and information on bond directions can be obtained. This has been covered in detail by Brouder (1990).

At high photoelectron energies the Hankel functions which appear in (10) may be approximated by their asymptotic forms, which are exponentials. The angular momentum sums may then be performed analytically and we find that

the expression for the EXAFS function reduces to

$$\chi_{PW}^{(1)}(k) = (-1)^l (1/kR^2) |f(k, \pi)| \sin(2kR + 2\delta + \psi) \quad (11)$$

in which $f(k, \pi)$ is the usual electron-backscattering factor. We thus obtain the expression of Sayers *et al.* (1971) as the high-energy limit of the exact expression. Higher-order contributions may also be written in this form (Boland, Crane & Baldeschweiler, 1982). In fact this so-called plane-wave approximation is *never* a good one, although it does serve to show the physical origins of EXAFS. For it to be valid we require $kR \gg l(l+1)$ for all significant partial waves. However, the phase shifts are only significantly different from zero for a maximum angular momentum given by $kR < 2l_{\max}$. Thus, the required inequality can never be satisfied in normal scattering conditions.

Equations (10) and (11) relate to a single scattering atom. To get the total EXAFS signal we need to sum over all scattering atoms. This process introduces the pair distribution function $g_{\alpha\beta}(r)$ so that

$$\chi_{\alpha}^{(1)}(k) = \sum_{\beta} \rho(\beta) \int 4\pi r^2 dr g_{\alpha\beta}(r) \chi_{\alpha\beta}^{(1)}(r) \quad (12)$$

in which $\rho(\beta)$ is the mean density of atoms of type β and $g_{\alpha\beta}(r)$ measures the number of atoms of type β at a distance r from an atom of type α . $\chi_{\alpha\beta}(k)$ is the EXAFS function [equation (10) or (11)] on an absorption edge of an atom of type α due to a single scattering atom of type β at a distance r away. We note the presence of just a single sum over atom type (*cf.* diffraction studies) – the type α is fixed by the edge.

Equation (12) is rarely used, except in reverse Monte Carlo simulations (Gurman & McGreevy, 1990). Usually, we assume that $g_{\alpha\beta}(r)$ may be written as a sum of Gaussian peaks, centred at R_j with mean-square deviation σ_j^2 and containing N_j atoms. We then find, assuming the form of (11) for integration purposes, that the EXAFS function due to a single peak is given by

$$\chi_{\alpha}^{(1)}(k) = \sum_{j\beta} N_j \exp(-2\sigma_j^2 k^2) \chi_{\alpha\beta}^{(1)}(k, R_j). \quad (13)$$

Apart from factors describing inelastic processes, which will be considered in §2.3, this is the form originally proposed by Sayers *et al.* (1971) except that we now have the possibility of using exact forms such as the FCW theory for the single-atom EXAFS function $\chi_{\alpha\beta}(k, R_j)$.

The assumption of a Gaussian peak shape may be relaxed by use of the cumulant expansion (Bunker, 1983) in which the contribution to (12) of each peak in $g_{\alpha\beta}(r)$ is written in terms of the exponential of a power series in (ik) . Odd powers contribute to the phase of the EXAFS, even powers to its amplitude. The coefficients of the power series are used as fitting parameters (usually three terms are sufficient) and the shape and size of the peak may then be recovered from these fitted values.

2.3. Inelastic processes

The description of the theory of XAS given above completely neglects inelastic processes. Such processes arise from the interaction between the photoelectron and the other electrons, both on the excited and scattering atoms, and must therefore be discussed in terms of many-body theory. The effect of inelastic processes is always to diminish the amplitude of the XAS signal, since they contribute to the absorption but not to the interference.

A proper many-body analysis of X-ray absorption would consider all electrons in the sample together. However, we may, to a good approximation, separate the interaction between the photoelectron and the other electrons on the excited atom, known as *intrinsic* processes, from those between the photoelectron and the other electrons which it meets during the scattering process, known as *extrinsic* processes.

Intrinsic processes include the effects of the finite lifetime of the core hole plus shake-up and shake-off processes, which involve the rearrangement or removal, respectively, of other electrons on the excited atom as part of the photoabsorption event. These latter two can be dealt with in the *sudden approximation* (Carlson, Nestor, Tucker & Malik, 1968). In this we write the many-body electron wavefunction for the N electrons on the excited atom as a product of N one-electron wavefunctions, the Hartree approximation. The expression for the absorption coefficient then becomes

$$\mu \simeq \sum | \langle i | \epsilon \cdot \mathbf{r} | f \rangle |^2 \delta(e_i - E_f + \hbar\omega) \prod_{i=1}^{N-1} | \langle c_i | c_i' \rangle |^2, \quad (14)$$

the extra factor arising from the $N-1$ passive electrons, those not directly involved in the photoabsorption. The wavefunctions of these differ between the initial and final states because of the presence of the core-hole potential in the latter.

The one-electron contribution to (14) is that where *none* of the passive electrons changes its state. It is therefore given by the last factor of (14) with $\langle c_i |$ the wavefunctions of the passive electrons on the unexcited atom and $|c_i'\rangle$ those of the passive electrons *in the same quantum states* in the potential of the excited atom with a core hole. This factor is necessarily less than unity. There is a sum rule which states that the overall absorption is unchanged by the inclusion of many-body effects: the extra contribution of multiple-electron excitations allows for this. Thus, the effect of shake-up and shake-off processes on the XAS signal is to multiply it by an amplitude factor $A(k)$ given by

$$A(k) = \prod_{i=1}^{N-1} | \langle c_i | c_i' \rangle |^2, \quad (15)$$

a result originally due to Rehr, Stern, Martin & Davidson (1978). This factor may be calculated fairly easily from tables of bound-state wavefunctions, those in the presence of the core hole being approximated by the wavefunctions

of the next atom in the Periodic Table, the so-called $Z + 1$ approximation. We find that $A(k)$ takes values between 0.6 and 0.9 for all atoms and all hard ($E > 4$ keV) X-ray edges. In this approximation $A(k)$ is, in fact, independent of k and this is found generally to be a fairly good approximation in the EXAFS regime.

The lifetime of the core hole also influences the EXAFS: interference can only occur if the returning photoelectron wave sees the same potential as the outgoing wave. The effects of core-hole lifetime are normally included as a mean free path type of factor derived from a constant imaginary part of the photoelectron energy equal to the energy uncertainty corresponding to the lifetime (this is one contribution to the width of the edge step) so that $\lambda_{\text{core}} \propto k$. Tabulations of core-hole lifetimes are available (Keski-Rahkonen & Krause, 1974).

The extrinsic process of interest in EXAFS is inelastic scattering of the photoelectron. The major source of this is plasmon excitation by the photoelectron as it travels through the sample. This problem has been considered within the local density approximation (LDA) by Lee & Beni (1977). The result of this analysis is that the potential seen by the photoelectron becomes energy-dependent, owing to the energy dependence of the exchange contribution, and it also acquires an imaginary (absorptive) part owing to plasmon excitation when the energy of the photoelectron is sufficiently high. This potential may be calculated using standard routines. It forms the basis of the *FEFF* series of data-analysis programs (Mustre de Leon, Rehr, Sabinsky & Albers, 1991) and also of the current version (*EXCURV92*) of the Daresbury Laboratory program. In a simpler approximation used in earlier EXAFS studies (up to about 1988!) the imaginary part was approximated by a constant, a form commonly used in LEED theory. This again gives rise to a mean free path type of factor with $\lambda_{\text{plasmon}} \propto k$. In general, use of the complex energy-dependent LDA potential gives better results.

3. Obtaining structural information

XAS is mostly used to determine the local structure around the excited atom in amorphous solids, liquids, complex crystals and biological molecules, *i.e.* it is the EXAFS which is generally of most interest. The chief problem of data analysis is how best to obtain this structural information. In order to treat this problem and the methods employed to solve it, we shall use the form of the EXAFS function given as (1), the PWA. In practice, wave curvature effects are always important, as we noted in §2.2, so we need to use (10). Multiple-scattering contributions may also be significant. Although these effects greatly complicate the programs used in practice, they do not alter the principles of data analysis.

The first stage in data analysis is to extract the EXAFS function $\chi(k)$ from the measured absorption (or fluorescence or total yield) data. The first step is to remove the contributions of lower energy edges from that due to the

edge of interest. This is performed by fitting a smooth function, such as the Victoreen expression, to the absorption coefficient below the edge and extrapolating this to higher energies. Subtracting this from the data gives the $\mu(k)$ used in (6). Similarly we obtain $\mu_0(k)$ by fitting such a smooth form to the edge contribution to obtain the EXAFS function defined by (6). This process is usually fairly straightforward although the small size of the EXAFS function compared to unity means that the fitting procedure used to obtain $\mu_0(k)$ must be rather accurate.

The simplest form of analysis, and the one which was almost exclusively used in the early (1970–1980) days of EXAFS studies, is to Fourier transform $k\chi(k)$ with respect to $\sin(2kr)$ or $\exp(-2ikr)$. The latter is to be preferred since taking the modulus of a complex transform removes some of the problems associated with a finite data range. We may usefully state at this point that one of the major limitations on the usefulness of EXAFS comes from the fact that we do not have data down to $k = 0$ owing to the presence of the threshold energy E_0 [equation (5)]: the lower limit k_{min} is usually $2\text{--}3 \text{ \AA}^{-1}$.

The result of a Fourier transform is a series of peaks, one corresponding to each shell of atoms contributing to the EXAFS, which may overlap. There are also peaks due to noise in the spectrum and to the effects of the finite data range: these last may be minimized by use of a window function at the cost of some peak broadening. There may also be a strong contribution at an unphysically short distance: this is usually a sign of poor background subtraction. The peaks due to real shells are shifted from the true interatomic distances by the effects of the extra phase factor $2\delta + \psi$ and their widths are dominated by the effects of the finite data range, *not* in the majority of cases by the Debye–Waller factor. To improve this simple analysis we may weight the spectrum by a higher power of k , k^3 being most commonly used, to counteract the decrease in amplitude with increasing k arising from the Debye–Waller factor and the fall off in $|f(k, \pi)|$: a function with constant amplitude gives a sharper Fourier transform. We might also take the transform with respect to $\exp[-i(2kR + 2\delta + \psi)]$ using calculated phases for the strongest contribution. This moves all peaks close to their true interatomic distances since the phase is dominated by the excited-atom contribution.

A simple Fourier transform gives a good idea of the amount of information in the experimental EXAFS spectrum and of the principal interatomic distances in the sample. To obtain more information we must fit to $\chi(k)$. This is always best done by fitting to the *raw* data.

Fitting the experimental spectrum in k space involves calculating a spectrum using an assumed set of structural parameters and scattering data and varying the structural parameters until a best least-squares fit is obtained. The accuracy of the fit, and of the resulting structural parameters, clearly depends on the quality of the scattering data used and much work has gone into evaluating methods of calculating electron-scattering phase shifts. At present, the

best results are obtained using complex energy-dependent potentials based on the LDA (Lee & Beni, 1977; Mustre de Leon *et al.*, 1991). k -space fitting can be rather time-consuming computationally but it does extract the maximum amount of structural information. It is also amenable to statistical analysis (Joyner, Martin & Meehan, 1987): this enables reliable estimates of the uncertainties of the (often correlated) structural parameters to be obtained. It also helps to avoid obtaining *more* information than is actually present!

The whole question of the amount of structural information contained within an EXAFS spectrum and the consequent uncertainties on the fitted parameters obtained in a fitting analysis is of major importance and is often neglected. This problem has been thoroughly considered by the International Workshop on Standards and Criteria in XAFS and the recommendations of their report (Bunker, Hasnain & Sayers, 1991) are required reading for all X-ray absorption spectroscopists.

The preset parameters in the curve-fitting analysis of an EXAFS spectrum are the atomic scattering data, including inelastic effects and the core-hole lifetime, and the amplitude factor $A(k)$, obtained from standard values or by fitting the spectrum from a sample of known structure. This process also acts as a check on the accuracy of the scattering data used. In a free analysis run the user sets the number of shells to be included and the type of atom making up each shell. The parameters varied during the least-squares fitting process are the correlated pairs of parameters (E_0 , R_j) and (N_j , σ_j^2) which control the phase and amplitude, respectively, of the EXAFS signal. Correlation between parameters is a major problem in EXAFS analysis, more so than in diffraction analysis because of the lack of data going down to $k = 0$, and this greatly increases the uncertainties on the fitted parameters. The presence of correlation means that a proper statistical analysis of the quality of the fit is *essential*. A good data-analysis program will search for a best fit automatically, varying those parameters selected by the user. Fitting tends to proceed interactively and iteratively, fixing the phase by varying E_0 and R_j , then the amplitude using N_j and σ_j^2 , then the phase and so on until a good fit, defined by a good reliability factor, is obtained. At this final stage a statistical package will give the uncertainties on the fitted parameters.

With good experimental data, over as long a k range as is possible, and well separated shells, we may expect to obtain interatomic distances with an accuracy of $\pm 0.02 \text{ \AA}$ or a little better. N and σ^2 , which are strongly correlated by the lack of low- k data, can be fitted to about $\pm 10\%$. The variation in $f(k, \pi)$ is such that we can reliably identify atoms whose atomic numbers differ by about ten or more: such identification can, of course, often be made more exact by using other chemical information or the bond lengths.

Surface EXAFS (SEXAFS) experiments are quite often considered as distinct from EXAFS. This is because the requirements of the surface physics equipment mean that indirect (fluorescence or total electron yield) methods

have to be used to obtain the absorption spectrum and also because the use of single-crystal samples means that polarization and beam direction effects (§2.2) are important. In low-symmetry situations, these require the use of a full polarization-dependent calculation (Gurman, 1988; Brouder, 1990) in the fitting procedure. In higher symmetry situations, the majority studied to date, the standard analysis described in the previous paragraph can be used. The fitted coordination numbers N_j are then effective coordinations, being equal to the true coordination numbers multiplied by a beam and polarization factor (less than unity) which can be easily calculated from the assumed symmetry of the surface environment. In this way the identity and symmetry of adsorption sites on surfaces can be determined, along with the interatomic distances between adsorbate and substrate.

In the curve-fitting method of EXAFS analysis described above, the EXAFS data is the *only* information used. In complex systems, containing many different shells of scattering atoms, the large number of parameters required cannot be justified by the information content of the EXAFS spectrum. The refinement is then underdetermined and a large number of solutions become possible, with no clearly defined minimum in the fit index. This is a problem which occurs particularly in biological studies. The only solution is to increase the amount of information available by including other data. The techniques of restrained and constrained refinement (Binsted, Strange & Hasnain, 1992) have been developed for this purpose.

As an example of the inclusion of extra information, consider a system containing a well defined chemical unit, such as an imidazole ring, which is bonded to the central atom. The atoms in this unit are not independent, as would be assumed in a free fit, since it is known that the structure of such units varies little between molecules. In *constrained* refinement the unit is treated as absolutely fixed in internal structure and the refinement only uses a distance parameter, from the central atom to the bonded atom in the unit, plus at most three angular parameters to define the orientation of the unit. We thus have a major reduction in the number of fitting parameters, especially if multiple scattering has to be included (as it usually does for such rigid structures). The refinement process is therefore much more determinate. Total constraint has a problem in that it neglects small but significant variations which may occur in the unit structure. This is overcome in a *restrained* refinement. In this, a common practice in protein crystallography, departures from the ideal structure are permitted, but these differences contribute to the fit index which is being minimized. Depending on the weighting applied to these changes, more or less flexibility is allowed. Again the result is to lessen the number of free parameters.

Another method of including extra information is used in reverse Monte Carlo simulations (Gurman & McGreevy, 1990) for the analysis of EXAFS data from solids and liquids. In these simulations, *all* (or as many as possible) EXAFS spectra from the sample are fitted simultaneously. The calculated spectra are built up by summing the contri-

butions of each atom pair in an array of perhaps 1000 atoms. The external constraints are the density and composition of the array. No *a priori* assumptions as to peak shapes are applied. In the data-analysis process atoms are moved at random, moves being accepted always if they lower the fit index and with a probability, determined randomly, if they raise it. Eventually convergence is achieved and the partial radial distribution functions of the final array of atoms represent those of the sample. The density constraint is very powerful and the simultaneous fitting of several spectra also acts as a strong constraint on the system.

4. Conclusions

The introduction of synchrotron radiation has made possible the measurement of high-resolution low-noise X-ray absorption spectra. Extraction of the oscillatory structure (EXAFS and XANES) from these spectra provides information on the local atomic environment in molecules and condensed material by way of the theory of the electron scattering which gives rise to the structure.

The theory of photoelectron scattering has reached a high level of development over the past 20 years. It now provides an essentially complete description of the processes leading to EXAFS and XANES. It shows how structural information is contained in the spectrum as well as the effects of inelastic processes.

Data-analysis programs based on the theory have also reached a high level. Several curve-fitting programs now exist which can rapidly and accurately extract the maximum amount of information from an experimental data set and, perhaps as important, the uncertainties on these parameters.

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