

## Progress and challenges in the theory and interpretation of X-ray spectra

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There has been dramatic progress over the past decade both in theory and in *ab initio* calculations of X-ray absorption fine structure (XAFS). Rapid progress is now being made in understanding X-ray absorption near-edge structure (XANES). This presentation reviews the developments in this field by many groups leading up to the current state of the art. These developments have led to several *ab initio* codes, such as *FEFF*, which yield results comparable to experimental results for XAFS, and permit an interpretation of the spectra in terms of geometrical and electronic properties of a material. The review begins with a summary of the key theoretical developments that are essential for achieving a quantitative agreement with experiment for XAFS. The same high-order multiple-scattering (MS) theory of XAFS can also give an approximate treatment of XANES, but this approach can fail close to an edge, where full MS calculations are often necessary. However, a fully quantitative treatment of XANES remains challenging, largely as a result of a number of many-body effects, *e.g.* the approximate treatment of the core-hole, multiplet effects, the photoelectron self energy and inelastic losses. Finally, natural extensions of the theory to other spectroscopies, such as anomalous X-ray scattering, DAFS (diffraction anomalous fine structure) and XMCD (X-ray magnetic circular dichroism) are briefly discussed. These developments are illustrated with a number of applications.

**Keywords:** XAFS; XANES; multiple scattering.

### 1. Introduction

Advances in theory over the past decade have revolutionized the technique of extended X-ray absorption fine structure (EXAFS) for local structure determinations. Indeed, the basic theory is now well understood, as discussed in a recent review (Rehr & Albers, 2000). Significant progress has also been made in understanding X-ray absorption near-edge structure (XANES), *i.e.* the structure within about 30 eV of threshold where multiple-scattering contributions are important. Curved-wave multiple-scattering (MS) theory now provides a unified treatment of the structure in both EXAFS and XANES; hence the term XAFS (Zabinsky *et al.*, 1995). Here we also use the acronym XAS to refer more generally to XAFS and other X-ray absorption spectroscopies [*e.g.* X-ray magnetic circular dichroism (XMCD)]. These theoretical advances have led to the development of *ab initio* codes for XAS calculations in arbitrary systems. Currently popular codes include, for example, *CONTINUUM* (Natoli *et al.*, 1980), *EXCURVE* (Binsted, Campbell *et al.*, 1991; Binsted, Strange & Hasnain, 1991), *FEFF* (Rehr *et al.*, 1991; Zabinsky *et al.*, 1995; Ankudinov *et al.*, 1998), *GNXAS* (Filipponi & Di Cicco, 1995), and *WIEN98* (Blaha *et al.*, 1990, 1998). The development of EXAFS code was revolutionary in that it provided accurate theoretical standards which eliminated the need for tabulated standards (Teo & Lee, 1979; McKale *et al.*, 1986) and greatly simplified the analysis of experimental data. Despite this progress, however, a fully quantitative treatment of XAS remains elusive, due to a host of complications, *e.g.*

full potential corrections and many-body effects, such as the treatment of the core-hole, inelastic losses and multiplet effects. In this short review, we outline the key concepts that have led to the current theory, together with the challenges for future improvements.

### 2. Key developments in XAS theory

The basic MS theory of XAS (Lee & Pendry, 1975; Rehr & Albers, 2000) is now well established. Formally, the X-ray-absorption coefficient  $\mu$  for a given X-ray energy  $\hbar\omega$  is given by Fermi's 'golden rule',

$$\mu(E) \simeq \sum_f |(i|\mathbf{A} \cdot \mathbf{p}|f)|^2 \delta(E - E_f), \quad (1)$$

where  $E = \hbar\omega - E_i$  is the photoelectron energy,  $\mathbf{A} \cdot \mathbf{p}$  is the coupling to the X-ray field, and the sum is over unoccupied final states. Most practical calculations are based on the dipole approximation and the reduction of the 'golden rule' to a one-electron approximation. However, the question of precisely which one-electron states to use is not unambiguous. Much current work is based on the final-state rule, in which the final states are calculated in the presence of an appropriately screened core-hole, and all many-body effects and inelastic losses are lumped into a complex valued optical potential. This theory is the basis for *FEFF* and many other codes.

Another commonly used approach for calculating XANES is the atomic multiplet theory (de Groot, 1994; Kotani, 1997). However, neither of these approaches is fully satisfactory. The one-electron approach ignores atomic multiplet effects, which are important for transition-metal *L*-shell XAS, while the atomic multiplet theory uses a crystal-field parameterization of solid-state effects and ignores delocalized states. Also, as a result of local field effects, a screened X-ray field can be important for soft X-rays (Zangwill & Soven, 1980). A challenge for the future is to improve on these approximations.

#### 2.1. Real-space Green's function (RSGF) formalism

An important formal development in XAFS theory is the RSGF approach (Schaich, 1973; Lee & Pendry, 1975). The need to calculate final states in the 'golden rule' is generally a computational bottleneck and can only be carried out efficiently for highly symmetric systems such as atoms, small molecules, or crystalline solids. However, many systems of interest lack symmetry. In addition, band-structure methods, which are often used for XANES calculations (Müller *et al.*, 1982; Blaha *et al.*, 1998), generally ignore important effects such as the core-hole and lattice vibrations, which spoil the assumed crystalline symmetry. Thus instead of explicitly calculating the final states, it may be preferable to re-express  $\mu$  in terms of the photoelectron Green's function or propagator  $G(\mathbf{r}', \mathbf{r}, E)$  in real space,

$$\mu(E) \simeq -(1/\pi)\text{Im} \langle i | \hat{\epsilon} \cdot \mathbf{r}' G(\mathbf{r}', \mathbf{r}, E) \hat{\epsilon} \cdot \mathbf{r} | i \rangle. \quad (2)$$

Within MS theory,  $G(\mathbf{r}', \mathbf{r}, E) = \sum_{L,L'} R_L(\mathbf{r}) G_{L,L'} R_{L'}(\mathbf{r}')$ , so the expression for  $\mu$  can be reduced to a calculation of atomic dipole-matrix elements  $M_L = \langle i | \hat{\epsilon} \cdot \mathbf{r} | L \rangle$  and a propagator matrix  $G_{L,L'}$ . The matrix  $G_{L,L'}$  can be re-expressed formally as a sum over all MS paths that a photoelectron can take away from the absorbing atom and back (Lee & Pendry, 1975), and thus gives rise to the path expansion for EXAFS. The relativistic generalization (Ebert, 1996) is similar in form. Relativity is important for the treatment of spin-orbit effects, which are largest in the atomic cores. Thus, we have found that relativistic effects are most important for the matrix elements have only weak effects on scattering. In *FEFF* they are treated to high accuracy with a relativistic Dirac-Fock atom code (Ankudinov *et al.*, 1996) and an interpolative approach (Ankudinov & Rehr, 1998).

Since  $G_{L,L'}$  naturally separates into intra-atomic contributions from the central atom and from MS, one obtains  $\mu = \mu_0(1 + \chi)$ , and hence the structure in  $\mu$  depends both on the atomic background  $\mu_0$  and on the MS signal  $\chi$ . This result is consistent with the experimental definition of XAFS,  $\chi = (\mu - \mu_0)/\Delta\mu_0$ , where  $\Delta\mu_0$  is the jump in the smooth atomic-like background. For XANES, however, the MS expansion is often carried to all orders (full MS) by matrix inversion (Durham *et al.*, 1982; Natoli *et al.*, 1980) and is then equivalent to ‘exact’ treatments, *e.g.* the KKR (Koringa–Kohn–Rostoker) band-structure method (Schaich, 1973).

## 2.2. Curved-wave multiple-scattering theory

Another key theoretical development is curved-wave scattering theory. Because of curved-wave effects, exact MS calculations are extremely time-consuming and at high energies can only be carried out with the path expansion for low-order MS paths (Gurman *et al.*, 1986). To overcome this bottleneck, we introduced an efficient method, referred to as the Rehr–Albers (RA) scattering matrix formalism, for curved-wave calculations based on a separable representation of the free propagator  $G(E)$  (Rehr & Albers, 1990). With separable propagators, the MS expansion can be re-expressed as a sum over MS paths,

$$\chi(k) = S_0^2 \sum_{\text{paths}} [f_{\text{eff}}(k)/kR^2] \sin(2kR + \Phi_k) \times \exp(-2R/\lambda_k) \exp(-2\sigma^2 k^2), \quad (3)$$

where  $k = [2(E - E_0)]^{1/2}$  is the wavenumber measured from threshold  $E_0$ ,  $\lambda_k$  is the XAFS mean-free path, and  $\sigma$  is the root-mean-square (r.m.s.) fluctuation in the effective path length  $R = R_{\text{path}}/2$ . This expression has the same form as the famous XAFS equation of Sayers *et al.* (1971), which has inspired much work on XAFS. However, all quantities must be redefined to include curved-wave and many-body effects. For example, instead of the plane wave back-scattering amplitude,  $f_{\text{eff}}(k)$  is an effective curved-wave scattering amplitude (from which *FEFF* is named) and  $S_0^2$  is a many-body amplitude reduction factor accounting for intrinsic losses, which was not in the original formula. Because of the path-dependent phase shift  $\Phi_k$ , theoretical calculations are essential in order to analyse experimental XAFS data beyond the nearest neighbors, because of the difficulty of obtaining suitable experimental standards. Curved-wave effects lead to phase shifts of order  $l(l + 1)/kR$  in each partial wave, and hence  $f_{\text{eff}}(k)$  differs significantly from the plane-wave back-scattering amplitude, even at the highest photoelectron energies of  $\sim 1500$  eV. With the RA approach,  $f_{\text{eff}}$  can be expressed both efficiently and accurately as a product of low-order (typically  $6 \times 6$ ) matrices for all XAFS energies, thus making high-order path expansions practicable. For XANES, however, exact propagators are needed. It turns out that the RA approach still provides a stable and efficient algorithm (Manar & Brouder, 1995), which we have implemented in *FEFF8*. At low energies, only small angular momenta are involved, so the matrix dimensions are still relatively small.

## 2.3. Path filters and high-order MS calculations

The introduction of an automated path enumeration scheme and ‘path filters’ that restrict the number of MS paths being considered (Zabinsky *et al.*, 1995) was another key development in EXAFS theory. We found that the vast majority of MS paths are numerically insignificant, so this step permits efficient fits of EXAFS data to local structure extending well beyond the nearest neighbor. The most important MS paths in EXAFS tend to be either linear or triangular. To automate the path selection procedure, the contribution of a given

MS path is estimated using the plane wave approximation, and only those paths of amplitude larger than a given cutoff are retained. With such filters, only of the order of  $10^2$  distinguishable MS paths need to be calculated to yield XAFS to within experimental accuracy of a few percent. For the near edge, more paths (typically of the order of  $10^3$ ) are generally needed, but often, a high-order MS treatment suffices to describe all XANES features, including ‘white lines’ and pre-edge structure (Farges *et al.*, 1997; Ankudinov *et al.*, 1998). Another application of near-edge XAFS (NEXAFS) is the simulation of ‘shape resonances’, *i.e.* the strong shape-dependent peaks observed, *e.g.* in hydrocarbons. Such resonances are well described by high-order MS calculations (Rehr *et al.*, 1995; Haack *et al.*, 2000) and their positions are good measures of bond length.

## 2.4. Scattering potentials

A simple approximation for the scattering potentials in EXAFS was also important. The calculation of such potentials simplifies for electrons of moderate energy since scattering depends strongly on the density in the core of an atom, where spherical symmetry is a good approximation. Thus the Coulomb part of these potentials is well described by an overlapped self-consistent field (SCF) atomic charge density and the overlapped ‘muffin-tin’ approximation (*i.e.* the Matheiss prescription), and the exchange term can be well approximated by a local self energy (see below). This latter approximation, however, can be inadequate for XANES, where chemical effects and charge transfer are important; in this case self-consistent (SCF) calculations are necessary. The SCF approach implemented in *FEFF8* also yields an accurate estimate of the Fermi energy  $E_F$ , eliminating an important fitting parameter from XAFS analysis. ‘Muffin-tin’ corrections can also be important in XANES, especially in highly anisotropic systems, and hence the development of self-consistent full-potential approaches remains a challenge for the future.

## 2.5. Self-energy and mean free path

Yet another key development is an efficient algorithm for calculations of the electron mean free path and self-energy shifts. A crucial difference between ground-state electronic structure calculations and excited states is the need in the latter for a complex energy-dependent ‘self-energy’  $\Sigma(E)$  to account for (extrinsic) inelastic losses. The XAFS mean free path is  $\lambda_k \simeq k/(|\text{Im}\Sigma| + \Gamma/2)$ , where  $\Gamma$  is the inverse core-hole lifetime. The self-energy is essentially a dynamically screened exchange interaction, which is the analog of the exchange-correlation potential  $V_{\text{xc}}$  of density functional theory. Indeed, the self-energy varies by about 10 eV over EXAFS energies and leads to systematic shifts of XAS peaks from their ground-state locations. Thus its effect can be more important than self-consistency (Mustre de Leon *et al.*, 1991). *FEFF* and other XAFS codes often use the Hedin–Lundqvist self-energy, but this self-energy tends to overestimate losses; occasionally other options such as the Dirac–Hara exchange are better. However, these approximations are based on electron-gas theory and can be inaccurate for XANES. One of the major challenges for future work is to develop better approximations.

## 2.6. Thermal and configurational disorder

The effects of disorder are of crucial importance in XAFS, as the approximation of a static structure yields large errors in XAFS amplitudes. Thus a key theoretical development is the cumulant expansion for an efficient parameterization of such thermal and configurational disorder (Crozier *et al.*, 1988; Dalba & Fornasini, 1997) in terms of a few moments or cumulants of the vibrational

distribution function. The *FEFF* codes treat only the mean square variation in bond length and ignore angular variations, which leads to a Gaussian Debye–Waller factor  $\exp(-2\sigma^2k^2)$  for each MS path. The thermal contributions to this factor can often be fit to a correlated Debye model (Beni & Platzman, 1976). The first cumulant  $\sigma^{(1)}$  is the thermal expansion, while the third  $\sigma^{(3)}$  characterizes the anharmonicity or asymmetry in the pair distribution function. Relations between the cumulants have been derived (Frenkel & Rehr, 1993) which show that  $\sigma^{(1)} \propto \sigma^2(T)$  and that  $\sigma^{(3)}$  is also related to  $\sigma^2(T)$ . If the third cumulant is neglected in the analysis, bond distances obtained from EXAFS are too short. Additional cumulants are usually not useful in fits. Improved treatments of XAFS Debye–Waller factors have been developed which go beyond the Debye approximation (Poiarkova & Rehr, 1999) and permit fits of Debye–Waller factors to local spring constants. Such treatment is important in highly anisotropic materials, such as biological systems. Another approach is to parameterize the  $N$ -particle distribution as in *GNXAS* (Filipponi & Di Cicco, 1995). Molecular-dynamics approaches are promising (McCarthy *et al.*, 1997), representing less phenomenological approaches, but accurate *ab initio* treatments require expensive total-energy calculations and remain a challenge for the future. Another challenge is the need for better algorithms for treating disorder in full MS XANES calculations.

### 2.7. Many-body amplitude reduction factor $S_0^2$

The amplitude reduction factor  $S_0^2$  is typically between 0.7 and 0.9 and arises from intrinsic losses in the creation of the core-hole, *i.e.* the multi-electron shake-up and shake-off excitations (Rehr *et al.*, 1978). Partly because of the difficulty of calculating or estimating  $S_0^2$ , the determination of coordination numbers from EXAFS is typically accurate only to  $\pm 1$ . Recently, however, a quasi-boson formalism has been introduced for such calculations, which treats both extrinsic and intrinsic losses, as well as interference between them (Hedin, 1989; Rehr *et al.*, 1997). The interference terms tend to suppress excitations near the threshold, which may explain why the existence of sharply defined multi-electron peaks in XANES has been controversial (Filipponi & Di Cicco, 1996). Preliminary numerical results for  $S_0^2$  from this approach are quite promising. However, a fully quantitative treatment of such many-body effects is lacking and remains a challenge for the future.

### 2.8. Atomic XAFS

There is now both theoretical and experimental evidence for weak oscillatory structure in  $\mu_0$ . The origin of this atomic XAFS or AXAFS (Holland *et al.*, 1978; Rehr *et al.*, 1994) is the scattering of a photoelectron at the periphery of an ‘embedded atom’ as a result of intra-atomic charge contributed from neighboring atoms. This effect is important for the analysis of EXAFS, since if not removed by background subtraction, it can show up as a peak in the EXAFS Fourier transform at about half the near-neighbor distance (Wende *et al.*, 1997). AXAFS is also important for the interpretation of XANES since it is sensitive to the bonding potential (Koningsberger *et al.*, 1999).

### 2.9. Fast XANES calculations

Because of the need for matrix inversion in full MS calculations, which scale in time as the cube of system size, XANES calculations are much more time-consuming than EXAFS. Indeed, XANES calculations become computationally intractable in the EXAFS regime or for cases (*e.g.* low- $Z$  atoms) where the mean free path is

very long. Thus one of the big challenges in XANES theory is to increase the computational speed. Promising methods include the recursion method (Filipponi, 1991; Ankudinov & Rehr, 2000), repartitioning (Fujikawa, 1993) and iterative approaches (Wu & Tong, 1999; Ankudinov & Rehr, 2000), which can provide substantial improvements on the conventional LU (lower-upper) decomposition. However, much more dramatic reductions can be obtained from parallel computational algorithms, which scale as  $A + B/N$ , where  $N$  is the number of processors, and hence can provide one–two orders of magnitude further improvement (Bouldin *et al.*, 2000). Parallelization has been implemented in *FEFF8* with the MPI (message-passing-interface) protocol (Gropp *et al.*, 1994). As a result, XANES calculations, even for very large systems of the order of  $10^3$  atoms, can now be carried out in about 1 h on large parallel computers, *e.g.* systems with 32–64 processors.

### 2.10. Quantitative interpretation of EXAFS and XANES

In parallel developments, robust EXAFS analysis procedures have been developed based on the high-order MS path approach. These include novel automated background-removal methods (Bridges *et al.*, 1995) and fitting codes (Newville *et al.*, 1995; George, 1999; Filipponi & Di Cicco, 1995; Binsted, Campbell *et al.*, 1991; Binsted, Strange & Hasnain, 1991; Binsted & Hasnain, 1996), which permit accurate refinements of structural parameters from XAFS data, as briefly reviewed in these proceedings (Newville, 2001). Challenges for the future include the need for improved error analysis methods (Krappe & Rossner, 2000), increased automation and graphical interfaces. Considerable effort has also been directed toward the interpretation of XANES data (Brown *et al.*, 1977; Mansour *et al.*, 1984; Binsted & Hasnain, 1996). However, the quantitative analysis of XANES is still not well developed and remains a challenge. There is also a need for a reliable inverse-method of extracting chemical and geometrical structure from XANES. On the other hand, there has been significant recent progress. Although the XANES signal depends sensitively on the geometrical structure, its shape directly reflects the excited-state electronic structure in a material. The reason is that the local projected density of states (LDOS)  $\rho$  has a form analogous to XAFS, *i.e.*  $\rho = \rho_0(1 + \chi)$ , and hence  $\rho \propto \gamma\mu$ , where  $\gamma = \rho_0/\mu_0$  is a smooth atomic ratio. This and analogous relations have recently been exploited to interpret charge counts from XANES and spin and orbital moments from XMCD, as reviewed in these proceedings (Ankudinov *et al.*, 2001).

## 3. Applications to X-ray spectroscopies

We have implemented the RSGF formalism outlined above into *FEFF8* for self-consistent calculations of both XAS and electronic structure. The code has already been applied extensively, as discussed elsewhere [see, for example, Ankudinov *et al.* (2000) for the XANES of Pt clusters]. Moreover, tests show that *FEFF8* yields LDOS in good agreement with full-potential band-structure codes such as *WIEN98*. The code is also highly automated and intended to be ‘user friendly’, requiring a minimum of input and few adjustable parameters. Because the underlying physics is similar, the same RSGF approach can be applied to many other spectroscopies, *e.g.* electron energy loss spectra (EELS) (Schaich, 1984; Sikora *et al.*, 2000). *FEFF* has also been adapted for studies of diffraction anomalous fine structure (DAFS) (Cross *et al.*, 1998) and more recently for the X-ray elastic scattering amplitude (Ankudinov & Rehr, 2000). In our approach, both real and imaginary parts of the anomalous X-ray scattering amplitude are calculated simultaneously in the complex

energy plane, without the necessity of a Kramers–Kronig transform. The presence of XAFS gives rise to very significant solid-state contributions in the anomalous-scattering amplitudes, which are ignored in the standard tables (Cromer & Liberman, 1970). Our approach includes dipole–quadrupole and quadrupole couplings and thus also permits calculations of X-ray natural circular dichroism (XNCD) and the X-ray anomalous cross scattering amplitude (XACS)  $F_{\pi\sigma}$ , which are both caused entirely by solid-state effects (Natoli *et al.*, 1998). Similarly, calculations of X-ray magnetic circular dichroism (XMCD) have been carried out (Ankudinov & Rehr, 1995, 1997); calculations of XMCD for the *K* shell emphasize the importance of spin-orbit relativistic effects in the final state. RSGF techniques have also been used for photoelectron diffraction (PD) (Fadley, 1991). Unfortunately, these applications are not yet highly automated and the development of integrated codes remains a challenge for the future. Toward this end, the latest *FEFF* code under development is modularized to simplify both the automation and extensions to various spectroscopies and analysis tools as they are developed.

#### 4. Conclusions

RSGF theory and the *FEFF* codes now make possible a general treatment of XAS, encompassing both XAFS and XANES as well as a number of other X-ray spectroscopies. The availability of a quantitative theory is key to an interpretation of XAS spectra in terms of local geometrical structure and electronic structure, such as LDOS, and spin and orbital moments. XAFS is now highly quantitative and widely used. Although significant progress has been made in XANES theory, the development of a fully quantitative treatment remains challenging. Improved treatments of the scattering potential, going beyond the ‘muffin-tin’ approximation, and better many-body theory, including accurate treatments of core-hole, multiplet and other effects, are all necessary. Nevertheless, rapid progress is now being made and XANES is slowly realising its promise as a tool for elucidating chemical and electronic structure.

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