

Chapter 2

Theory and Analysis of XAFS

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2.1 Theory of EXAFS

2.1.1 Introduction

Owing to its element specific and short-range nature, core-level X-ray absorption spectroscopy (XAS) is now routinely used to elucidate the local structural, vibrational, and other physical properties of complex, aperiodic materials. XAS encompasses both extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge spectra (XANES) [1, 2], where the terms refer, respectively, to the structure in the X-ray absorption spectrum $\mu(\omega)$ at high and low energies relative to the absorption edge with the crossover typically at about 20–30 eV above the edge. The acronym XAFS refers to the fine structure at all energies. The extraordinary capabilities of these spectroscopies come at a price: they depend on comparisons with quantitative simulations of the spectra. Remarkably, however, theories of X-ray spectra have become increasingly accurate and sophisticated, generally overcoming this limitation [2–5].

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Formally, the theory of XAS is based on Fermi's golden rule

$$\mu(\omega) \sim \sum_F |\langle 0|D|F\rangle|^2 \delta(\omega + E_0 - E_F), \quad (2.1)$$

which requires a summation over exact many-body final states $|F\rangle$, with energies E_F . However, practical calculations depend on the reduction of this relation to an effective, independent particle theory that takes into account several important many-body effects. The theoretical advances in recent years are the result of an improved understanding of these effects and accurate new approximations, in particular for inelastic losses and vibrational damping [6]. These developments rely on physics beyond the usual independent-particle approaches of quantum chemistry and condensed matter such as Hartree–Fock or density functional theory (DFT). Moreover, they involve different limits and time-scales, requiring a variety of approximations and computational methods like Green's function and Lanczos techniques. Besides XAS, these advances are applicable to a number of core-spectroscopies involving electronic excitations, including non-resonant inelastic X-ray scattering (NRIXS, also called X-ray Raman scattering or XRS) [7], and electron energy-loss spectroscopy (EELS) [8–11]. In this chapter we review these advances, focusing on the ideas behind the key approximations needed for a quantitative theory of EXAFS (Sect. 2.1) and XANES (Sect. 2.2). Section 2.3 contains a review of modern XAFS analysis methods, and Sect. 2.4 a number of illustrative structural modeling applications.

2.1.2 The EXAFS Equation

One of the key developments in the history of EXAFS was the famous equation of Sayers, Stern, and Lytle, which represents the normalized fine structure $\chi(\omega) = [\mu(\omega) - \mu_0]/\mu_0$ in XAS in terms of oscillatory contributions from near-neighbor atoms. Here μ_0 is the jump in the XAS at the edge. Although their model was heuristic, it included two key many-body effects, namely the mean free path of the photoelectron and vibrational damping [12]. This key observation demonstrates both the failure of any independent particle interpretation and the need to include both electronic and vibrational effects in quantitative theories. It also shows that XAS is a short-range order phenomenon, and cannot be described using conventional band-structure methods. Remarkably, an exact treatment based on the multiple-scattering (MS) path expansion can be cast in a similar form [1], namely

$$\chi(k) = S_0^2 \sum_R \frac{|f_{\text{eff}}(k)|}{kR^2} \sin(2kR + \Phi_k) e^{-2R/\lambda_k} e^{-2\sigma_R^2 k^2}, \quad (2.2)$$

except that all quantities are redefined to include curved-wave and many-body effects implicitly. In particular f_{eff} is the effective curved wave scattering amplitude

for a given photoelectron wave number k defined relative to the absorption threshold (or Fermi level μ) for X-ray absorption, i.e., with $k^2 = 2(E - \mu)$, λ_k the inelastic mean free path, and σ_R^2 the mean square relative vibrational amplitude of path R . The sum is over all multiple scattering paths, R being the half-path length, S_0^2 the many-body reduction factor which is typically about 0.8 as discussed below, and Φ_k a smoothly varying phase shift. Remarkably, the expansion generally converges rapidly away from the edge, with only of order 10^2 multiple-scattering paths in the EXAFS. This simplification is a consequence of the smallness of λ_k which is generally of order 5–20 Å. This representation also explains why the dominant peaks in the EXAFS Fourier transform $\chi(R) = \text{FT}[\chi(k)]$ are close to the geometrical near-neighbor distances in a material, but shifted by system dependent phase shifts, $\delta R \approx \frac{1}{2} d\Phi_k/dk$. Moreover this MS path representation permits an analysis of experimental XAFS signals in terms of geometrical and vibrational properties of a material, provided one has a reasonable approximation of the phase shifts and λ_k .

2.1.3 Many-Body XAS Formula

Perhaps the easiest way to incorporate many-body effects is to follow the two-step approach derived by Campbell et al. [13]. The first step is the production of the photoelectron, by photoexcitation from a particular core-state, given by an effective one-body (i.e., quasi-particle) absorption $\mu^{(1)}(\omega)$. Second is the effect of inelastic losses and secondary excitations, e.g., plasmons and electron-hole pairs, that can be represented by an energy-dependent “spectral function” $A(\omega, \omega')$, which subsequently broadens and shifts the spectrum. This yields an exact representation of the many-body XAS in terms of a convolution

$$\mu(\omega) = \int d\omega' A(\omega, \omega') \mu^{(1)}(\omega - \omega'). \quad (2.3)$$

The shape of the spectral function $A(\omega, \omega')$ typically consists of a sharp “quasi-particle” peak of width related to the inverse mean free path, together with a broad satellite. Consequently the EXAFS problem can be factored into two parts: an effective quasi-particle XAS $\mu^{(1)}(\omega)$ and a part that accounts for inelastic losses. The quasi-particle XAS can be calculated using an independent-particle Fermi’s golden rule, with the Δ SCF approximation, i.e., with the final single-particle states $|f\rangle$ calculated with the final state Hamiltonian in the presence of the core-hole

$$\mu^{(1)}(\omega) \sim \sum_f |\langle i | d | f \rangle|^2 \delta(\omega + E_i - E_f), \quad (2.4)$$

where $d = \vec{e} \cdot \vec{r}$ is the dipole operator and P the projection operator onto unoccupied states. Although this is a considerable simplification to Eq. (2.1), the

calculation and summation over final states in the golden rule is a serious computational bottleneck at high energies: the sum can only be carried out efficiently for highly symmetric systems such as atoms, small molecules, or periodic solids. On the other hand, many systems of interest lack symmetry. Reciprocal space (i.e., band structure) methods [14, 15] often ignore the effects of the core-hole and lattice vibrations, which spoil crystal translation symmetry, although the former can be treated approximately with super-cell approximation. Instead, different methods are needed. Remarkably, it is preferable computationally to re-express the XAS in terms of the photoelectron Green's function or propagator G in real space rather than explicitly calculating the final states. This formulation implicitly sums over all final states as can be seen by using the spectral representation of G for which $-\frac{1}{\pi} \text{Im} G = \sum_f |f\rangle \delta(E - E_f) \langle f|$, so that the golden rule can be rewritten exactly as a single matrix element

$$\mu^{(1)}(\omega) = -\frac{1}{\pi} \text{Im} \langle c | d G(r, r', E) d' | c \rangle. \quad (2.5)$$

This approach turns out to be advantageous for XAS calculations even in perfect crystals, since inelastic losses (i.e., the mean free path) limit the range probed by XAS experiment to clusters typically of order a few hundred atoms about a given absorption site.

2.1.4 Real-Space Multiple-Scattering Theory

We now briefly summarize the real-space multiple scattering (RSMS) theory used for practical calculations of EXAFS. The starting point of the theory is the separation of the potential into contributions from “scattering potentials” v_R localized on each atomic site R ,

$$v_R(r) = v'_{\text{coul}} + \Sigma(E) = \sum_R v_R(r - R). \quad (2.6)$$

Here v'_{coul} is the Hartree potential calculated for the final state in the presence of a core hole, and $\Sigma(E)$ is the energy-dependent self-energy. With this separation and the approximation of local spherical symmetry at each site, the propagator is also separable

$$G(r, r', E) = \sum_{L, L'} R_L(r) G_{LR, L'R'} R_{L'}(r'), \quad (2.7)$$

so that the expression for the XAS can be reduced to a calculation of atomic-like dipole-matrix elements $M_L = \langle c | \epsilon \cdot r | LR \rangle$ and matrix elements of $G(r, r', E)$.

$$\mu(E) = -4\pi e^2 \frac{\omega}{c} \sum_{LL'} M_L(E) G_{LL'} M_{L'}(E), \quad (2.8)$$

where $L = (l, m)$ denotes the angular momentum variables at each site R . Here and elsewhere we interchangeably use either the photoelectron energy E or the photon frequency ω to characterize the photoelectron energy. Interestingly, the relativistic generalization, which is needed for heavy atoms like Pt [16], is identical in form but with relativistic angular momentum variables (k, m) . Relativistic corrections are essential for the treatment of spin-orbit effects, which are biggest in the atomic cores and hence crucially important for the transition matrix elements in heavy atoms. However, relativity has only weak effects on scattering of non-relativistic electrons in EXAFS. In FEFF, relativistic effects and spin-orbit corrections are treated to high accuracy using a relativistic Dirac–Fock prescription [17]. In addition the calculation of the scattering potentials at each site simplifies for electrons even of moderate energy (i.e., above about 10 eV of kinetic energy), where the scattering depends strongly on the density in the core of an atom, and hence spherical symmetry is an excellent approximation. Thus, self-consistency is not usually important in calculations of scattering in EXAFS. It is needed, however, to obtain an accurate estimate of the threshold (or Fermi energy E_F) and fractional occupations of the various valence states.

In RSMS, the propagator $G_{LL'}(E)$ naturally separates into intra-atomic contributions from the central atom G_c and multiple scattering contributions from the environment G^{sc} , so that $G = G_c + G^{sc}$. Consequently, the XAS μ naturally factors as

$$\mu(\omega) = \mu_0(\omega)[1 + \chi(\omega)], \quad (2.9)$$

where χ is the X-ray absorption fine structure (XAFS). Thus the net structure in the XAS μ depends both on the atomic background $\mu_0(\omega)$ and on the fine structure χ due to MS: $\chi = \text{Im Tr}_m G_{LL'}^{sc}$. Since $\mu_0(\omega)$ varies weakly with energy, these results are consistent with the experimental definition of the normalized XAFS $\chi = (\mu - \mu_0)/\Delta\mu_0$, where $\Delta\mu_0$ is the jump in the atomic background absorption at threshold. Formally, the matrix $G_{LL'}(E)$ can also be expressed as a sum over all MS paths that a photoelectron can take away from the absorbing atom and back [2], and thus gives rise to the multiple-scattering *path expansion*

$$G^{sc} = e^{i\delta'} [G^0 T G^0 + G^0 T G^0 T G^0 + \dots] e^{i\delta}, \quad (2.10)$$

where the successive terms represent single, double, $\dots$ scattering processes and δ and δ' are partial-wave phase shifts. As noted above, this expansion converges rapidly for EXAFS with of order 10^2 paths. Remarkably, the sum sometimes converges adequately in XANES, particularly in cases with a short core-hole lifetime as in deep core levels in heavy elements. However, the path expansion is not always reliable near the edge, as discussed in Sect. 2.2. Due to the large dimension of $G_{LR,L'R'}(E)$, exact calculations with the path expansion can only be

carried out for very few low-order MS paths [18]. To overcome this computational bottleneck, an efficient approximation was devised based on the Rehr-Albers (RA) scattering matrix formalism [19]. The RA approach yields curved-wave calculations of the effective scattering amplitude f_{eff} (from which the FEFF code takes its name) in terms of a separable representation of the free propagator $G^0(E)$. With this representation the MS expansion can be re-expressed as a sum over MS paths R in a form essentially the same as the original EXAFS equation of Sayers, Stern, and Lytle [12], but with renormalized ingredients in all terms.

2.1.5 Mean Free Path

Two of the crucial differences between ground state electronic structure and excited states in core-level spectra are (1) the need for an energy dependent self-energy $\Sigma(E)$ instead of an exchange-correlation functional like DFT, and (2) the need for a screened core-hole. The self-energy is essentially a dynamically screened Hartree–Fock exchange interaction, and is the analog of the exchange-correlation potential V_{xc} of DFT. The real part of the self-energy varies by about 10 eV over XAS energies, slowly turning off in the classical limit, while the imaginary part is negative and varies by about 5 eV. The imaginary part accounts for (extrinsic) inelastic losses or final-state broadening, and can be expressed in terms of a mean free path and a core-hole lifetime Γ ,

$$\lambda = k/[|\text{Im } \Sigma| + \Gamma]. \quad (2.11)$$

The real part of $\Sigma(E)$ accounts for systematic shifts in peak positions compared to those calculated with DFT, leading to a stretching of the energy scale at low energies of about 10 %. One of the key developments in practical XAS codes is an efficient algorithm for calculations of $\Sigma(E)$ based on the GW approximation of Hedin [20]. For example, FEFF and several other XAS codes by default typically use a local density approximation for $\Sigma(E)$ based on the plasmon-pole dielectric constant. This approximation works well for EXAFS, and reduces to the ground state exchange-correlation potential near threshold. However, the plasmon-pole self-energy tends to overestimate losses in the XANES. This deficiency can be overcome by using a many-pole model, as discussed by Kas et al. [21] (see also Sect. 2.2).

2.1.6 Many-Body Amplitude Reduction Factor S_0^2

The effect of the convolution in the exact expression for the XAS in Eq. (2.3) is to average the one-electron XAS over the spectral function, so

$$\mu = \langle \mu_0 \rangle \left[1 + \sum_R \langle \chi_R \rangle \right]. \quad (2.12)$$

Since the atomic absorption μ_0 is smoothly varying, the average $\langle \mu_0 \rangle \approx \mu_0$ has little effect. Here $\chi_R \sim \text{Im}[\exp(2ikr)]$ is the XAFS contribution for a given path. Then, averaging χ_R over the quasi-particle peak gives rise to a damping factor $\exp(-2R/\lambda_k)$ from the mean free path, while the broad structure in the spectral function gives an additional factor denoted by S_0^2 , which turns out to be only weakly dependent on R . Physically the mean free path term is dominated by the extrinsic losses, while S_0^2 is dominated by intrinsic losses. A more detailed analysis shows that this factorization is most appropriate at high energies in the EXAFS regime. Near the edge, one expects interference terms to suppress these effects and hence the energy dependence of these contributions to be important.

2.1.7 Thermal Vibrations and XAFS Debye–Waller Factors

The effects of thermal and structural disorder lead to strong exponential damping of the fine structure, and thus are of crucial importance in XAFS. This damping is dominated by an *XAFS Debye–Waller factor* $\exp(-2\sigma^2 k^2)$, where σ^2 is the mean square relative displacement (MSRD) of the near-neighbor bonds, and typically varies inversely with the local bond strength. Higher moments of the pair distribution function are sometimes important, especially in temperature dependent investigations of XAS. One of the key theoretical developments in the theory of vibrational damping in XAFS is the cumulant expansion, which yields an efficient parameterization of such thermal and configurational disorder [22, 23] in terms of a few moments or *cumulants* $\sigma^{(n)}$ of the pair distribution function. Formally this expansion yields a complex Debye–Waller factor $\exp\left[\sum_n (2ik)^n \sigma^{(n)}/n!\right]$ in G^{sc} , which contributes both to the amplitude and phase of the XAFS.

The thermal contributions to σ^2 often can be fit to a correlated Debye model [24]. The corrections to the dominant second cumulant depend on anharmonicity. The first cumulant $\sigma^{(1)}$ is the net thermal expansion, while the third $\sigma^{(3)}$ characterizes the asymmetry or skew of the pair distribution function. These odd order contributions can strongly affect the phase of the fine structure, especially at high energy, giving a contribution $2k\sigma^{(1)} - 4k^3\sigma^{(3)}/3 + \dots$. Relations between the cumulants have been derived [25] which show, to leading order in the anharmonicity parameter, that $\sigma^{(1)} \propto \sigma^2(T)$ and $\sigma^{(3)}$ is related to $\sigma^2(T)$. The third cumulant is important in bond distance determinations and in interpretations of thermal expansion. If the third cumulant is neglected in the analysis, bond distances obtained from EXAFS typically appear unphysically short. Improved treatments of XAFS Debye–Waller factors have recently been developed which go beyond the correlated Debye approximation. They are described in more detail in Sect. 2.4.

2.2 Theory of XANES

2.2.1 Basic Interpretation of XANES

As discussed in the previous section, the formal theories of XANES and EXAFS are essentially the same, and are both given by Fermi's golden rule, i.e., $\mu(\omega) \sim \sum_F |\langle 0|D|F\rangle|^2 \delta(\omega + E_0 - E_F)$, where $|0\rangle$ and $|F\rangle$ are many-body initial and final electronic states. When an effective single-particle description of the spectrum is reasonable, this leads to

$$\mu(\omega) \sim \sum_f |\langle i|d|f\rangle|^2 \delta(\omega + \varepsilon_i - \varepsilon_f), \quad (2.13)$$

where $|i\rangle$ denotes the core orbital in question, $|f\rangle$ are unoccupied single-particle states, and $d = \vec{e} \cdot \vec{r}$ is the dipole operator. The basic interpretation of this equation is that the core-level electron is kicked out of the core-level by the photon (dipole transition operator) and into an unoccupied excited state of energy $\varepsilon_f = \varepsilon_c + \omega$, as required by energy conservation. The deep core electrons are very nearly angular momentum eigenstates, e.g., the K-edge is a transition from a 1s orbital. This fact, coupled with the dipole selection rule $l \rightarrow l \pm 1$, provides an interpretation of the spectrum in terms of the angular momentum projected density of states (LDOS) and smoothly varying transition matrix elements. For example, transitions from a 1s core-level are related to the p-DOS of the system, while transitions from a 2p core-level are related to the s-DOS and the d-DOS. In many cases the latter dominates and the spectrum can be interpreted in terms of the d-DOS alone. Although the dipole approximation is usually very good, there are some systems for which the pre-edge peaks are due to quadrupole transitions. In this case the selection rules are $\Delta l = 0, \pm 2$, e.g., transitions from the 1s state are related to the s- and d-DOS.

2.2.2 Differences Between XANES and EXAFS

Several of the approximations appropriate for the EXAFS regime (beyond about ~ 20 – 30 eV above the edge) are not valid in the near edge regime, with some of these related to the reduction of the many-body formulation to an effective single-particle description, as in Eq. (2.13). For example, in highly correlated systems such as transition metal oxides and f-electron systems, many-body effects can change the qualitative behavior of the near edge spectrum [26], while the main effect on the EXAFS region is simply an overall reduction in the amplitude of the fine structure, which is taken into account by the S_0^2 factor in the EXAFS equation, Eq. (2.2). Even in simpler systems, the approximations made to construct an effective single-particle Hamiltonian, i.e., quasiparticle self-energy models such as the plasmon

pole model, are most appropriate in the EXAFS regime. When calculating XANES they must be augmented, e.g., with the many-pole self-energy model [21]. Another approximation has to do with the description of vibrational and structural distortions. In particular, vibrational effects damp the EXAFS via the Debye–Waller factor $\exp(-2k^2\sigma^2)$. In the XANES, the effects of vibrations and disorder are sometimes more related to symmetry breaking, which allows transitions to states that were previously dipole forbidden, resulting in additional peaks in the near edge spectrum.

EXAFS is also less sensitive to the non-spherical details of the potentials, and a simple overlapped atomic muffin tin potential is adequate for most practical calculations. On the other hand, near-edge spectra can be quite sensitive to details of charge transfer and changes in Fermi level due to solid state effects. Thus the use of self-consistent potentials and often non-spherical symmetry are essential for accurate calculations of XANES. Finally, calculations of the single particle Fermi golden rule must be treated differently in the near edge region because the path expansion detailed in Eq. (2.10) often fails to converge (or converges very slowly) for low energy photoelectrons. This slow convergence is caused by two factors. First, the inelastic mean free path becomes large for low energy electrons so that very long paths must be included in the expansion. Second, large angle scattering amplitudes are not small at low energies, so that the XANES signal is not dominated by nearly linear scattering paths, and all multiple scattering paths must be taken into account.

2.2.3 Full Multiple Scattering

Although the path expansion method of calculation is not appropriate for the XANES, one can instead sum the expansion to all orders for any finite cluster of atoms via matrix inversion, so that instead of Eq. (2.10) we have

$$G = [1 - G^0 T]^{-1} G^0. \quad (2.14)$$

The matrices in this equation are represented in a site and angular momentum basis $|L, R\rangle$, so the rank of the matrix to be inverted is $N(l+1)^2$, where N is the number of atoms in the cluster, and l is the maximum angular momentum of an expansion in spherical harmonics. Matrix inversion can be expensive computationally for large matrices, since the time to invert scales like the cube of the rank of the matrix. Therefore, practical calculations must limit the cluster size and truncate the sum over angular momentum states. The cluster size cannot be too large, typically ~ 1000 atoms or less for most computations. Fortunately, one does not usually need such large clusters for XANES calculations since the finite core-hole lifetime keeps the inelastic mean free path from becoming too large. In addition, reasonable accuracy requires that $l_{\max}$ is of order $k_{\max} R_{\text{mt}} + l_{\text{occ}}$, where l_{occ} is the largest

angular momentum of the occupied states and $k_{\max}^2 \sim E_{\max}$ in Rydberg units. Thus, in the XANES region one can safely set the maximum angular momentum to 4 at most, while at higher energies in the EXAFS matrix inversion becomes impractical. In the intermediate energy regime, Lanczos techniques can be used. In addition, the Green's function $G(E)$ is parameterized by the energy of the photoelectron, thus one inversion must be performed for each energy point in the spectrum. This makes the calculations parallelize naturally and can be done very efficiently on parallel computers [27].

2.2.4 Self-Consistent Potentials

The Green's function can also be used to calculate the total electron density, i.e.,

$$\rho(\vec{r}) = -\frac{1}{\pi} \int_{-\infty}^{\mu} \text{Im}[G(\vec{r}, \vec{r}, E)] dE. \quad (2.15)$$

Thus the Green's function naturally replaces all the orbitals used in standard density functional theory codes, and the Kohn–Sham Hamiltonian can be solved self-consistently using the Green's function [1]. In the real-space multiple scattering code FEFF, this works as follows:

1. Atomic Dirac–Fock eigenfunctions and densities are calculated for each type of atom, and an overlapped atom approximation to the density is used as the initial guess in the self-consistency loop.
2. The density and exchange correlation functional is used to create a Kohn–Sham (LDA) potential.
3. The spherical muffin-tin approximation is applied.
4. The Green's function is calculated at each energy using a scattering state basis.
5. A new chemical potential μ is found by requiring that the total number of

electrons N_e , is conserved, i.e., $N_e = -\frac{1}{\pi} \int_{-\infty}^{\mu} \int d^3r \text{Im}[G(\vec{r}, \vec{r}, E)] dE$.

6. New densities are calculated from the new Green's function and chemical potential.
7. Steps 2–6 are repeated until the output density is sufficiently close to the input density.

Figure 2.1 shows the structure of the FEFF program, along with details of the self-consistency algorithm. Several other approximations made in FEFF are worth mentioning. First, FEFF allows the user to treat several atoms as identical, even if they are physically different, i.e., two oxygen atoms in different local environments can be constrained to have the same potentials. Second, the integral over space

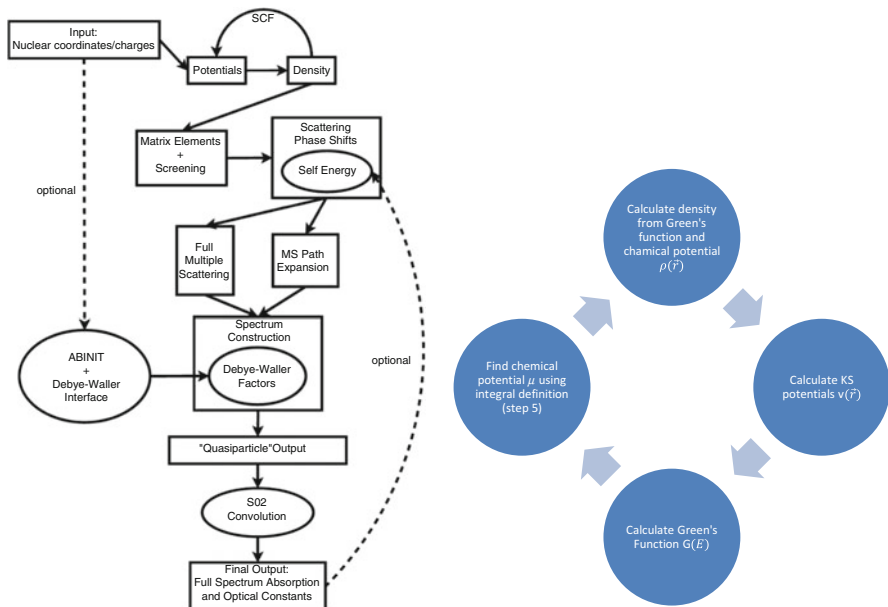


Fig. 2.1 Diagram showing the overall structure of calculations using the FEFF program (*left*) and an expanded view of the SCF procedure (*right*) detailed in the text

shown in step 5 above is approximated by a sum of integrals about each atom. Each of these integrals spans the volume of a sphere (the Norman sphere) defined such that the total overlapped atomic charge (including the nucleus) is zero.

Self-consistency of the densities and potentials can be very important for XANES calculations. For example, if an initial guess of the Fermi energy is too high, pre-edge peaks are missing. Self-consistency and the shift in the Fermi energy due to solid state effects also play a role in chemical shifts, and are very important in systems with multiple, physically unique absorbing sites, such as nanoparticles on a support.

2.2.5 Many-Body Effects: Quasiparticle Self-Energy Models

Many-body effects also play a large role in the XANES, and are responsible for energy dependent shifts and broadenings associated with the quasiparticle self-energy, as well as satellite peaks brought about by multi-electron excitations. While simple models such as the plasmon pole self-energy [28, 29] have been quite successful for calculations of EXAFS, more accurate models must be used near the edge. Most current calculations of these effects are based on the *GW* approximation of Hedin [30], i.e.,

$$\Sigma(E) = i \int \frac{d\omega}{2\pi} G(E - \omega) W(\omega) e^{-i\eta\omega}, \quad (2.16)$$

where G is the electron Green's function and $W = \epsilon^{-1}v$, is the screened Coulomb interaction. In the interest of retaining the efficiency of the plasmon pole model, we have developed a many-pole model self-energy which uses multiple poles to represent the loss function $L(\vec{q}, \omega) = -\text{Im}[\epsilon^{-1}(\vec{q}, \omega)]$ [21], i.e.,

$$L(\vec{q}, \omega) = \frac{\pi}{2} \sum_i g_i \omega_i \delta(\omega - \omega_i(\vec{q})). \quad (2.17)$$

The dispersion of the excitations is approximated by a polynomial $\omega_i(\vec{q})^2 = \omega_i^2 + v_F^2 q^2 + \frac{q^4}{4}$ which retains the high momentum transfer limit [29]. The amplitudes g_i are fixed by matching to the loss function in the zero momentum transfer limit ($q \rightarrow 0$), giving $g_i = -[2\Delta\omega / \pi\omega_i]L(0, \omega_i)$. In this way the model is consistent with the inverse and first moments of the spectrum for any number of poles, and thus convergence with number of poles is relatively fast. Given this model of the dielectric function, the total self-energy can be expressed as a sum of single plasmon pole self-energies arising from interactions with “plasmons” at different frequencies, i.e., $\Sigma(E) = \Sigma_x + \sum_{(i)} g_i \Sigma_1(E, \omega_i)$. This model has been shown to produce reasonably accurate quasiparticle self-energies in comparison with more accurate, but much more time consuming calculations. The many pole model self-energy has been applied to a variety of systems and gives improved results for amplitudes and phases in XANES calculations using FEFF. The model can also be applied in a post processing step as a convolution of the spectrum with an energy dependent Lorentzian [31], as seen in Fig. 2.2, which shows a comparison of theoretical and experimental results for the Li K-edge XANES of LiF [4].

In addition to quasiparticle energies, we can also calculate the inelastic mean free path (IMFP) [34], which is related to the imaginary part of the self-energy, i.e., $\lambda_k(E) = k/|\text{Im}[\Sigma(E)]|$. Figure 2.3 shows a comparison between calculated and experimental IMFP values for Cu, along with results from the plasmon pole model. These results show clear improvement in the agreement with experiment over the plasmon pole model, which is clearly inaccurate below ~ 100 eV.

Multi-electron excitations can also be calculated given the quasiparticle self-energy, via a convolution of the spectrum with an effective spectral function as in Eq. (2.3) [13, 21]. These calculations are based on a quasi-boson model, which also gives an estimate of the amplitude reduction factor S_0^2 . In addition, the calculations yield the satellites on the spectrum which roughly show up as “replica” peaks in the spectrum, shifted by the energy of the main bosonic excitations of the system, and are reflected by peaks in the observed loss function.

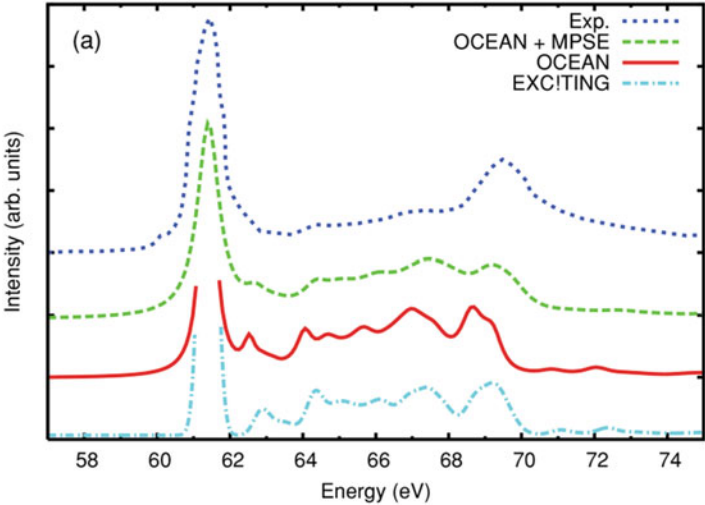


Fig. 2.2 Results for the Li K-edge XANES of LiF from the EXCITING BSE code (cyan dot-dashed) [32], the OCEAN BSE code (red), OCEAN plus the self-energy convolution (green dashed), and experiment (blue dashed) [33]. Figure taken from Ref. [4]

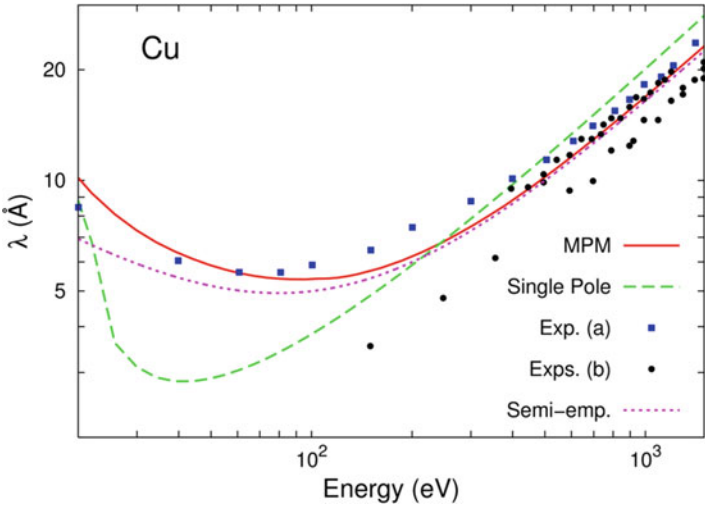


Fig. 2.3 Inelastic mean free path of Cu calculated using a single plasmon pole (green dashes), the many pole model (solid red), and a semi-empirical model (pink dots), compared to experimental data from (a) Ref. [35] (blue squares) and (b) Ref. [36] (black circles)

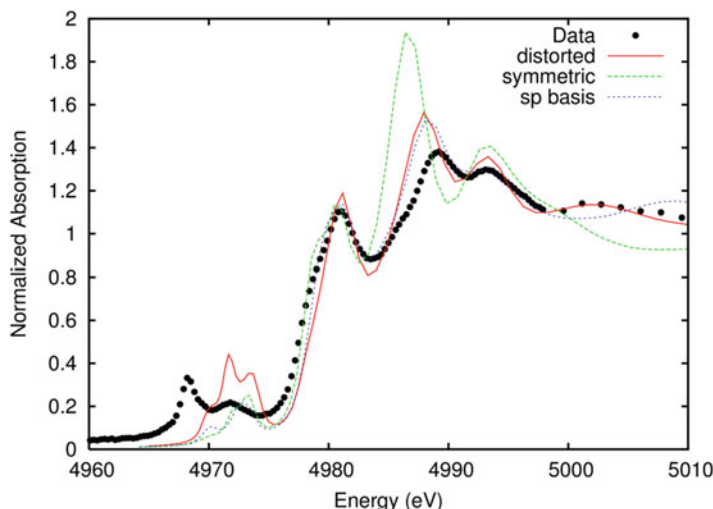


Fig. 2.4 Ti K-edge XANES of PbTiO_3 calculated using a distorted crystal structure (*solid red*), the same but with the basis limited to s- and p-states (*thin blue dots*), and using the ideal centrosymmetric crystal structure (*green dashes*), compared to experimental results (*black circles*)

2.2.6 Information in XANES: Atomic and Electronic Structure

XANES can be used to probe a variety of properties, including local electronic and chemical structure, atomic structure, and sometimes vibrational properties. For example, $L_{2,3}$ -edges of transition metals can be related to the number of holes in the d-orbitals [37]. Shifts in the onset of the spectrum can also indicate charge transfer to and from a metallic particle, or changes in formal oxidation state. While EXAFS is extremely sensitive to the first shell distances and, to a lesser extent, to coordination numbers, XANES is complementary in the sense that it is more sensitive to the local symmetry around the absorbing atom [38]. For example, the spectrum of an atom with four nearest neighbors in tetrahedral symmetry changes appreciably when the symmetry is changed to square planar. Another effect of local symmetry is symmetry breaking due to vibrational effects [39]. An example of symmetry breaking is shown in Fig. 2.4, which displays the Ti K-edge spectrum of PbTiO_3 with and without distortions that break centro-symmetry.

2.2.7 Use of Configurational Averaging for Vibrational and Static Disorder

For complicated systems such as amorphous materials or systems at higher temperatures, the EXAFS can be calculated via Debye–Waller factors which damp each path at high k . The XANES is more difficult, since changes in symmetry can

allow previously forbidden transitions, resulting in new peaks in the spectrum. Thus a more accurate method for calculating XANES is to perform averaging over physically unique absorbing sites. This configurational averaging must be performed even when disorder is not present if the system in question has more than one physically unique absorber. For example, magnetite has both tetrahedrally and octahedrally coordinated iron atoms, thus one calculation should be performed for each of these sites, and the final signal obtained from weighted average of the calculated results, where the weighting depends on the site stoichiometry. Doped systems can also require this kind of configurational averaging if the doping concentration is high. Also, in nanoparticles there can be a large number of physically unique sites, based on the proximity to the surface of the particle, interaction with the support, and interaction with adsorbed molecules. All of these effects cause distortions, which ideally should be modeled along with the dynamic, temperature dependent effects. This can be done using, for example, *ab initio* molecular dynamics to obtain snapshots of the structure of the system [40–42]. The XANES can be calculated for each snapshot by averaging over unique sites, and an average over snapshots gives the final result. There are several approximation applied in the FEFF code that can affect the outcome of such calculations. First, core level shifts due to charge transfer can be important in the final averaged result, since these cause red or blue shifting of the absorption edge. Second, the chemical potential found by FEFF must be calculated carefully since this also causes shifting of the edge. For example, all calculations performed on a static nanoparticle should result in the same (or very nearly the same) chemical potential. This sometimes requires that a unique potential be defined for each type of atom, although atoms with similar chemical surroundings can in many cases be defined as the same type without much loss of accuracy in the results.

2.2.8 Other Spectroscopies: EELS, XES, NRIXS, RIXS, Compton, etc.

Many other spectroscopies are related to XAS as they involve similar physics and an analogous golden rule formalism. In particular, electron energy loss (EELS), X-ray emission (XES), and non-resonant inelastic X-ray scattering (NRIXS) are all similar to XAS, the main difference being that they probe different states, either because the transition operator is different, as in EELS and NRIXS, or because the initial and final states are different, as in XES. XES is particularly useful since it probes the occupied states of the system via the dipole operator, and is thus complementary to XAS [43]. EELS and NRIXS both obey a Fermi's golden rule with transition operators $e^{i\vec{q}\cdot\vec{r}}$ replacing the dipole operator, where $\vec{q}$ is the momentum transfer due to the scattering of the electron or photon [7, 44]. This momentum transfer can be controlled by adjusting the angle of detection, and thus the dipole limit can be reached in which case the signal is equivalent to XAS, with

$\hat{q}$ replacing the polarization direction. The EELS amplitude contains a factor that damps the high momentum transfer signal, so that it is usually within the dipole limit, while NRIXS does not contain this factor, making it possible to probe the local unoccupied density of states for all angular momenta [45]. In addition, NRIXS is useful as a bulk probe of low energy edges, since the energy loss is required to match the edge energy, and high energy X-rays can still be used as the probe [46].

Resonant X-ray emission (RXES) is given by the Kramers–Heisenberg formula, which is similar to Fermi’s golden rule, but includes a resonant energy denominator that focuses on a given transition. Although the formula is more complicated than XAS, the RXES spectrum can be approximated by the convolution of an effective XAS signal with the XES spectrum [47], i.e.,

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{\omega}{\Omega} \frac{\int d\omega_1 \mu_{\text{XES}}(\omega_1) \bar{\mu}(\Omega, \Omega - \omega - \omega_1 + E_b)}{|\omega - \omega_1 + i\Gamma_b|}, \quad (2.18)$$

where μ_{XES} is the XES spectrum, $\bar{\mu}$ is the effective XAS spectrum, and E_b and Γ_b are the core level energy and broadening corresponding to the initial (deep core) excitation, respectively. This formula can be used to estimate both core to core resonant inelastic X-ray scattering, core-valence RXES, and high energy resolution fluorescence detection (HERFD) XAS. Finally, Compton scattering can be calculated within the impulse approximation from the density matrix,

$$\rho(\vec{r}, \vec{r}') = -1/\pi \int_{-\infty}^{\mu} dE \text{Im}[G(\vec{r}, \vec{r}', E)],$$

making multiple scattering a natural formalism for these calculations [48].

2.3 Analysis of EXAFS and XANES

The analysis of EXAFS and XANES begins with a good quality experimental spectrum, and at least some understanding of the physical and chemical environment of the sample that gave that spectrum. Because EXAFS can be measured in a number of modes, and over a wide range of sample conditions and concentration of the absorbing element, care must be taken to ensure that the spectrum being analyzed has been corrected for systematic measurement errors such as over-absorption effects [49, 50] and detector saturation [51]. These topics are beyond the scope of the present chapter, but must be considered in order to get meaningful results from EXAFS and XANES analysis. Here, a good measurement of $\mu(E)$ is simply assumed. The key steps for reducing $\mu(E)$ to “the EXAFS” $\chi(k)$ are shown, the EXAFS Fourier transform presented, and the analysis of the EXAFS equation, Eq. (2.2), to extract coordination numbers, distances, and atomic species of the near-neighbors of the absorbing element is discussed. Finally, a simple approach to

analysis of experimental XANES spectra in terms of linear components of model spectra is outlined. Many treatments [52–56] give more complete and detailed discussions of EXAFS and XANES analysis.

2.3.1 Data Reduction

For all XAFS data, whether measured in transmission or emission mode, the data reduction and analysis are essentially the same. First, the measured intensity signals are converted to $\mu(E)$, normalized to unity edge jump, and then reduced to $\chi(k)$. Normalized $\mu(E)$ is suitable for XANES analysis, while EXAFS modeling using the EXAFS equation requires background-subtracted $\chi(k)$. In this section, we go through these steps of data reduction in some detail.

For transmission measurements, the Beer–Lambert law

$$I = I_0 e^{-\mu t}, \quad (2.19)$$

can be used to convert measured intensities to a quantity proportional to the absorption coefficient, $\mu(E)$. Here I_0 is the X-ray intensity incident on a sample, I is the X-ray intensity transmitted through the sample, and t is the sample thickness. This can be rearranged (and t ignored as a constant) to give

$$\mu(E) = \ln\left(\frac{I_0}{I}\right). \quad (2.20)$$

Usually neither I_0 nor I is an absolute intensity by itself, but signals from ion chambers, photodiodes, or other detectors that are proportional to these intensities. Thus, it is customary to see experimental values reported for “raw” $\mu(E)$ in the literature that do not have dimensions of inverse length, but rather are proportional to $\mu(E)$ in inverse length. Since the $\mu(E)$ will be re-scaled early in the data reduction, this not a problem. For measurements made by detecting emission of the excited atom (including X-ray fluorescence, Auger, and optical luminescence), $\mu(E)$ is given as

$$\mu(E) = \frac{I_f}{I}, \quad (2.21)$$

where I_f is the emitted signal of interest. As with transmission measurements, there is no need to worry about getting absolute intensities, and one can use the ratio of measured intensities.

2.3.2 Pre-edge Subtraction and Normalization

The experimental $\mu(E)$ is reduced to a *normalized* $\mu(E)$, representing the absorption of one X-ray by the element and absorption edge of interest, for both XANES and EXAFS analysis. The resulting normalized $\mu(E)$ will have a value near 0 below the edge and be approximately 1 well above the edge. The first step in this process is to identify the edge or threshold energy, E_0 . Since chemical differences can easily move the threshold by several eV, and because calibrations vary between monochromators and beamlines by similar amounts, the most important feature of the E_0 identified at this point is consistency. Though a crude approximation with little theoretical justification, the most common approach is to take the maximum of the first derivative of $\mu(E)$. This is easily reproduced, and readily applied to any spectrum, but may require refinement during fitting of the EXAFS.

Instrumental drifts from detectors and the expected E^{-3} dependence of $\mu(E)$ can be approximated by a polynomial dependence of $\mu(E)$. As a first approximation, a simple linear fit to the pre-edge range of the spectrum can be extrapolated and subtracted from the full spectrum. A slightly better approximation is to fit to the so-called Victoreen pre-edge function, $E^n\mu(E)$, where n is typically 1, 2 or 3. This is especially helpful for data measured in fluorescence with a solid-state detector for dilute species, where elastic and Compton-scattered X-ray intensity can leak into the energy window of the fluorescence peak of interest, and where this leakage decays as the incident energy increases.

Finally, the edge step $\Delta\mu$ is found, and the pre-edge subtracted $\mu(E)$ is divided by this value. Typically, a low-order polynomial is fit to $\mu(E)$ well above the edge (so as to avoid the XANES region), and the value of this polynomial is extrapolated to E_0 to give the edge step. It should be emphasized that this convention is fairly crude and can introduce systematic biases in the result for $\Delta\mu$.

These steps are illustrated in Fig. 2.5 for transmission XAFS data at the Fe K -edge of FeO. For XANES analysis, this amount of data reduction is generally sufficient. For both XANES and EXAFS analysis, the most important part of these steps is the normalization to the edge step. For XANES analysis, spectra are generally compared by amplitude, so an error in the edge step for any spectrum will directly affect the weight given to it. For EXAFS, the edge step is used to scale $\chi(k)$, and so is directly proportional to coordination number. Good normalization (such that $\mu(E)$ goes to 1 above the edge) is generally not hard, but requires some care, and it is important to assess how well and how consistently this normalization process actually works for a particular data set. Most analysis packages do these steps reasonably well, especially in making spectral normalization consistent for similar datasets, but it is not unusual for such automated estimates of the edge step to need an adjustment of 10 %.

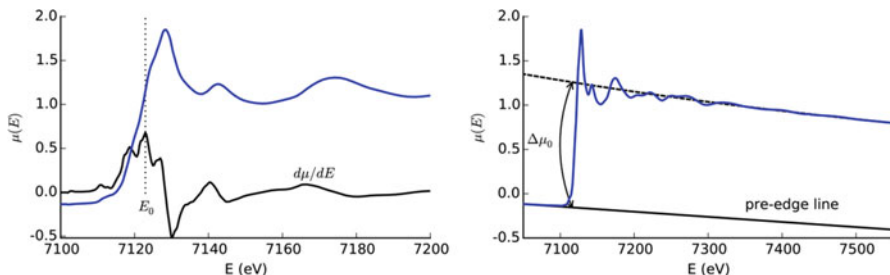


Fig. 2.5 *Left:* The XANES portion of the XAFS spectrum (blue), and the identification of E_0 from the maximum of the derivative $d\mu/dE$ (black). *Right:* XAFS pre-edge subtraction and normalization. A line or low-order polynomial is fit to the spectrum below the edge, and a separate low-order polynomial is fit to the spectrum well above the edge. The edge jump $\Delta\mu_0$ is taken as the difference between these two curves at E_0 . Subtracting the pre-edge polynomial from the full spectrum and dividing by the edge jump gives the normalized XAFS

2.3.3 Background Subtraction

In order to model the EXAFS with equation Eq. (2.2), the EXAFS $\chi(k)$ must be separated from the absorption coefficient, using

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu_0}. \quad (2.22)$$

Here, $\mu_0(E)$ represents the absorption coefficient of the absorbing atom without photoelectron scattering from the neighboring atoms, and $\Delta\mu_0$ is the edge step. Since $\mu_0(E)$ cannot be measured readily (if at all), it is approximated mathematically. Usually a piece-wise polynomial or *spline* is used for $\mu_0(E)$. While an ad hoc approach, and capable of being abused, this can be made robust with a small amount of care. The main challenge is to decide how flexible the spline should be, so as to ensure that it does not follow $\mu(E)$ closely enough to remove the EXAFS. That is, $\mu_0(E)$ should follow the slowly varying parts of $\mu(E)$ but not $\chi(E)$, which varies more quickly with E .

A simple approach that works well for most cases relies on the Fourier transform to mathematically express this idea that $\mu_0(E)$ should match the slowly varying parts of $\mu(E)$ but not the quickly varying parts of $\mu(E)$. The Fourier transform is critical to EXAFS analysis, and will be discussed in more detail shortly, but for now the most important point is that it gives a weight for each frequency making up a waveform. The EXAFS Fourier transform converts χ from wavenumber k to distance R .

For determining the background $\mu_0(E)$, the spline function should remove the low- R components of χ , while retaining the high- R components. Conveniently, distinguishing “low- R ” from “high- R ” can be made physically meaningful using the approximate distance to the nearest neighboring atom. As a realistic rule of thumb,

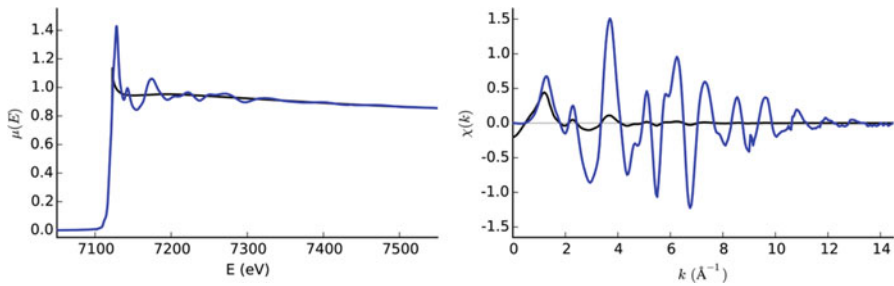


Fig. 2.6 *Left:* Background subtraction for Fe K-edge EXAFS of FeO. A smooth spline function (black) that matches the low- R components of $\mu(E)$ (blue), in this case using $1 \text{ \AA}$ for R_{bkg} , is used to approximate $\mu_0(E)$. *Right:* the EXAFS $\chi(k)$ (black) isolated after background subtraction. The EXAFS decays quickly with k , and weighting by k^2 (blue) amplifies the oscillations at high k

atoms are rarely closer together than about $1.5 \text{ \AA}$ —this is especially true for the heavier elements to which EXAFS is usually applied. Thus, a spline can be used for $\mu_0(E)$ that makes the resulting χ have as little weight as possible below some distance R_{bkg} (typically, $1 \text{ \AA}$), while ignoring the higher R components of χ . While this approach [57] is not always perfect, it can be applied easily to any spectrum and has some physically meaningful basis. Figure 2.6 shows a typical background spline found for FeO, using a R_{bkg} of $1.0 \text{ \AA}$, and the resulting $\chi(k)$.

2.3.4 EXAFS Fourier Transforms

The Fourier transform is central to the understanding and modeling of EXAFS data. While many resources describe Fourier transforms and their properties, a few important points about the use of Fourier transforms for EXAFS are made here. Figure 2.7 illustrates the EXAFS Fourier transform for the Fe K-edge data of FeO shown in Fig. 2.6. Two peaks are clearly visible below $3 \text{ \AA}$, corresponding to the Fe–O and Fe–Fe distances in the rock-salt structure of FeO. Thus the Fourier transformed EXAFS separates different coordination spheres around the absorbing atom.

In Fig. 2.7, $|\chi(R)|$ almost looks like a radial distribution function, $g(R)$. While EXAFS does depend on the partial pair distribution—the probability of finding an atom at a distance R from an atom of the absorbing species—it must be emphasized that $|\chi(R)|$ is not a pair distribution function. This can be seen from the additional parts to the EXAFS equation, including the non-smooth k dependence of the scattering factor $f_{\text{eff}}(k)$ and phase-shift $\Phi(k)$. An important feature of $\chi(R)$ is that the positions of the peaks are shifted to lower R from the interatomic distances of $g(R)$. For FeO, the first main peak occurs at $1.6 \text{ \AA}$, while the FeO distance in FeO is $\sim 2.1 \text{ \AA}$. This is not an error, but is due to the scattering phase-shift—recall that the EXAFS goes as $\sin[2kR + \Phi(k)]$. For most systems involving single-scattering, $\Phi(k) \sim -k$ is a

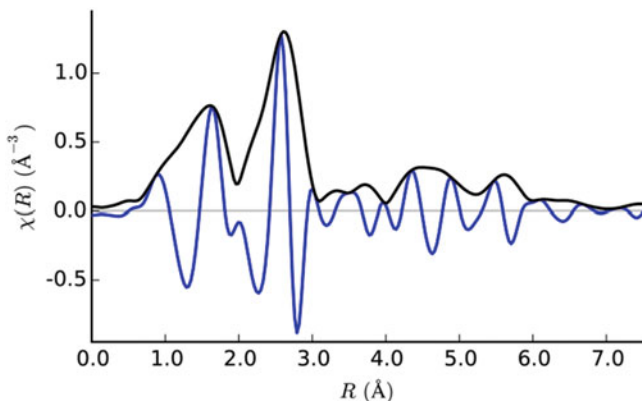


Fig. 2.7 The XAFS Fourier Transform, $\chi(R)$. The magnitude $|\chi(R)|$ (black) is the most common way to view the data, showing peaks corresponding to scattering from neighboring atoms. The Fourier transform $\chi(R)$ is a complex function, with both a real (blue) and imaginary parts

decent if crude approximation to the phase-shift, which gives a shift to the peaks in $\chi(R)$ of $-0.5 \text{ \AA}$ or so relative to the actual interatomic distances.

The Fourier transform is inherently complex, and gives a complex function for $\chi(R)$ even though $\chi(k)$ is a strictly real function. It is common to display only the magnitude of $\chi(R)$ as shown in solid in Fig. 2.7, but the real (blue) and imaginary components contain important information that cannot be ignored when modeling EXAFS. In contrast to the standard form, the Fourier transform for EXAFS analysis uses conjugate variables of k and $2R$, reflecting the EXAFS equation. For numerical analysis, a discrete Fast Fourier transform is used. The data must be interpolated onto a uniformly spaced set of values in k . Typically, a spacing of $\delta k = 0.05 \text{ \AA}^{-1}$ and an array size of $N = 2048$ k values are used. This gives a spacing of R points in the discrete $\chi(R)$ of $\delta R \approx 0.0307 \text{ \AA}$.

Prior to the transform, $\chi(k)$ is usually multiplied by a power of k , typically k^2 or k^3 , as shown in Fig. 2.6. This weighting helps compensate for the strong decay with k of $\chi(k)$. In addition, $\chi(k)$ is multiplied by a window function $\Omega(k)$ which smooths the resulting $\chi(R)$ and removes ripples and ringing that would result from a sudden truncation of $\chi(k)$ at the ends of the data range. Since Fourier transforms are used in many fields, there is an extensive literature on such window functions and many choices available in most EXAFS analysis packages.

In many analyses, the inverse Fourier transform is used to select a particular R range and transform this back to k space, *filtering* out most of the spectrum and leaving only a narrow band of R values in the resulting filtered $\chi(k)$. This can isolate the EXAFS signal for a single shell of physical atoms around the absorbing atom, and was the basis of most early EXAFS analyses. This approach should be used with caution since, for all but the simplest of systems, it can be surprisingly difficult to effectively isolate the EXAFS contribution from an individual scattering atom

this way. It is almost never possible to isolate a second neighbor coordination sphere in this way. For this reason, many modern analyses of EXAFS will use a Fourier transform to convert $\chi(k)$ to $\chi(R)$, and use $\chi(R)$ for data modeling, without trying to isolate shells of atoms.

2.3.5 XAFS Data Modeling

The FeO data shown above is convenient to illustrate many aspects of EXAFS data modeling. FeO has a simple rock salt structure, with Fe surrounded by 6 O, with octahedral symmetry, and then 12 Fe atoms in the next shell. Starting with this simple structure, the scattering amplitudes $f_{\text{eff}}(k)$ and phase-shifts $\Phi(k)$ can be calculated theoretically using the FEFF formalism described above. These theoretical scattering factors (along with a calculation of the mean free path λ_k) can be used in the EXAFS equation to refine structural parameters R , N , and σ^2 to match a set of data. Typically, E_0 (the energy for which $k = 0$) is also adjusted to best match data, to compensate for the crude estimate made in the initial processing. While one can do the refinement with the measured $\chi(k)$, working with the complex $\chi(R)$ is generally preferred, as higher coordination shells can be selectively ignored. The examples shown here are done with the FEFF6 [2, 58] program to construct the theoretical factors, and the IFEFFIT [59–61] package to do the analysis. Some aspects of the analysis shown here may depend on details of these particular programs, but similar results can be obtained with any of several EXAFS analysis programs.

2.3.6 Running and Using FEFF for EXAFS Calculations

In order to calculate the $f_{\text{eff}}(k)$ and $\Phi(k)$ needed for the analysis, the FEFF program [58] uses a cluster of atoms, builds atomic potentials from this, and simulates a photoelectron with a particular energy being emitted by a particular absorbing atom and propagating along a set of scattering paths [62]. As detailed above, FEFF includes many subtle but quantitatively important effects. Because one starts with a cluster that represents the atomic structure, the FEFF fitting process is a *refinement* of the path lengths and coordination numbers for those paths. Conveniently, FEFF breaks up the results in a way that can be put into the standard form of the EXAFS equation, even for multiple-scattering paths. This allows analysis procedures to easily refine distances, apply multiplicative factors for coordination numbers and S_0^2 , and apply disorder terms. Because the outputs have a uniform format, results from different runs of the programs can readily be mixed, which is important for modeling complex structures with multiple coordination environments for the absorbing atom.

2.3.7 First-Shell Fitting

To model the first shell EXAFS of FeO, a simulation of the EXAFS for the Fe–O scattering path is calculated by FEFF from a cluster derived from the known crystal parameters for FeO. Setting S_0^2 to 0.75, values for N , R , σ^2 , and E_0 are refined until the model for χ best matches the complex $\chi(R)$ of the measured data. The results of this refinement are shown in Fig. 2.8, with best-fit values and estimated uncertainties for the refined parameters given in Table 2.1. These values are not perfect for crystalline FeO, especially in that the distance is contracted from the expected value of 2.14 Å, but they are reasonably close for a first analysis.

It is instructive to look at this refinement more closely and discuss a few details. The refinement was done on the $\chi(R)$ data, after a Fourier transform of $k^2\chi(k)\Omega(k)$ for both data and model, where $\Omega(k)$ represents a Hanning window with a range between $k = [2.5, 13.5]$ Å^{−1}, and with a dk parameter of 2 Å^{−1}. Both real and imaginary components of $\chi(R)$ between $R = [1.0, 2.0]$ Å were used. Figure 2.8 shows that the higher frequency components from the second shell of Fe–Fe dominate $k^2\chi(k)$. This is a useful reminder of the power of the Fourier transform in XAFS analysis: it allows one to ignore shells of higher frequency even if they have larger overall amplitude.

The refinement used a nonlinear least-squares fit to minimize a standard statistical definition for the chi-square statistic

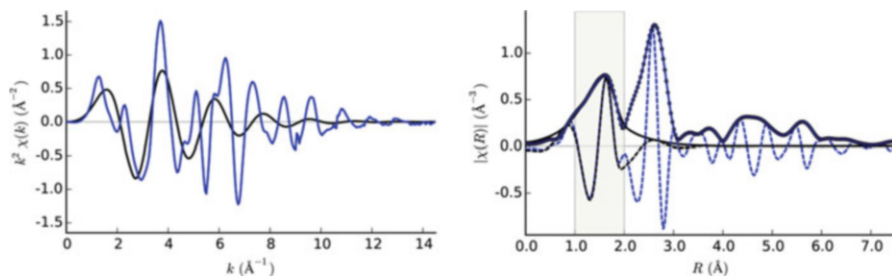


Fig. 2.8 First shell fit to EXAFS for FeO. *Left*: XAFS $k^2\chi(k)$ for data (blue) and best-fit model (black). *Right*, the real (dashed) and magnitude (solid) components of $\chi(R)$ for the data (blue) and best-fit model (black). The fitting range of $R = [1.0, 2.0]$ Å is highlighted, showing that the model matches the data very well

Table 2.1 Best values and uncertainties (in parentheses) for the refined first shell parameters for FeO. The refinement fit the components of $\chi(R)$ between $R = [1.0, 2.0]$ Å after a Fourier transform using $k = [2.5, 13.5]$ Å^{−1}, a k -weight of 2, and a Hanning window function. S_0^2 was fixed to 0.75

Shell	N	R (Å)	σ^2 (Å ²)	ΔE_0 (eV)
Fe–O	5.5(0.6)	2.10(0.01)	0.015(.002)	−3.4(1.1)

$$\chi^2 = \sum_i^{N_{\text{data}}} \frac{[y_i^{\text{data}} - y_i^{\text{model}}(x)]^2}{\varepsilon^2}, \quad (2.23)$$

where y_i^{data} is the experimental data, $y_i^{\text{model}}(x)$ is the model constructed from the EXAFS equation and the variable fitting parameters x , ε is uncertainty in the data, and N_{data} is the number of points being fit. As mentioned above, the real and imaginary components of $\chi(R)$ were used as y for both data and model, though fitting to $k^2\chi(k)$ data is not uncommon. A crude estimate of ε can be made from the high frequency noise in $\chi(k)$ [63]. Historically, the problem of identifying N_{data} has been controversial. For any signal, the Nyquist–Shannon sampling theorem gives the resolution R (the smallest detectable difference in distances) based on k_{max} , the maximum measured value of k , as $\delta R = \pi/2k_{\text{max}}$. From this, it follows [64, 65] that the maximum number of independent measurements that can be extracted from an EXAFS spectrum is

$$N_{\text{ind}} \approx \frac{2\Delta k \Delta R}{\pi} + 1, \quad (2.24)$$

where Δk and ΔR are the range of useful data in k and R . For the first shell of FeO with $k = [2.5, 13.5] \text{ \AA}^{-1}$ and $R = [1.0, 2.0] \text{ \AA}$, this gives $N_{\text{ind}} \approx 8$. The number of variables in a fit should not exceed this value.

2.3.8 Second-Shell Fitting

Including the second shell in the model for the FeO EXAFS involves adding the path for Fe–Fe scattering to the sum in the EXAFS equation. Variables for R , N , and σ^2 for the Fe–Fe shell will be included, while a single value for E_0 will be used for both the Fe–O and Fe–Fe paths. The fit range will be extended to $R = [1.0, 3.1] \text{ \AA}$, increasing N_{ind} to ≈ 15.7 , while the number of variables increases to 7. Results for this fit are shown Fig. 2.9 and Table 2.2. The structural values for distances and coordination number are consistent with the known crystal structure of FeO, though the Fe–O distance is a bit shorter than expected, and the Fe–Fe is a bit longer than expected, both suggesting that there may be some contamination of a ferric iron phase in the sample. Figure 2.9 shows the fit to be quite good, especially in the real part of $\chi(R)$, which is actually used in the fit. Figure 2.10 shows the individual contributions to the total best-fit spectrum. In k -space, the contribution from Fe–Fe is seen to have a shorter period than Fe–O due the longer interatomic distance. In addition, the Fe–Fe contribution persists to higher k due to the dependence of $f_{\text{eff}}(k)$ on Z of the scatterer. In R -space, substantial overlap can be seen between the two shells, even though there is a strong dip in $|\chi(R)|$ at $2 \text{ \AA}$. Indeed, the inclusion of the Fe–Fe shell did subtly alter the best-fit results (though within the estimated uncertainty) for the Fe–O shell.

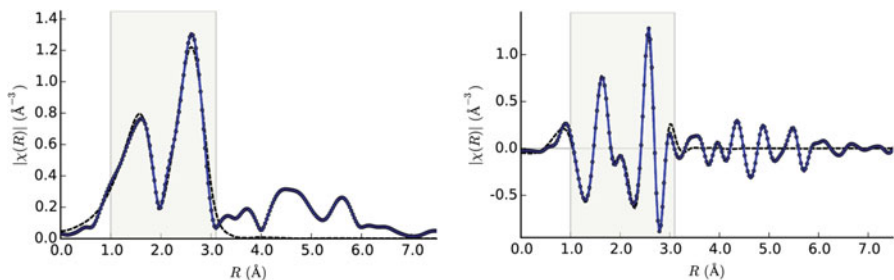


Fig. 2.9 EXAFS $|\chi(R)|$ (left) and $\text{Re}[\chi(R)]$ (right) for FeO data (blue) and best-fit model (black) for the first two shells around Fe, including Fe–O and Fe–Fe scattering paths. The fitting range of $R = [1.0, 3.1]\text{Å}$ is highlighted

Table 2.2 Best fit values and uncertainties (in parentheses) for the Fe–O and Fe–Fe shells for FeO. The refinement fit of $\chi(R)$ between $R = [1.0, 3.1]\text{Å}$ with all other parameters as in Table 2.1

Shell	N	R (Å)	σ^2 (Å ²)	ΔE_0 (eV)
Fe–O	5.4(0.7)	2.11(0.01)	0.013(.002)	−1.5(0.6)
Fe–Fe	12.6(1.4)	3.07(0.01)	0.015(.001)	−1.5(0.6)

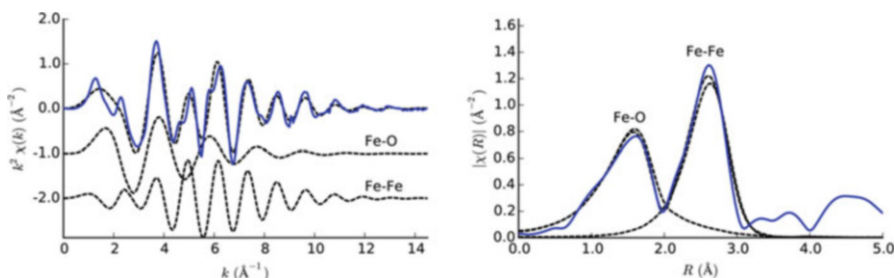


Fig. 2.10 Contributions of the first and second shell to the model for the FeO EXAFS. Left: the fit (black) matches the data (blue) in k -space much better than in Fig. 2.8. Right: the fit (black) and data (blue) for $|\chi(R)|$. In both, contributions from the Fe–O and Fe–Fe shells are shown in dashed lines

2.3.9 XANES Analysis

As discussed in Sect. 2.2.6, XANES is uniquely sensitive to oxidation state, coordination chemistry, and the partial density of unoccupied electronic states, and XANES spectra are much richer in spectral features than EXAFS, making it an excellent spectroscopic technique for almost every element [66]. Unfortunately, the EXAFS equation breaks down at low k , where λ_k diverges, so that a huge number of scattering paths contribute. With no readily parameterized XANES equation, quantitative XANES analysis has traditionally relied on fitting idealized

peak-shapes to spectral features or matching spectra to linear combinations of spectra from known systems. These approaches are reasonably well justified in many specific cases, but are not easy to generalize. Some work [67, 68] has been done to try adapt a suite of calculations to best-match experimental data using a reverse Monte-Carlo approach, which has the advantage of being able to use both the XANES and EXAFS portions of a spectrum, but is computationally slow. In the soft X-ray regime, and for certain 3d metal pre-edge peaks, quantitative analysis based on multiplet analysis is also robust and very useful for assigning electronic transitions [69].

Although the XANES cannot be numerically parameterized in terms of oxidation state or coordination chemistry, these can be determined using simpler spectroscopic analysis methods. For example, the pre-edge peaks in the K and L edges of 3d metal are very rich at identifying coordination chemistry and hybridization of electronic levels, even if the precise intensities of the different transitions is complicated to calculate accurately. To make analysis quantitative, fitted intensities of such peaks can be compared to calibration curves made from spectra of known materials. While such analysis is not *ab initio*, it can be robust and reliable with minimal effort. As an illustration of such XANES peak analysis, the left-hand side of Fig. 2.11 shows the pre-edge peaks of Fe_2O_3 , and a fit to this edge structure using several peaks—in this case 3 separate Voigt functions and one error function. These peaks can be assigned as the atomic-like multiplet orbitals, and the 1s-4p transition. When applied over a range of experimental compounds, clear trends emerge and the XANES peak intensities can give excellent precision in oxidation state [70–72].

A second common approach to XANES analysis is to treat the spectra as a signature or fingerprint of a material, and determine the fractional composition of

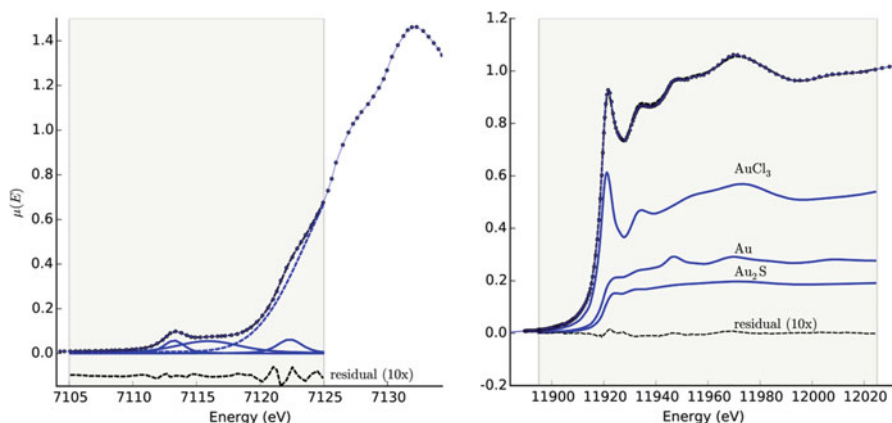


Fig. 2.11 *Left:* XANES pre-edge peak fit (black) for the Fe K edge data (blue dots) of Fe_2O_3 , over the shaded fit range of $E = [7105, 7125]\text{eV}$. The fit used three Voigt peaks (blue, solid) and an error function (blue, dashed). The fit residual (black), has been multiplied by 10, and offset. *Right:* XANES fit of an unknown Au LIII-edge spectrum to a linear combination of spectra from model compounds (gold chloride, metal, and sulfide), with contributions of individual components (blue) and the fit residual. After Lengke et al. [76]

spectra from well-characterized materials. This approach uses simple linear statistical analysis, and so can build on a wide literature, including Principal Component Analysis [73] and related methods [74, 75]. As an illustration, the L_{III} -edge XANES spectrum of an experimental gold compound [76] is shown on the right-hand side of Fig. 2.11, along with the weighted components used to fit the spectrum. This approach relies heavily on the use of the correct components, and care must be taken to ensure that standard spectra are correctly calibrated in energy and normalized in intensity.

2.4 Theoretical Modeling of EXAFS and XANES

2.4.1 Introduction

The great success of EXAFS and XANES stems from the insights they provide into the atomic and electronic structure of complex materials. This has been especially important for catalytic systems, as discussed elsewhere in this volume. As shown in the previous sections, this success was aided in part by the development of robust theoretical methods to simulate a broad range of X-ray spectroscopies [1, 2, 19]. Although these methods have often been highly successful, a limitation is that the accuracy of the predicted spectra depends on the quality of the structural models used in the simulations. This is particularly important in XANES simulations. In the past, this drawback has been sidestepped by either the use of known crystallographic information, or by a combination of EXAFS modeling and chemical know-how of the nature of the material in order to build more complete structural models [77]. In recent decades, however, materials research has begun to focus on complex materials under *operando* or extreme conditions. Typical examples of these types of systems are supported nanocatalysts [40, 42, 78], solvated ions [41], and shocked materials. Reliable simulations under those conditions require more sophisticated models that capture the heterogeneous nature of the materials. Thus, the field of XAS modeling has recently progressed towards the interfacing of spectroscopy codes with existing software for calculations of structural and electronic properties [6]. In the following sections we present a few examples that highlight the power of this blend of spectroscopy, materials science, condensed matter physics and quantum chemistry methods.

2.4.2 Use of Modeling to Enhance EXAFS Analysis

While the fitting of EXAFS spectra using theoretical scattering amplitudes and phase-shifts is now a well-established methodology, the calculation of other parameters of the EXAFS equation, Eq. (2.2), such as path lengths, number of

near-neighbors N_R and mean-square relative displacements (MSRD) σ_R^2 have only recently become feasible on a routine basis. While many theoretical methods lack the accuracy needed to rival fitted EXAFS path lengths, they may be well suited to distinguish between alternative conformations, and provide good approximations to both the N_R and σ_R^2 , thus making the fitting of the path lengths much more reliable in many complicated materials. In this section we discuss two ways in which theoretical modeling can enhance EXAFS fits: First, we focus on the calculation of ab initio Debye–Waller factors for systems where σ_R^2 can be described well using a combination of static and vibrational disorder. Second, we highlight the simulation of EXAFS spectra for systems with large dynamic disorder.

2.4.2.1 Ab Initio Debye–Waller Factors

The theory behind MSRDs or XAFS Debye–Waller factors and how to compute them ab initio is now fairly well established [79–82]. Briefly, the MSRD or σ_R^2 for a path R is defined by the thermal average:

$$\sigma_R^2 = \langle (R - \bar{R})^2 \rangle, \quad (2.25)$$

where R and $\bar{R}$ are the instantaneous and mean path lengths, respectively. In the quasi-harmonic approximation, the average can be computed as a sum over vibrational or phonon eigenmodes [81] or, alternatively, in terms of the projected vibrational density of states $\rho_R(\omega)$ or VDOS, and the Debye integral

$$\sigma_R^2(T) = \frac{\hbar}{2\mu_R} \int_0^\infty \frac{1}{\omega} \coth\left(\frac{\beta\hbar\omega}{2}\right) \rho_R(\omega) d\omega, \quad (2.26)$$

where μ_R is the reduced mass for path R . Poiarkova and Rehr [79, 80] have shown that the VDOS can be calculated efficiently from the imaginary part of the lattice dynamical Green’s function matrix element:

$$\rho_R(\omega) = -\frac{2\omega}{\pi} \text{Im} \langle 0 | \frac{1}{\omega^2 - \mathbf{D} + i\varepsilon} | 0 \rangle \cong \sum_{v=1}^N w_v \delta(\omega - \omega_v). \quad (2.27)$$

Here $|0\rangle$ is a vector representing a normalized mass-weighted displacement of the atoms along the multiple-scattering path R . Efficient calculations of the lattice dynamical Green’s function can be accomplished using a continued fraction representation obtained with the iterative Lanczos algorithm that yields an N -pole representation for the VDOS where ω_v and w_v are, respectively, the pole frequencies and weights of pole v . $\mathbf{D}$, the dynamical matrix of force constants, or Hessian, is the main ingredient required for the calculation of theoretical MSRDs and is defined as:

$$D_{jl\alpha,j'l'\beta} = (M_j M_{j'})^{-1/2} \frac{\partial^2 E}{\partial u_{jl\alpha} \partial u_{j'l'\beta}}, \quad (2.28)$$

where $u_{jl\alpha}$ and M_j are the $\alpha = \{x, y, z\}$ Cartesian displacement and mass of atom j in unit cell l , respectively, and E is the internal energy of the system. For molecular systems, $\mathbf{D}$ is routinely computed with quantum chemistry packages like Gaussian [83], NWChem [84], and ORCA [85], and the accuracy of different methods is well-established [86, 87]. For solids, the dynamical matrix can be computed, e.g., using ABINIT [88–90], VASP [91], and Quantum Espresso [92]. The MSRDS can be extracted from the output of these and other programs by using interface programs included in FEFF [6] and used directly to replace the values provided by phenomenological Einstein or Debye models. A typical example of the quality of the results that can be obtained for molecular ion complexes such as the one shown in Fig. 2.12 are presented in Table 2.3. The $\text{Ru}(\text{bpy})_2(\text{AP})(\text{H}_2\text{O})^{++}$ complex was optimized and its Hessian calculated using the B3LYP exchange correlation functional, while using the SDD effective core potential and associated basis sets for all atoms. The agreement between the experimental [93] and theoretical coordination

Fig. 2.12 Structure of $\text{Ru}(\text{bpy})_2(\text{AP})(\text{H}_2\text{O})^{++}$ highlighting the near-neighbor sites used for computing the MSRDS shown in Table 2.3

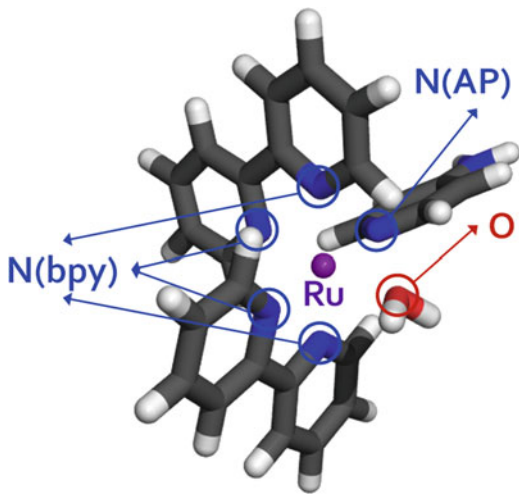


Table 2.3 Comparison between the experimental [93] and theoretical near-neighbor distances and MSRDS (σ^2) for the $\text{Ru}(\text{bpy})_2(\text{AP})(\text{H}_2\text{O})^{++}$ complex shown in Fig. 2.12

Path	$R_{\text{M-L}}$ (in Å)		σ^2 (in 10^{-3} Å^2)	
	Theory	Expt.	Theory	Expt.
	2.08		2.49	
	2.04		2.32	
Ru-N (bpy)	2.10	2.05 ± 0.01	2.60	2.6 ± 0.9
	2.09		2.50	
Ru-N (AP)	2.14	2.10 ± 0.03	2.61	4 ± 3
Ru-O	2.22	2.06 ± 0.05	4.93	9 ± 7

distances for the tightly bound N near-neighbors is good, despite being slightly outside the EXAFS error bars. For the weakly bound water molecule, the theoretical distance is slightly overestimated, but still reasonable.

The agreement for the MSRDS (σ^2) is quite good and, given the error margins from the EXAFS fit, could be used “as is” in the EXAFS fit to replace the fitted values. In particular, the theoretical results provide a good alternative for the weaker bonds, where the EXAFS-fitted values have large uncertainties.

In practice, however, a better approach may be to set up a fitting model where the near-neighbor MSRDS are scaled by a single parameter. This approach is quite useful for systems with mixed coordination shells with different MSRDS where the number of EXAFS parameters becomes large and highly correlated.

2.4.2.2 Simulating EXAFS of Dynamic Systems

The standard approach to vibrational disorder in EXAFS assumes that the local environment surrounding the absorbing atom is relatively rigid, with small distortions that are harmonic, thus resulting in an approximately Gaussian pair distribution function [22]. Although broadly applicable, this approach can give poor results for systems like ions in solution or liquid materials, where the bonds between the absorber and its near-neighbors are continuously breaking and reforming. In such cases using an optimized structure plus vibrations is not sufficient, and an explicit sampling over the dynamical fluctuations is needed. A method of choice to obtain this sampling is molecular dynamics (MD) in conditions of temperature, pressure, and concentration that closely resemble those used in the experiments. MD simulations rely on the calculation of atomic forces that can be computed based on either model or ab initio potential energy surfaces [94, 95]. The former results in very efficient calculations, but have the drawback of requiring the parameterization of a model potential that might or might not be transferable to other systems and conditions. The latter, on the other hand, can be applied to a very broad range of conditions although at a very high computational cost. Both approaches have been applied successfully to the simulation of ions in solution [96, 97]. For example, Fulton et al. [41] have demonstrated near-quantitative prediction of EXAFS spectra for charged transition metal ions in solution. Figure 2.13 shows the module and imaginary parts of the real-space fine structure for Cr^{+3} in aqueous solution, compared to theory. The theoretical results were obtained from FEFF simulations using conformations sampled from a QM/MM MD simulation. Remarkably, these simulations do not include any type of experimental parameter and the thermal broadening of the distribution arises naturally from the averaging.

2.4.3 Use of Modeling to Enhance XANES Analysis

The theoretical modeling of XANES spectra poses bigger challenges than that of EXAFS due to two main reasons: (a) It demands more computationally intensive

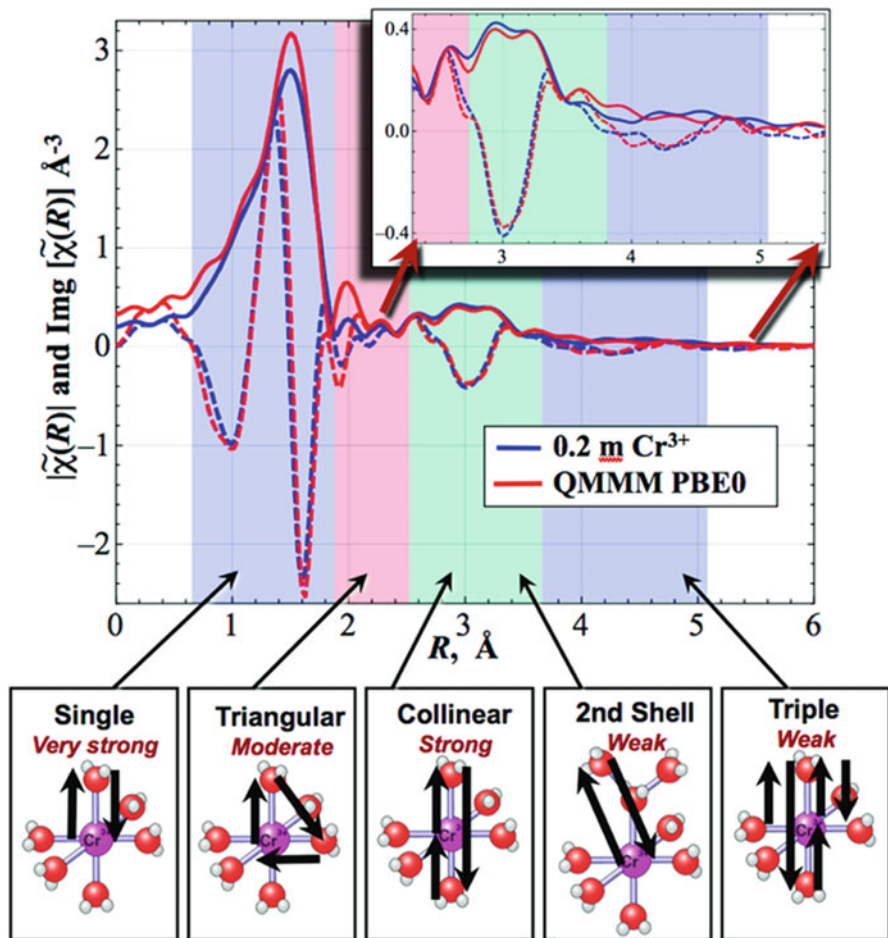


Fig. 2.13 k^2 -weighted $|\tilde{\chi}(R)|$ (solid lines) and $\text{Im}[\tilde{\chi}(R)]$ (dashed lines) for hydrated Cr^{3+} . The highlighting of different spectral regions shows the assignments to different types of single and multiple scattering events, as illustrated. The inset expands the view for the longer multiple scattering region (Reproduced with permission from Ref. 41)

simulations and, (b) generally there is incomplete information about the structure of the system under study. These two aspects result in the need for theoretical generation of structural models by means of optimizations or MD simulations. As in the case of EXAFS, the former are quite useful for quasi-rigid systems, while the latter are required for systems with dynamic fluctuations and bond-breaking. As opposed to EXAFS, XANES spectra are often less sensitive to the quality of the structural model, thus permitting the direct use of theoretical structures in the simulations. The advent of accurate and efficient DFT simulations has virtually eliminated the need to guess possible structures since one can now optimize accurate models based on simple external information such as composition

[98, 99]. Moreover, one can also take advantage of other information resulting from simulations such as thermodynamic properties, charge distribution (see below), and vibrational properties (see discussion on MSRDS above). In light of the current trend towards multi-spectroscopy, *operando* experimental approaches [100], this broad range of theoretical properties facilitates a more holistic interpretation of the experimental results. In the following sections we focus on two aspects of theoretical modeling of XANES. First, we discuss the importance of including dynamical disorder in XANES simulations to be able to reproduce experiment. Second, we focus on the enhanced understanding that emerges from the atomistic information provided by simulations.

2.4.3.1 Effects of Dynamical Disorder on XANES

As in the case of EXAFS, dynamic structural disorder plays a very important role in the accurate simulation of XANES [40, 78, 100]. For systems where the experiment naturally samples a large number of conformations, the XANES simulations must usually include similar sampling to be able to reproduce experiment. The most common way to do structural sampling theoretically is by means of molecular dynamics simulations over a suitable time-frame. These simulations can rely on model potential energy surfaces, as discussed for EXAFS above, or on *ab initio* DFT potentials (i.e., DFT/MD). In practice, the former is quite efficient and provides a good understanding of the structural properties for systems with a mixture of covalent and soft interactions. But, for other examples of dynamic systems with metallic bonds such as supported metal clusters, the use of DFT/MD is highly recommended. This approach also has the added bonus of providing very useful information about the electronic structure of the material. A classic example of this type of problem is the case of Pt and PtSn nanoclusters on γ -Al₂O₃ [40, 42], where modeling is needed to understand their intra-particle heterogeneity and their structural and electronic changes under realistic conditions. DFT/MD simulations reveal that the nanoscale structure and charge distribution are inhomogeneous and dynamically fluctuating over several time-scales, ranging from fast (200–400 fs) bond vibrations to slow fluxional bond breaking (>10 ps). To help visualize this fluctuating behavior, Fig. 2.14 shows an average of snapshots extracted from the MD simulations at two different temperatures. At low temperature (165 K), the cluster “rocks” over the surface. While mostly maintaining its shape, it is clearly less rigid than the surface. At high temperature (the catalyst *operando* temperature of 573 K), however, the cluster becomes highly fluxional due to the large number of bond-breaking events and is capable of diffusing over the surface.

The effects of the dynamic disorder on the XANES are very significant. Figure 2.15 shows a comparison between the experimental XANES spectra and those obtained from MD and Boltzmann sampling of the conformations. Despite the large fluctuations indicated by the standard deviation bars, the MD-sampled spectra are in very good agreement with experiment, capturing both the enhancement of the white line at high temperatures and the red shift of the edge. In contrast, the spectra

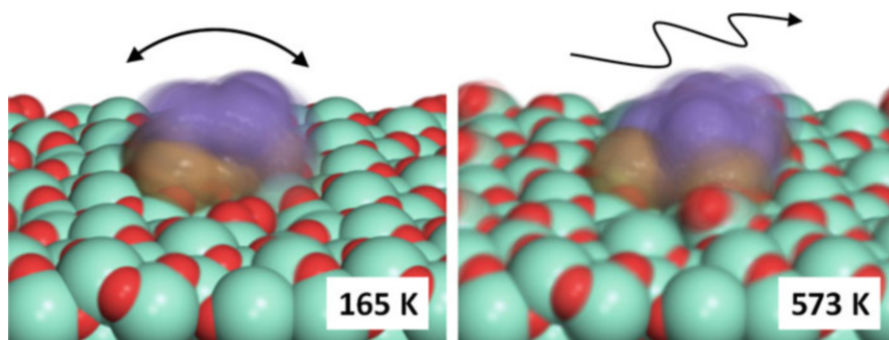


Fig. 2.14 Average image showing the dynamic behavior of Pt_{10} on $\gamma\text{-Al}_2\text{O}_3$ generated from snapshots of MD simulations at 165 and 573 K where the “blurriness” of the atoms indicate their mobility. The gold and purple spheres indicate Pt atoms that are oxidized ($+\delta$) or reduced ($-\delta$), while the red and teal ones represent the O and Al atoms, respectively. At 165 K, the cluster rocks on the same surface site while at 573 K it moves over the surface

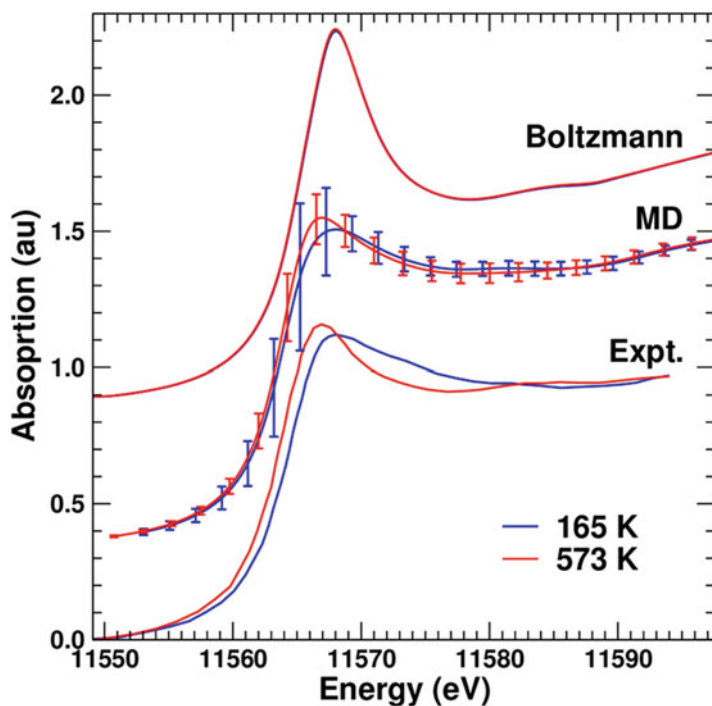


Fig. 2.15 Pt K edge XANES spectra for Pt_{10} on $\gamma\text{-Al}_2\text{O}_3$. The MD results were generated by averaging over conformations sampled from 6 ps runs and the error bars indicate the standard deviation of the spectrum. For comparison, results are also shown for a Boltzmann-average over conformations obtained by quenching the same MD samples

obtained from the Boltzmann-average of quenched conformations show little difference between both temperatures, and severely overestimate the intensity of the white line. The main difference between the MD and quenched conformation samplings stems mainly from the important role played by breaking and reforming bonds.

2.4.3.2 Understanding Electronic Structure Changes Through Modeling

Perhaps one of the most useful features of theoretical modeling is the possibility of directly visualizing atomistic changes in electron density distribution. This is particularly important since global probes such as EXAFS and XANES reveal the ensemble characteristics of materials while missing details of their internal structure. Moreover, changes in spectral features such as edge position and white line intensity that are commonly associated with charge density fluctuations in a qualitative way can be studied quantitatively and in detail. An excellent example of the atomistic understanding that is gained through modeling arises again in the case of Pt₁₀ on γ -Al₂O₃ [40]. Figure 2.14 shows that the cluster is roughly separated into two layers, with one layer in contact with the surface (golden spheres) and another resting on top (purple spheres). The atoms in the contact layer become positively charge or “oxidized,” while the others are neutral or slightly negatively charged (“reduced”). The MD simulations show that at high temperature, the number of contacts with the surface increases, thus removing more charge from the cluster which results in the expected red shift in the absorption edge position and increase in the white line intensity. Moreover, these charge fluctuations can be correlated with other observed trends such as negative thermal expansion in Pt clusters [40], and species segregation and differential reactivity in PtSn alloy clusters [42, 78]. This detailed atomistic understanding can only be achieved through the close integration of modeling and experiment.

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