Chapter 2

XAFS THEORY, EXPERIMENTATION AND DATA ANALYSIS

The basic physical quantity that is measured in X-ray Absorption Fine Structure (XAFS) spectroscopy is the X-ray absorption coefficient $\mu(E)$, which describes the probability of X-rays being absorbed as a function of incident X-ray energy $E$. Generally $\mu(E)$ smoothly decreases as the energy increases (approximately as $1/E^3$), i.e. the X-rays become more penetrating. However, at specific energies that are characteristic of the atoms in a material, the absorption co-efficient increases rapidly and these discontinuities are called X-ray absorption edges. These occur when the incident X-ray photon has sufficient energy to knock out electrons from the low-energy bound states in the atoms. The X-ray absorption cross section, a quantity that is proportional to $\mu(E)$, is shown in Fig. 2.1 for different elements.

Figure 2.1 Variation of X-ray absorption cross section with incident photon energy.
Absorption edges were first measured in 1913 by Maurice De Broglie. In 1920, using M. Siegbahn’s vacuum spectrograph, Hugo Fricke first observed the “fine structure”– energy-dependent variations in the $\mu(E)$ – in the vicinity of the X-ray absorption edges of a number of elements. An example is shown in Fig. 2.2.

![X-ray Absorption fine structure spectrum.](image)

Figure 2.2 X-ray Absorption fine structure spectrum.

Despite some early successes and intermittent progress, the correct theoretical explanation of XAFS eluded researchers for another five decades. In particular, a controversy existed as to whether a model based on the long-range order (LRO) or short-range order (SRO) in the sample was more accurate. This confusion was removed around 1970 when Stern, Sayers, and Lytle [4], [5], [9], [10] formulated a viable theory of XAFS, and further demonstrated that XAFS could be a practical tool for local structure determination.

The term “XAFS” is a broad one that comprises several different techniques: EXAFS (Extended X-ray Absorption Fine Structure); XANES (X-ray Absorption Near Edge Structure); NEXAFS (Near Edge XAFS, which is basically XANES in the soft X-ray regime); and SEXAFS (Surface EXAFS). Although the basic physics of these techniques is
fundamentally the same, different approximations, techniques, terminology, and theoretical approaches are employed in different situations, particularly in the low-energy (soft X-ray) and high-energy (hard X-ray) regimes.

2.1 Development of EXAFS equation

In 1931-32, Kronig [1]–[3] first attempted to explain EXAFS and germinated the idea of a short range theory for diatomic molecules which came to be known as short range order (SRO) theory. It had the basic physics of the modern theory of EXAFS i.e. the final state energy spectrum is that of a free electron and the EXAFS is due to the modulations of the final state wave function of the photoelectron caused by the backscattering from the surrounding atoms. In 1941, Kostarev [11] concluded that the SRO theory is accurate for both molecules and matter in the condensed state. The lifetime of the excited photoelectron and the corresponding core-hole state was first calculated by Sawada et. al. [12] in terms of a mean free path. Further correction to the theory was introduced by Schmidt [13] who pointed out that the interference of the backscattered waves from atoms at a given average distance will not all be in phase due to the disorder in the distances of the backscattering atoms, as a consequence of structural or thermal vibrations. Hence a Debye-Waller factor was incorporated based on the Debye theory of lattice vibrations. In the period of 1971-75, E. A. Stern and D. Sayers [4], [5], [9], [10] postulated that the photoelectron wavefunction would be modified by the scattering from its nearest neighbour atoms and the interference between the backscattered and outgoing waves would modulate the absorption matrix elements. They had further suggested that a Fourier transform of EXAFS spectrum with respect to the photoelectron wavenumber would peak at distances corresponding to nearest neighbour coordination shells of atoms. In 1975, Lee and Pendry [14] gave first reasonable quantitative theory for calculating EXAFS including multiple scattering effects. A significant progress
towards computation was achieved when Rehr and his collaborators [15] developed a
computer code called FEFF in 1991 that allowed rapid calculations of EXAFS theoretical
spectra. The straightforward form of the EXAFS equation has been used in this thesis for
theoretical modelling of the data and the corresponding theory is explained in the next sub-
section along with inherent assumptions. Detailed mathematical derivation has been omitted
here which can be obtained from any standard text [16], [17].

2.1.1 Single Scattering EXAFS

XAFS which is intrinsically a quantum mechanical phenomenon does not occur for isolated
atoms and is only observed in condensed matter. In this work the non-relativistic
approximations have been assumed unless stated otherwise. The relativistic effects are
important mostly for heavy atoms. Interaction of X-rays with matter, in the photon energy
range of upto 40 keV, is dominated by photoelectric absorption where the incident photon is
completely absorbed, transferring its energy to eject an excited photoelectron and leaving a
core-hole in the atom. When the kinetic energy of the ejected photoelectron is about 15eV or
greater, this energy is large compared to the interaction energy (~3 eV) with the surrounding
atoms. Hence the interaction with the surrounding atom can be treated as a perturbation about
an isolated atom. A useful approximation is to treat the behavior of electrons in a many-
electron system as that of a single electron moving in the average field of the other electrons.

We are interested in the transition rate between a core level (e.g. 1s) and final states that is
induced by a weak time-dependent perturbation such as an electromagnetic wave. Time-
dependent perturbation theory tells us that the transition rate, to first order in the perturbation,
is proportional to the squared modulus of the transition amplitude (matrix element), also
known as the Fermi’s Golden rule:

\[
\frac{2\pi}{\hbar} |\langle \psi_f | H | \psi_i \rangle|^2
\]

(2.1)
where $|\psi_i\rangle$ and $|\psi_f\rangle$ are respectively the initial and final electron states, of energy $E_f$ and $E_i$, $\rho$ is the density of states, and $H$ is the interaction Hamiltonian between the electromagnetic field and the electrons. In the case of excitation by electromagnetic waves, to first order in the field (which, in quantized field picture, corresponds to single photon interactions)

$$H \propto A \cdot \vec{p}$$  \hspace{1cm} (2.2)

where $A$ is the vector potential of the wave and $\vec{p}$ is the momentum operator of the electron.

Using commutation relations with the Hamiltonian this can be written as

$$\mu \propto |\langle \psi_f | e^{i \vec{E} \cdot \vec{p}/\hbar} | \psi_i \rangle|^2 \rho (E_f - E_i - \hbar \omega)$$  \hspace{1cm} (2.3)

and $\epsilon$, $\hbar k$ and $\hbar \omega$ are the X-ray’s electric polarization vector, momentum, and energy.

It is useful to express the total absorption coefficient $\mu(E)$ as the isolated atom absorption $\mu_0(E)$ times a correction factor $\chi$:

$$\mu(E) = \mu_0(E) (1 + \chi)$$

or, $\chi(E) = (\mu(E) - \mu_0(E)) / \mu_0(E)$.  \hspace{1cm} (2.4)

This says that $\chi$ is the fractional change in absorption coefficient that is induced by the presence of neighbouring atoms. Within the context of the single scattering approximation (and others discussed below), Stern, Sayers and Lytle [5] derived a simple and extremely useful expression for $\chi$, which has come to be called the standard EXAFS equation. According to this theory, for $K$-edge (and $L_1$) excitations, an atom (index $i$) at relative distance $r_i$ makes the following contribution to the EXAFS

$$\chi(k) = S_0^2 \sum_i \frac{2\pi e^2 \delta_{r_i}^2}{\hbar^2} |f_i(k)| e^{-2Q_i} \sin (2\hbar r_i + 2\delta_{1i}(k)) + \arg (f_i(k))$$  \hspace{1cm} (2.5)

where $k = \sqrt{\frac{2m(E_{k} - E_0)}{\hbar^2}} \approx \sqrt{\frac{2625(E_{k} - E_0)}{\hbar^2}}$ in eV, Å units), $\theta$ is the angle between the X-ray polarization vector $\epsilon$ and the vector $\vec{r}_i$ connecting the central atom with the atom in question. Here, $|f_i(k)|$ and $\arg (f_i(k))$ are the modulus and phase of the complex electron
scattering amplitude for each atom: $\delta_1(k)$ is the $l = 1$ partial wave phase shift; and $S_0^2$ and the photoelectron mean free path $\lambda_e$ account for losses of coherence due to multi-electron excitations. The $1/r^2$ factor accounts for the $1/r$ decrease in intensity of the photoelectron wave propagating out to the scatterer and then back to the central atom. The overall structure of the simple equation is that of a sum of damped sine waves: a $k$-dependent amplitude pre-factor times the sine of a phase which is approximately linear in $k$. In other words, each atom contributes a sinusoidal signal which, when plotted as a function of $k$, oscillates more rapidly if the distance is larger, thus rapid oscillations in the EXAFS mean long distances. Stronger scattering amplitude generates a larger signal and in an oriented sample, the signal from a given atom is largest when its radius vector lies along the direction of the X-ray polarization vector.

In an experiment one effectively averages over many sites in the sample, and the instantaneous positions of atoms may vary because of thermal and quantum zero point motion and structural heterogeneity. XAFS essentially takes a snapshot of the instantaneous configurations of atoms, because the lifetime of the excited state is limited by the lifetime of the core hole (i.e. the vacancy in the initial $1s$ state), and core-hole level widths $\Delta E$ usually are 1 eV or greater, corresponding to time scales of $\tau = \hbar/\Delta E < 10^{-15}$ sec. Because of the rapid spatial variation of the phase factor $\sin(2kr + \delta)$ compared to other $r$-dependent factors, often the variation of the latter is neglected. The configurational disorder is manifested in the spectra mainly through variations in total path length. The average of the phase factor $\langle e^{ikr}\rangle$ is 1 at $k = 0$ (if the distribution is normalized to 1), so evidently we can expand $\ln \langle e^{ikr}\rangle$ in a Taylor series about $k = 0$ as $\ln \langle e^{ikr}\rangle = ika + (ik)^2b + \ldots$. where $a$ and $b$ are some constants. Exponentiating both sides we have $\langle e^{ikr}\rangle \approx e^{ika-bk^2}$. The first term gives an oscillatory contribution while the second term provides a Gaussian damping factor of the sort generally found in the averaged EXAFS equations. The damping occurs because the EXAFS is a
superposition of oscillations of different wavelengths. At low k the wavelengths are long, so all the contributions add together in phase. As k increases, however, the wavelengths become shorter, and the signals of slightly different path length destructively interfere with each other. These damping factors are called EXAFS Debye–Waller factors in analogy with similar quantities in diffraction theory. For randomly oriented polycrystalline or solution samples an isotropic average over angles must be performed. In this case, the contributions from atoms of the same atomic number and at similar distances from the absorbing atom may not be resolvable from each other, and the atoms must be conceptually grouped together into “coordination shells”. For small variations in distance within a shell, the equation becomes:

\[ \chi(k) = \sum_j \frac{2N_j}{kR_j^2} |F_j(k)| e^{-2\sigma_j^2} e^{-2k^2\sigma_j^2} \sin (2kR_j + \delta_j(k)) \]  

(2.6)

where \( N_j \) is the number of atoms in the coordination shell, and \( \sigma_j^2 \) is the mean square variation of distances about the average \( R_j \) to atoms in the \( j \)th shell. This is the classic EXAFS equation of Stern, Sayers, and Lytle [4],[5] for an un-oriented sample with Gaussian disorder with corrections for many body effects incorporated. This equation has been employed for all the theoretical fitting in the present thesis.

2.1.2 Approximations

- **Dipole approximation**

The exponential in the matrix element in Equation 2.3 can be expanded as

\[ < \psi_F | e^{i \frac{k}{2} \vec{R} \cdot \vec{r}} | \psi_i > \approx | < \psi_F | e^{i \frac{k}{2} \vec{r}} | \psi_i > | + i | < \psi_F | (e^{i \frac{k}{2} \vec{r}})(\vec{r} \cdot \vec{r}) | \psi_i > + \ldots \]

The first term is the dipole term; the second term is the quadrupole term. The ratio of the quadrupole to dipole matrix elements for Fe, \( Z = 26 \), is about 10\%, and the ratio of the transition probability is about 1\%, for \( K \)-edges. This shows that dipole approximation is good, but that quadrupole transitions are not always negligible. They can be readily observed in some situations when not masked by allowed dipole transitions, for example in the pre-edge
region of transition metal complexes. The quadrupole/dipole ratio grows quadratically with Z, so that it can be expected to be substantial for heavier atoms, and for $L$-edges because of size of the initial state wavefunction. Multipoles of higher order than quadrupole are usually negligible.

- **Orientation dependence**

Summing over final states of different energies, in the dipole approximation we can rewrite the expression for the absorption probability as

$$\mu \propto \mathbf{e} \cdot \mathbf{M} = \sum_{jK} M_{jK} \mathbf{s}_j \mathbf{s}_K$$

where $\mathbf{s} = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$ is the X-ray polarization vector expressed in spherical coordinates $\theta, \phi$. Although the tensor can be diagonalized by choosing an appropriate coordinate system at one energy, it is not generally possible to do this at all energies. However, when the sample itself has certain symmetries the form simplifies considerably. An important special case is if the sample is isotropic (e.g. solution or randomly oriented polycrystalline, or is of cubic symmetry) the absorption tensor is proportional to the identity matrix — it may as well be taken as a scalar. Now suppose that we have a pair of atoms aligned along the $z$ axis, and we excite them with X-rays. Evidently we can expect both $\cos^2 \theta$ and $\sin^2 \theta$ angle dependencies, where $\theta$ is the angle between the polarization vector and the vector connecting the atoms. Calculation shows that in $K$-edges the $\sin^2 \theta$ contribution dies off rapidly with energy above the edge, leaving only the $\cos^2 \theta$ dependence. However, it must be remembered that the $\sin^2 \theta$ term is generally present in the near-edge region, as it is for $L$-edges [18], [19].

- **Selection rules**

The core state from which the electron is removed, is deeply bound, and the dominant interaction of the electron is with the nucleus and electrons of the central (photo absorbing) atom. As a consequence, the initial state is well approximated as an atomic-like state of angular momentum quantum numbers $l$ and $m$. The transition operator in the dipole
approximation is proportional to the vector \( \vec{r} \). The final-state wavefunction can be expressed as a linear combination of functions with specific \( l, m \), which are eigenfunctions of the operators \( L^2 \) and \( L_z \). Because of the orthogonality of spherical harmonics, the transition matrix element projects out only the part of the final-state wavefunction that has the appropriate symmetry for an allowed transition. Electric dipole selection rules tell us that \( \Delta l = \pm 1 \), and quadrupole selection rules \( \Delta l = \pm 2, 0 \). Dipole selection rules therefore imply that for \( K \)- and \( L_1 \)-edges, allowed transitions are to states containing \( p \) symmetry. For \( L_2 \)- and \( L_3 \)-edges, allowed transitions are to final states containing \( d \) and \( s \) symmetry.

- **Small atom approximation**

In this approximation the spherical wave incident on a backscattering atom is approximated by a plane wave. It is only valid when the effective size of the backscattering atom is small compared to the distance between the atom and the central atom, which is true for a photoelectron with high \( k \)-value. At low \( k \) values, this approximation breaks down.

### 2.1.3 Corrections

- **Many body effects**

  (a) **Passive electron effect:** As a consequence of absorption of the incident photon, a core electron is knocked out from the excited atom. The atomic electrons of this excited atom perceive a modified potential, which can be approximated by that of an atom with its \( Z \) increased by 1. Thus the nucleus attracts the other electrons more, pulling in the wave functions of the original atom and relaxing them to a lower energy. These are called *passive electrons* because they are not directly excited by the x-ray, in contrast to the core electron. In the independent particle model, the wave function of the atom is a product of the wave functions of each electron. If relaxation is neglected, the passive electron states do not change as the atom is excited by the incident photon, and their contribution to the matrix element consists of the product of their overlaps before and after excitation as below:
\[
\prod_i \left| \langle \varphi_i | \varphi_i \rangle \right|^2 = 1
\]

where \( |\varphi_i \rangle \) is the wave function of the \( i^{th} \) passive electron. However, if this electron relaxes to some other state \( |\varphi'_i \rangle \) in the excited atom, the overlap contribution of the passive electron becomes

\[
\int_i \left| \langle \varphi_i | \varphi'_i \rangle \right|^2 < 1
\]

The product \( S_0^2 \) is less than 1 because \( |\varphi'_i \rangle \) is normalized and its overlap with \( |\varphi_i \rangle \) can be 1 at the most when \( |\varphi'_i \rangle = |\varphi_i \rangle \). Hence, \( S_0^2 \) is a parameter slightly less than unity that accounts for the less overlap between the wave functions of the passive electrons in the initial and final states. Thus the many body relaxation effect reduces the value of \( \mu \) by the factor \( S_0^2 \) which is in the range of 0.7 – 0.9 in typical cases.

**(b) Mean free path:** Another key ingredient for accurate calculations at high energies is to account for the fact that the photoelectron interacts dynamically with the gas of other electrons in the material, and its behaviour is substantially modified by these many-body effects. The “leaking away” of probability from the wavefunction effectively introduces a mean free path into the formalism, which means a loss of coherence as the electron propagates through the material. Probability is lost from the main single electron (quasiparticle) channel into a large number of multi-electron channels that need not be explicitly calculated. The effect limits the range of the photoelectron, so the spectra are sensitive only to the short range order in the sample. The electron mean free path is energy dependent, of magnitude ~ 5–10 Å, which limits the sensitivity of XAFS to regions of about nanometer scale or less.
• **Multiple Scattering**

The neglect of multiple scattering in the simple equation implies that the total $\chi(k)$ is a simple linear sum of contributions from backscattering atoms. This is a useful first approximation, but it is well known that multiple scattering is often important in EXAFS, particularly when the absorbing atom and scatterers are collinear as shown below.

![Diagram of scattering paths](image)

Figure 2.4 Possible nearest neighbour (NN) and next nearest neighbour (NNN) scattering paths.
Most multiple scattering approaches currently employ the “muffin-tin” approximation, in which the atomic potentials are approximated as spherically symmetric out to a finite radius, and the interstitial potential between the atomic sphere is approximated as a constant. This approximation tends to work well for close-packed structures, but is less successful with open structures. A muffin-tin potential is sketched in Fig. 2.5. Typically the muffin-tin radii are chosen so that the charge inside equals that of the atom (Norman criterion). In practice the muffin-tin radii often are scaled up so that they overlap slightly, which experience has shown partially makes up for deficiencies in the muffin tin approximation. In the EXAFS region, the kinetic energy of the electron is large enough that small variations in the interstitial potential do not make much difference, and the muffin-tin approximation works well.

![Figure 2.5 Schematic of muffin-tin (MT) potential.](image)

\[ V(r) = V_T(r) - V_{MTZ} \]

- for \( r < r_{MTZ} \)
- for \( r \geq r_{MTZ} \)

*Anharmonicity*

If the disorder is too large for the Gaussian Debye–Waller factor to suffice, additional terms must be included in the exponential and new terms are introduced into the phase. If these terms are substantial, but are ignored, serious errors in the interatomic distance and other
parameters can occur. The cumulant expansion is particularly useful for describing anharmonic systems and thermal expansion.

It is remarkable that, when spherical wave effects, many body interactions, etc. are included, the basic structure of the original EXAFS equation is preserved as long as the plane wave scattering amplitude $f(k)$ is replaced by an effective scattering amplitude $f_{\text{eff}}(k; r)$: the scattering amplitude acquires a weak $r$ dependence.

2.2 XANES interpretation

In the vicinity of the absorption edge, the interaction of the ejected photoelectron with the potential of the neighbouring atoms is still strong so the simplifying single scattering assumption leading to EXAFS is not possible. The EXAFS equation breaks down at low-$k$, due to the $1/k$ term and the increase in the mean-free-path at very low-$k$. In the near-edge (XANES) region the muffin-tin approximation is less satisfactory for quantitative analysis and the interpretation of XANES is complicated since there is no simple analytic description of XANES. However, useful information regarding the chemical environment can be obtained from the XANES region. The absorption edge position and shape is sensitive to formal valence state, ligand type, coordination geometry and can be used as a fingerprint to identify phases.

The final states of K and L1 edges are $p$-states, and the final states in L2 and L3 edges are a mixture of $d$ and $s$ character. The $p$ final states of K and L1 edges are more diffuse than the localized $d$ final state of L2 and L3 edges. All of these edges may show strong peaks at the top of the edge (the “principal maximum”). Historically these were called “white lines,” because that was how they appeared on photographic plates. For K shell absorption, where the core-level is a $1s$ state, the photo-electron has to end up in a $p$ state according to the selection rules of transition. Thus, even if there are available states with the right energy,
there might be no $1s$ absorption if there are no available $p$ states. For EXAFS, where the energies are well-above the threshold energy, this is rarely an important concern. For XANES, on the other hand, this can play a very important role. From a molecular orbital point of view, the bound states in the pre-edge region consist of linear combinations of orbitals that have specific symmetry properties. If the Hamiltonian is symmetric under inversion, states of opposite parity cannot mix to make an eigenstate of the Hamiltonian. This implies that $p$ states (odd parity) can only mix with $d$ or $s$ states (located at the central atom) if the Hamiltonian (and therefore the local environment) is not totally symmetrical under inversion. Since the final state in $K$- and $L_1$-edges are of $p$ symmetry (by dipole selection rules), any strong transition near the energy of the metal $3d$ orbitals indicates a breaking of inversion symmetry. Transition metal oxides, for example, usually have many unfilled $3d$ electrons near the Fermi level, and a filled $3p$ band. There are empty $2p$ electron states from the oxygen, but these are too far away to appreciably overlap with the metal $1s$ band. Therefore, the metal $3d$ electrons do not normally participate in the absorption process unless there is a strong hybridization of the $O\ 2p$ and metal $3d$ levels. The XANES spectra are especially sensitive to such hybridization. For ions with unfilled $d$-electron bands, the $pd$ hybridization is dramatically altered depending on the coordination environment, with much stronger hybridization for tetrahedral coordination than for octahedral coordination. Since the photo-electron created due to a $1s$ core level (a K-shell) must have $p$-like symmetry, the amount of overlap with the $d$-electron orbitals near the Fermi level can dramatically alter the number of available states to the $p$-electron, causing significant changes in the XANES spectrum. This argument would suggest that the pre-edge transition strength should be identically zero for inversion symmetric sites. However, quadrupole transitions can be weakly present because the transition Hamiltonian contains small terms that are non-dipolar
as previously discussed in section 2.1.2. Such terms can be observed in the pre-edge of most transition metal complexes.

Another important and common application of XANES is to use the shift of the edge position to determine the valence state. Fig. 2.6 shows the valence dependence of Fe metal and oxides of Fe$^{2+}$ and Fe$^{3+}$ (and a mixture of these two). With good model spectra, Fe$^{3+}$/Fe$^{2+}$ ratios can be determined with very good precision and reliability. The heights and positions of pre-edge peaks can also be reliably used to empirically determine oxidation states and coordination chemistry.

![Figure 2.6 XANES spectra of standard Fe metal and oxides.](http://xafs.org/Tutorials; Fundamentals of XAFS, Matthew Newville, Consortium for Advanced Radiation Sources, University of Chicago, Chicago, IL)

For many systems, XANES analysis based on linear combinations of known spectra from “model compounds” is sufficient to estimate the ratios of valence states and/or phases. More sophisticated linear algebra techniques such as Principle Component Analysis and Factor Analysis can also be applied to XANES spectra. Some materials, such as the spinel and inverse spinel structures have metal ions in nonequivalent sites: 2/3 of the sites are
octahedral, and 1/3 of them are tetrahedral. Despite the dilution due to octahedral sites, the $3d$ pre-edge peaks are noticeably larger than the pure octahedral case. In some cases the states associated with pre-edge transitions are full ($3d^{10}$ configuration) in one charge state, but have a hole ($3d^9$) in another charge state. For example, the presence or absence of the $3d$ pre-edge transition can be used to detect the difference between $Cu^+$ and $Cu^{2+}$. Correlating formal charge state with absorption edge shifts is obvious from simple physical arguments that shifts of a few eV can indeed occur by transferring charge.

### 2.3 XAFS Experimental Technique

#### 2.3.1 Data Collection (TM, FL, TURBO)

EXAFS measurements with synchrotron radiation are generally carried out in two different modes. In the more conventional one the beamline uses a double-crystal monochromator (DCM) to select a particular energy from the incoming synchrotron beam, which is incident on the sample and the intensity of the transmitted beam passing through the sample or that of the fluorescence beam emerging out of the sample is recorded along with the incident intensity at each energy. The absorption data of the sample are then recorded by scanning the monochromator over the whole energy range of interest and hence this is called the Energy Scanning EXAFS mode.

![EXAFS setup diagram](image)

Figure 2.7 (a) Energy Scanning and (b) Energy Dispersive EXAFS modes.
However, it takes several tens of minutes to measure an EXAFS spectrum for dispersed species by the conventional energy scanning XAFS technique and thus it cannot monitor time-dependent structures during dynamic chemical processes. Rapid scanning monochromators have subsequently been developed that permit spectra to be collected in less than a minute [20] and much smaller energy ranges can be scanned at 10 Hz by use of a vibrating monochromator [21]. However, despite these advances, it is clear that energy scanning EXAFS mode is not yet suitable to monitor dynamic change of structures in msec time scale which is required for in situ monitoring of fast kinetics e.g., reaction processes of catalytic materials.

In the other mode of measurement, viz., the Energy dispersive EXAFS (EDXAS) mode, on the other hand, a bent crystal polychromator is used to select a band of energy from the white synchrotron beam horizontally dispersed and focused on the sample. The transmitted beam from the sample is recorded on a position sensitive CCD detector, thus enabling recording of the whole EXAFS spectrum around an absorption edge in a single shot. As no mechanical motion for monochromatizing X-rays is required in this technique, EXAFS spectra can be measured in 1s or even less. The EDXAS technique is applied for the elucidation of structural changes during catalyst preparation, chemical treatment, catalytic reaction, study of transient and short-lived species, phase transition under high pressure, etc. [22] [23]. The two experimental modes of EXAFS measurement are illustrated in Fig. 2.7.

XAFS can be measured either in transmission or fluorescence geometries. Transmission mode simply involves measuring the X-ray flux before and after the beam is passed through a homogeneous sample. Under these conditions, the transmitted flux $I$ is related to the incident flux $I_0$ by:

$$\frac{I}{I_0} = \exp(-\mu(E)x), \text{ or } \mu(E)x = \ln(I_0/I). \quad \text{(2.7)}$$
Transmitted mode measurements are useful for uniformly thick bulk samples having optimum concentration of the absorbing species.

In X-ray fluorescence, a higher energy core-level electron fills the deeper core hole, ejecting an x-ray of well-defined energy. The fluorescence energies emitted in this way are characteristic of the atom, and can be used to identify the atoms in a system, and to quantify their concentrations. For example, an L shell electron dropping into the K level gives the $K_\alpha$ fluorescence line. Since the fluorescence process is a secondary process of photoelectric absorption, all the features of the absorption spectra of a sample get reflected in its fluorescence spectra also and hence fluorescence spectra can also be used to study the EXAFS oscillations. In fluorescence mode one measures the incident flux $I_0$ and the fluorescence X-rays $I_f$ that are emitted following the X-ray absorption event and follows the relation:

$$\mu(E) \propto I_f/I_0$$

(2.8)

In EXAFS measurements, usually the fluorescence detector is placed at 90° to the incident beam in the horizontal plane, with the sample at an angle (usually 45°) with respect to the beam. This mode is suitable for dilute samples, liquid samples, thin films on thick substrates etc. Fluctuations in the number of elastically scattered X-rays are a significant source of noise in fluorescence XAFS, so the position of the detector is selected to minimize the elastically scattered radiation by exploiting the polarization of the X-ray beam. There are two main considerations for making good fluorescence XAFS measurements: solid angle and energy resolution. The fluorescence is emitted isotropically, and every effort is made to collect as much of the available signal as possible. The scatter is actually not emitted isotropically because the x-rays from a synchrotron are polarized in the plane of the synchrotron. It means that elastic scatter is greatly suppressed at 90 degrees to the incident beam, in the horizontal plane. Therefore, fluorescence detectors are normally placed at a right
angle to the incident beam. Energy discrimination is important because it can potentially allow us to completely suppress the scatter peak and other fluorescence lines, and collect only the intensity of the fluorescence lines of interest. This would greatly suppress the background intensity, and increase the signal-to-noise level. Energy discrimination can be accomplished either physically, by filtering out unwanted emission before it gets to the detector by using a Z-1 filter, or electronically after it is detected as shown in Fig. 2.8. To avoid re-radiation from the filter itself, a set of slits (Soller slits) is often used to preferentially collect emission from the sample and block the emission from the filter. Since we know which element is to be probed, we know the energy of the expected x-ray photon and we can establish a band of channels in the solid state detector. These spectra are useful in their own right for being able to identify and quantify the concentrations of other elements in the sample.

![Figure 2.8 The effect of "Z-1" filter on a measured fluorescence spectra.](image)

However, unwanted portions of the fluorescence spectra can also be completely rejected and thus these detectors can be used for XAFS measurements with concentrations down to ppm levels. This band of channels is referred to as a “window” and when we select this window to determine a specific absorption edge, the window is referred to as a “Region of Interest,” or
ROI. The two configurations (transmission and fluorescence) of EXAFS measurements are shown schematically in Fig. 2.9.

In principle, as per the optical layout of an Energy Dispersive set up as shown in Fig. 2.7(b), measurement is only possible is transmission geometry, which poses a problem for measurements on dilute samples and samples deposited on thin films. However, with a slight modification, an Energy Dispersive set up can also be used for EXAFS measurements in fluorescence based geometry which allows good data quality, offering a correct normalization due to the simultaneous recording of $I_0$ and $I_t$.

![XAFS measurements](image)

Figure 2.9 Transmission and Fluorescence mode of data collection.

In this modified configuration, first proposed by Pascarelli et al. [24] and known as turbo-XAS (T-XAS) a monochromatic beam is obtained at the sample (focus) position by placing a narrow slit in the energy-dispersed fan of radiation immediately before the polychromator set up as shown in Fig. 2.10. The incident signal is measured in a gas detector positioned before the focal point ($D_1$) while the fluorescence signal from the sample is detected by a fluorescence detector $D_2$ (Lytle-type of a Silicon drift detector-type). The whole EXAFS spectrum is recorded by scanning the slit precisely across the fan of beam. The simultaneous
recording of $I_0$ and $I_t$ implies that the experimental set-up is intrinsically less sensitive to beam instabilities. The experimental setup also profits from the small and stable horizontal focal point and high energy scale stability and reproducibility of the dispersive optics thanks to the decoupling of the monochromatization and of the focusing action. Finally, T-XAS also enables detection of decay channels, allowing time-resolved studies of surfaces and dilute samples or growth of nanoparticles using dispersive optics, in the transmission mode as well as in the fluorescence mode. Due to the possibility of obtaining a correct normalization of the data, T-XAS is also widely employed for the large number of static XAS experiments which need dispersive optics because of the small and stable focal spot, such as high-pressure experiments or which need a high stability of the energy scale, such as XMCD measurements.

Figure 2.10 A schematic diagram of the TURBO-XAFS experimental set up in an energy dispersive EXAFS beamline.

The EXAFS data presented in this thesis have been measured at the INDUS-2 synchrotron radiation source at RRCAT, Indore, India where a comprehensive EXAFS measurement facility, consisting of two beamlines, has been developed in recent years which
facilitate the two modes of XAFS measurements as described above viz., energy dispersive mode and energy scanning mode.[25] Both the beamlines are described briefly in the following section.

2.3.2 Energy Dispersive EXAFS beamline (BL-08)

A energy dispersive extended X-ray absorption fine structure (EXAFS) beamline using a bent crystal and position sensitive detector has been developed and installed at a bending magnet port of INDUS-2 for X-ray absorption studies in the energy dispersive geometry [26].

![Figure 2.11 Working principle of the Energy Dispersive EXAFS beamline (BL-08) at INDUS-2 SRS](image)

The beamline works in the dispersive mode using a 460-mm-long Si (111) crystal mounted on an elliptical bender and a position-sensitive CCD detector having 2048×2048 pixels. The beamline is designed to cover the photon energy range of 5 – 20 keV providing energy bandwidths of 0.3, 1.0 and 2.0 keV and with resolution of ~ 0.5, 1 and 2eV per pixels at photon energies of 5, 10 and 20 keV, respectively. The optical layout of the beamline is shown in Fig. 2.11. Here, a bent single crystal (C,C) forms part of an ellipse such that the source (S0) and the sample positions (S3) are situated at two focii of the ellipse. The elliptical
optics ensures all radiation emerging from one focus (S0) reach the other focus (S3) after reflection from the crystal and offers minimum aberration.

The emission from the synchrotron source is first passed through a Be window (B) of suitable thickness to cut off the unwanted low-energy part from the continuum and then through the beam aperture system consisting of two copper blocks (K,K) positioned at an angle of 15° to the beam path for collimation. The collimated beam with horizontal divergence of 1.5 mrad is then made to fall on the slit system (S,S) which defines the final horizontal and vertical divergence of the synchrotron beam using two sets of water-cooled tantalum jaws. The beam emerging from the slit system with required vertical and horizontal divergences falls on a vertically focusing mirror (M, M) at a grazing angle of incidence ~ 0.2°, which cuts off the higher energy part of the synchrotron beam. After reflection from the mirror, the beam falls on silicon crystal (C, C) mounted on a bender. Depending on the angle of incidence of the beam and its radius of curvature, the crystal reflects a particular central energy ($E_0$) with a certain band-width ($\Delta E$) and this spatially dispersed polychromatic radiation is focused at

Figure 2.12 Optical layout of BL-08.
the sample position (S3). The transmitted radiation from a sample diverges further and is detected by a position-sensitive detector (D,D). Thus, the energy dispersed absorption spectra of the sample over the whole bandwidth ($\Delta E$) around the central energy ($E_0$) can be simultaneously recorded by the detector.

A <111> oriented (2d = 6.2709 Å) Si single crystal has been chosen as the polychromator consequent to its narrow Darwin width, low thermal expansion coefficient and high thermal conductivity. The source to Si crystal distance ($p$) is fixed based on practical considerations is 20,000 mm. The horizontal beam divergence ($U_m$) is chosen to be 1.5 mrad taking into consideration the detector and crystal sizes and heat flux falling on different beamline components. The energy bandwidths ($\Delta E$) sought for meaningful EXAFS studies at different central energies within the energy regime of 5–20 keV have been decided considering practical values of the radius of curvature ($R$) of the crystal achievable by the crystal bender.

The values of other beamline parameters have been determined as follows. The Bragg angle $\theta_0$ for the central ray at the pole of the crystal is obtained from the central photon energy $E_0$ or wavelength $\lambda_0$ from the Bragg relation:

$$\sin \theta_0 = \frac{\lambda_0}{2d} \quad (2.9)$$

Since the source to crystal distance ($p$) and horizontal divergence ($U_m$) are fixed, the length of the illuminated portion of the crystal ($l$) corresponding to the central energy $E_0$ is then determined by the simple geometrical relation:

$$U_m = \left(\frac{l}{p}\right) \sin \theta_0 \quad (2.10)$$

For simplification of calculations, initially we have assumed the elliptical crystal to be a spherical cylinder having a uniform radius of curvature ($R_0$). Since $l$ is known, the radius of
curvature \((R_0)\) can be determined by the following relation for a pre-specified value of the energy bandwidth \((\Delta E)\) for all values of \(E_0\). \([27]\)

\[
\Delta E = E_0 \cot \theta_0 \left( \frac{1}{R_0} - \frac{\sin \theta_0}{p} \right)
\]  

(2.11)

Since the values of \(p\), \(\theta_0\) and \(R_0\) are known, the crystal to sample distance \((q)\) is then determined from the equation below

\[
\frac{1}{2 \sin \theta_0} = \frac{R_0}{2} + \frac{q}{2}
\]

(2.12)

The above calculations have been done for various photon energies between 5 and 20 keV.

It should be noted here that, following eqn. 2.11, the band width obtained at a particular central energy in such a set up is limited by the minimum radius of curvature attainable on the crystal by a mechanical crystal bender within the elastic limit of silicon. Thus in the energy dispersive EXAFS beamline described here, though one can get reasonably good band width of \(~1000\) eV at central energy of 10 keV, it reduces significantly in lower energy range with only \(~400\) eV of available band width at 6 keV. This poses a major limitation in utilization of the present energy dispersive beamline for probing elements whose X-ray absorption edges lie below 7 keV.

The CCD at BL-08 is an ANDOR make, Model no. DW 436-F0 Sr No.: CCD-3320 area detector with 2048 \times 2048 pixels each having a width of 13.5 \(\mu\)m. It has a theoretical resolution of 1eV/pixel, though this can be increased or decreased depending on the experimental requirements. Each element interacts with light to build up a charge – the brighter the light, and/or the longer the interaction, the more charge is registered. At the end of the measurement read out electronics pull the charge from the elements, at which point each individual charge reading is measured. A schematic diagram depicting the principle of action is shown in Fig. 2.13. CCDs require some degree of cooling to make them suitable for
high grade spectroscopy. Typically this is done using either water cooling, peltier cooling (suitable for temperatures down to -90°C), and liquid nitrogen cryogenic cooling. We have a water cooling system that maintains the detector temperature at –35°C.

![Schematic diagram of the working principle of a CCD.](image)

Figure 2.13 Schematic diagram of the working principle of a CCD.

A photograph of the beamline after final installation is shown in Fig. 2.14.

![Photograph of the Energy Dispersive EXAFS beamline (BL-08).](image)

Figure 2.14 Photograph of the Energy Dispersive EXAFS beamline (BL-08).

Fig. 2.15 shows the synchrotron beam spot on a CCD screen focused horizontally by the crystal bender and vertically by the mirror at the sample position for 20,000eV setting of the crystal. It should be noted that prior to the EXAFS measurement at any particular energy
edge in this Energy Dispersive set up, the uniformity of the focal spot at the sample position has been carefully checked. This has been done by illuminating different regions of the bent crystal sequentially by scanning a fine slit at the polychromator entrance and observing the intensity distribution of the focal spot recorded on a CCD screen kept at the sample position. Aberrations in the focal spot, if any, is corrected by precisely adjusting the two stepper motors connected to the crystal bender.

![Figure 2.15](image.png)

**Figure 2.15** Focussed beam spot at the sample position at 20 keV.

In some of the studies in the present thesis a closed cycle cryostat has been used to carry out temperature dependent EXAFS measurements. The major components of the closed cycle cryostat are the expander, compressor, vacuum shroud, and radiation shield. The expander, commonly referred to as the coldhead or cold finger, is where the refrigeration cycle takes place. It is connected to a compressor by two gas lines and an electrical power cable. One of the gas lines supplies high pressure helium gas to the expander, the other gas line returns low pressure helium gas from the expander. The compressor provides the necessary helium gas flow rate at the high and low pressure for the expander to convert into
the desired refrigeration capacity. The vacuum shroud surrounds the cold end of the expander in vacuum limiting the heat load on the expander caused by conduction and convection. The radiation shield is actively cooled by the first stage of the expander and insulates the second stage from the room temperature thermal radiation being emitted from the vacuum shroud. A schematic of the cryostat is shown in Fig. 2.16.

Figure 2.16 A schematic diagram of the closed cycle cryostat.

In addition to these major components the closed cycle cryo-cooler is accompanied by several support systems like a vacuum port and electrical feedthroughs, as well as a temperature controller to measure and adjust the sample temperature. The system also requires cooling water for the compressor and a vacuum pump for the sample space.

2.3.3 Energy Scanning EXAFS beamline (BL-09)

An Energy Scanning type EXAFS beamline has also been developed at BL-09 port of INDUS-2 synchrotron source and has been commissioned recently [28]. The beamline uses a
1.3 m long meridional cylindrical mirror with radius of curvature 11.2 Kms for vertical collimation of the beam. This mirror is followed by a fixed exit type double crystal monochromator (DCM). The DCM consists of two Si (111) crystals with 2d=6.2709Å and narrow Darwin widths. The fixed exit is realized by varying relative lateral and vertical distances between the two crystals at each energy setting, maintaining parallelism between them. The second crystal of the DCM is a saggital cylinder with variable radius of curvature in the range 1.2 m to flat, which provides horizontal focusing to the beam. A post mirror with meridional curvature is used upside-down for bending the beam path to horizontal direction again as well as for vertical focusing of the beam at the sample position. Higher harmonics are rejected by changing the angle of incidence at the second mirror. Each of the two cylindrical mirrors has two coating strips, viz., of Platinum (Pt) and Rhodium (Rh). Rhodium has the absorption edge at 23.2 KeV (K-edge) and Pt has L1, L2 and L3 absorption edges between 11.5 KeV to 13.9 KeV. So to cover the energy range of 4-25 keV, coatings of Rh and Pt are used. The optical layout of the beamline is given in Fig. 2.17(a), while the photograph is shown in Fig. 2.17(b).
The beamline has been installed with two separate sections namely the optics hutch and the experimental hutch. The optics hutch consists of the optical components e.g., slit system, grazing incidence X-ray mirrors, beam viewer, double crystal monochromator (DCM) and Beryllium window. The components in the optics hutch are at $10^{-9}$ torr vacuum and separated by front end and experimental hutch using 200μm beryllium windows. The experimental hutch is equipped to record EXAFS spectra of the samples both in transmission and fluorescence mode. In the transmission mode of measurement, the sample is placed between two ionization chamber detectors. The first ionization chamber measures the incident flux ($I_0$) and the second ionization chamber measures the transmitted intensity ($I_t$). A third ionization chamber is also used where reference metal foils are measured for energy calibration. The IC Spec ionisation chamber (Make: FMB Oxford) has been specially designed for high precision X-ray intensity measurements at Synchrotrons and is particularly suited for transmission X-ray absorption spectroscopy measurements. It has a large installed base and has been shown that it is capable of measuring EXAFS spectra with signal to noise of the order $10^5$. The operating voltage of these ionization chambers are 200 kV and a pressure of 100-1000 mbar.
is maintained at each of these detectors depending on the available flux and the absorption edge being probed. For dilute and thin film samples, measurements are done in fluorescence mode using a silicon drift detector, which is placed in front of the sample in 45° degree geometry. The Si drift detector (Model no. Vortex-60EX®, Make: Hitachi-High Technologies Science America, Inc.) which is generally produced from high purity silicon, feature excellent energy resolution (<133 eV FWHM at Mn K_{\alpha} is typical) and a high count rate capability (input rate >1 Mcps). At a very short peaking time of 0.25 µs, an output count rate of 600 kcps is achieved. A unique feature of these detectors is their ability to process high count rates with virtually zero loss in energy resolution and no peak shift with count rate. This detector is operated at room temperature and cooled by a thermoelectric cooler (TEC) and can be cycled as frequently as needed without any degradation in detector performance. Cool down times are typically less than 3 minutes. The detector spectroscopy system includes a detector unit and control box, which includes power supplies for the detector and TEC, a digital pulse processor with PI-SPEC Software. The complete detector also contains a charge-sensitive preamplifier and temperature stabilization system, which eliminates concerns of varying ambient temperature.

It is to be noted here that while the energy dispersive beamline (BL-08) is operational since 2009, the energy scanning beamine (BL-09) has only been in operation since 2014 and hence most of the studies presented in this thesis have been carried out in the energy dispersive beamline. However in my future course of work, the energy scanning beamline (BL-09) will be used in most of my studies particularly for doped, dilute and thin film systems, since it offers better signal to noise ratio, larger band width even for low energy edges and ease in measurement both in transmission and fluorescence mode, while the energy dispersive beamline (BL-08) will be used mostly for time-resolved in-situ studies for its short (msec) time scale of measurement.
2.3.4 Sample Preparation

In the transmission mode of measurement, ideally the sample should be homogeneous so that every ray of light interacts identically with every part of the sample. It should be uniform, of appropriate sample thickness of ~2 absorption lengths and it should be free from pinholes. In case of powder, the grains should be very fine grained (particle size should be comparable to less than one absorption length) and uniform. If the sample particles are large compared to an absorption length it implies some regions are very thick, while other regions have gaps (or leakage). The leakage problem distorts the data by decreasing white line height and altering the measured $\sigma^2$ of the EXAFS. In transmission experiments it has been observed that, if samples are too thick, most photons don’t get through and if it is too thin, most photons don’t interact. These thickness effects are particularly serious in the near-edge region where large amplitude, high-contrast structure may be found. A symptom of thickness effects is that the XAFS oscillations are compressed - they have reduced amplitudes, which has the effect of erroneously reducing the estimated coordination numbers that are obtained in data analysis. It is best to keep the sample edge step $\Delta \mu x$ to about 1.0 or less, and the total sample absorption $\mu x$ to less than 3 or so, preferably less. The exact amount of the sample required for a particular transmission EXAFS measurement can be estimated from:

$$\text{Weight} = \text{Surface} \times \frac{\mu x}{\sum_i g_i \left( \frac{\mu}{\rho} \right)_i}$$  \hspace{1cm} (2.9)

It turns out that for majority standard samples to satisfy the above conditions, the amount of sample required is generally not more than about 20-25 mg/square cm. For 12 or 15 mm diameter pellets, this is a very small amount. Hence, binders of very light non-reactive elements viz., Boron Nitride, graphite, zeolites, cellulose etc. are used to make self supporting pellets that will not crack.
For thick samples or lower concentrations (down to the ppm level and lower), monitoring the x-ray fluorescence is the preferred technique. However, a self absorption correction has to be applied to equation 2.8. The term self-absorption usually refers to the case where the penetration depth into the sample is dominated by the element of interest. Since all matter attenuates x-rays, the fluorescence intensity, and therefore the XAFS oscillations, can be damped due to this self absorption effect. In the worst case for self absorption (a thick sample of a pure element), the XAFS simply changes the penetration depth into the sample, but essentially all the x-rays are absorbed by the element of interest. The escape depth for the fluoresced x-ray is generally much longer than the penetration depth, so that essentially all absorbed x-rays cause a fluoresced x-ray. This severely dampens the XAFS oscillations. The two limits (very thin or thick, dilute samples) are the best cases for fluorescence measurements.

2.4 Data Analysis

The standard sequence of operations in EXAFS data analysis consists of the following steps: normalization of the data to unit edge step; background subtraction, conversion from energy to k-space; Fourier transformation to R-space and generation of experimental $\chi(R)$ vs. R spectra; windowing and inverse transformation; generation of theoretical $\chi(R)$ vs. R spectra using a crystallographic/amorphous model and fitting of the experimental spectra with the theoretical spectra by nonlinear least squares fitting. The normalization procedure, by which the data are divided by the size of the edge step, compensates for the uncertainties in the concentration and sample thickness. A common method of determining the edge step is to fit the data within a few hundred eV below the edge, and also above the edge, with low order polynomials (linear or quadratic), and then extrapolate them to the edge. The difference between the pre-edge and post-edge fits extrapolated to the edge energy is the edge step. To
convert to k-space, the value of $E_0$, the threshold energy (muffin tin zero level in the theory) must be specified. Fortunately the precise value is immaterial as long as it is within a rydberg or so of the edge, and that it is consistent for standard and unknown. Typically the half-maximum point on the edge is taken, or the first maxima of the derivative of the EXAFS signal. In the next step, background subtraction is performed, to isolate the oscillations in EXAFS from the atomic part of the absorption $\mu_0(E)$, and the background absorption or scatter from other elements in the beam path. In principle, the isolated atom absorption $\mu_0(E)$ (which is generally unknown) is subtracted from the absorption of the atom in condensed matter $\mu(E)$, and the result is divided by $\mu_0(E)$, which is a slow function of energy in the EXAFS region. Background subtraction is accomplished by ordinary linear least squares fitting, typically using cubic spline functions. Subsequently the data is converted to k space and is generally weighted by an increasing function of k (such as $k^3$) so that the data at high k (which are of small amplitude) becomes significant. At this point, the data consist of sums of damped sine waves corresponding to the different shells of atoms and hence Fourier transformation is carried out to generate the radial distribution function. The region below $k = 2 \text{ Å}^{-1}$ is excluded because of possible complications from multiple scattering etc. The transformed data ($\chi(R)$ vs. R) actually consist of a complex function, which has real and imaginary parts, or alternatively a modulus and phase. The modulus is the most frequently used quantity, but the real and imaginary parts are also useful. They exhibit significantly more structure than the modulus does, and they don't suffer from nonlinear interference and hence in all the cases discussed in this thesis the data fitting has been carried out on the modulus as well as separately on the real and imaginary parts.
A collection of computer codes have been developed by Dr. Bruce Ravel and co-workers [29], [30] providing a rich graphical interface to the extensive analytical and numerical capabilities of the popular IFEFFIT library [31]. It includes the four sub-routines: (i) ATOMS, a program to generate input data for the *ab initio*, multiple scattering, x-ray absorption spectroscopy code FEFF, (ii) ATHENA, a program for XAS data processing, (iii) ARTEMIS, a program for analysis of extended X-ray absorption fine structure (EXAFS) data using theoretical standards computed by the FEFF program [32], [33] and (iv) HEPHAESTUS, a collection of beamline utilities based on tables of atomic absorption data.

The raw experimental EXAFS data needs some pre-processing before a meaningful data analysis can be carried out to extract relevant information. The data processing includes such steps as conversion of raw data to $\mu(E)$ spectra, background subtraction, energy calibration of spectra, alignment of data, use of reference spectra, deglitching (i.e. the removal of spurious points from spectra), merging of data by calculating the average and standard deviation at each point in a set of spectra and finally Fourier transforming and plotting. The above steps are carried out in the ATHENA subroutine. Once the raw data has been processed appropriately, it is used in ARTEMIS for theoretical modelling and fitting.

ARTEMIS includes access to the functionality of the ATOMS program, which converts crystallographic data into a format suitable for FEFF. This interface can read crystallographic data either in the form of an ATOMS input file or a crystallographic information file (CIF). These data are then converted into a FEFF input file or can be converted into a form suitable for export to a molecule viewer. ATOMS was originally conceived as a tool for generating input files of the form needed by FEFF, an *ab initio* multiple scattering code used to generate theoretical fitting standards for EXAFS analysis and simulation of XANES spectra. FEFF performs its calculation in real-space on a specified
cluster of atoms and so requires a list of Cartesian coordinates of each atom in the cluster. The original purpose of ATOMS is to generate such a list from crystallographic structure data. The central algorithms in ATOMS are for interpreting space group symbols and constructing a description of a unit cell using space group symmetries and the input crystallographic data.

HEPHAESTUS is basically an application for several small utilities based on the periodic table of elements and on a database of absorption cross sections and other data for the elements. All calculations made by HEPHAESTUS use one of several published compilations of atomic cross sections. It provides relevant information regarding absorption and fluorescence line energies of the elements using a periodic table interface, computes the absorption length and quantity of sample required for measurement given the chemical formula and density of a material, displays chemical data such as melting point and electronegativity of the elements, computes the ideal gas mixture for ion chambers of various lengths and internal pressures, finds all absorption edges in the vicinity of a given energy etc.

In XAFS analysis, a theoretical model of the data is constructed containing unknown parameters and their values are determined by fitting. Parts of the theoretical model are well established, such as the basic theory of EXAFS. Other aspects of the model have been well tested, such as the electron scattering contributions in EXAFS that are computed by FEFF. The remaining parts of the model are less well established that must be defined by the data analyst and its accuracy depends on understanding of the problem. In particular, it is crucial to describe the distribution of atoms and the disorder in the structure most usefully and economically in terms of number of parameters. Formulation of these aspects of the model is the most subtle and tricky part of data analysis.

Each scattering path has a degeneracy $N$ (the number of equivalent atoms in single scattering paths), an effective distance $R$ (half path-length), and a mean square variation
parameter \( \sigma^2 \), as mentioned in the canonical EXAFS (equation 2.6). Once calculated, each of these paths can be easily modified to give a different \( N, R, \sigma^2 \), and even \( E_0 \) (if that is necessary). Of the remaining parameters in equation 2.6, \( f(k) \) and \( \delta(k) \) (the scattering amplitude and phase shift due to the neighbouring backscattering atom respectively) and the photoelectron mean free path \( \lambda(k) \) are calculated theoretically. In the past decade or so, calculations of these factors have become more accurate and readily available from the program FEFF and they have been shown to be accurate enough to be used in real analysis. In addition, the calculated factors are not restricted to the first shell and can account for multiple-scattering of the photo-electron. The parameters that are often determined from a fit to the EXAFS spectrum affect either the amplitude of the EXAFS oscillations (\( N, S^2, \sigma^2 \)) or the phase of the oscillations (\( \Delta E_0 \) and \( \Delta R \), the energy shift and the change in half path length respectively.)

The spectrum for a structure that is close to the reference structure can be computed without re-running FEFF, which makes it fast to do within a fitting loop. This is similar to the classical approach in which the spectrum of a standard compound was modified to fit a similar material of unknown structure. Artemis/IFEFFIT [31] works in this way where, the user needs to devise a set of fitting parameters that are adjusted by IFEFFIT to give the best fit to the data (usually over a selected region in \( r \)-space). This approach is particularly good for analyzing simple structures in which only a few paths (mostly single scattering) are important, and also for refining complex structures that are pretty much known, except for a few details. Hence this approach of data fitting has been taken for all the studies described in the present thesis. Although reasonable ad hoc assumptions or constraints can be made to limit the degrees of freedom, it seems more defensible to calculate the DWFs, validate them, and then use them as supplementary information in the fitting process. It is always good to first do a rough analysis of the data to get an overview, and then refine the analysis in later
steps. The fitting algorithms are intended to find a global minimum but it can get trapped in one of the numerous local minima and give misleading results. To verify the true minima, parallel minimizations using Levenberg-Marquardt with many random starting points must be performed, in order to find all the multiple minima. It is also best to start with the simplest hypothetical structure while modelling, and if the fit is inadequate for all rational choices of the parameters, further complexity can be introduced into the model.

In case of an unknown structure, it is a better methodology to model the data shell by shell. The first shell of the FT EXAFS signal is generally dominated by single scattering, even though the tails of multiple scattering contributions at larger $r$ may leak in. However, they have very trivial contributions and initially can be neglected. After approximate solutions are obtained, it is a good idea to fit the whole spectrum together as a unit, in order to account for residual overlap between the shells.

Some of the fitting parameters are correlated. For example, changing the coordination number affects the amplitude parameter uniformly as a function of $k$. Varying $\sigma^2$ also affects the amplitude, but it has a greater effect at high $k$ than at low $k$. Hence, if one of the correlated parameter is perturbed, the other will adjust accordingly to partially make up for it. A similar correlation is observed between $\Delta E_0$ and the distance $R$. Both affect the slope of the phase, but in different ways. The shorter the range of data in $k$ space, the more highly they will be correlated. The fitting problem becomes poorly determined and numerically unstable and introduces large error in parameter values. To avoid this problem one of the correlated parameters should be fixed during a fit. Adding unnecessary parameters may introduce correlations that will cause the error bars to inflate, so the information about the original parameters is masked. This raises the question: how many parameters can be reasonably fit? EXAFS data exist over a finite range in both $k$-space and $r$-space, and therefore they have limited information content. It is known from a Fourier series expansion that only a finite
number of coefficients are needed to represent a signal of fixed bandwidth. All of the data in
the FT exist on an array of $N$ points in size. If we assume that the $k$ window width is $\Delta k$ wide,
and the $r$-space data are contained in total width $\Delta R$, the grid spacings respectively are $\delta k$
and $\delta r$ where $\delta r = \pi/(N\delta k)$. The maximum $r$ value in the $r$ space is $(N/2)\delta r = \pi/(2\delta k)$, where
the factor of two comes in because half the space is allocated to negative frequencies which
offer no new information. The fraction of the total information contained within $\Delta R$ is then
$2\delta k\Delta R$. The number of $k$-space data points in the window is (about) $\Delta k/\delta k$. But most of these
data points actually carry no information, because the signal can be accurately represented
within only a fraction of the total $r$-space. Therefore the actual information content in the data
is number of $k$-space points $\Delta k/\delta k$ times the compression factor $2\delta k\Delta R$. This gives a total
“independent point” count of $N_{\text{ind}} = 2\Delta k\Delta R/\pi$. Stern [34] has argued that a more precise value
is $N_{\text{ind}} = 2\Delta k\Delta R/\pi + 2$.

A simple flow chart depicting the data analysis methodology is given below:

```
ATHENA*
Experimental data → $\chi(k)$ vs $k$ data → Experimental $\chi(R)$ vs $R$

Known Crystal structure → ATOMS program* 
Amorphous structure

FEFF program* → Theoretical $\chi(R)$ vs $R$

ARTEMIS* → $\chi^2$ fitting
```

*All the programs come within IFEFFIT software package. It is free and can be
downloaded from the following links: http://cars9.uchicago.edu/ifeffit/; http://sourceforge.net/projects/ifeffit/

2.4.2 ATHENA

The normal view of the ATHENA window is shown in Fig. 2.18. Data conversion from its
raw form is executed, creating $\mu(E)$ spectra from transmission or fluorescence experiments.
ATHENA also supports powerful pre processing of data as it is imported, including
automated deglitching, truncation, alignment and constraint of analysis parameters. Background subtraction is performed using the AUTOBK algorithm [35] which determines an empirical background spline based on a distinction between data and background in terms of Fourier components. Edge-step normalization of the data is determined by a linear pre-edge subtraction and regression of a quadratic polynomial beyond the edge. The difference between these two polynomials extrapolated to the edge energy $E_0$ is used as the normalization constant in the definition of:

$$\chi(E) = \frac{m(E-E_0)}{\sigma(E)}$$

Normalized data are typically presented after subtracting the curvature of the regressed quadratic and the difference in slope between the post- and pre-edge polynomials after the edge.

![Figure 2.18 The main window of ATHENA program.](image)
The data in E-space is converted to k-space and $\chi(k)$ is obtained by the formula

$$k = \sqrt{\frac{2m(E-E_0)}{\hbar^2}}$$  \hspace{1cm} (2.11)

The absorption edge $E_0$ is determined automatically as the data is imported by finding the first large peak in the first derivative of the $\mu_0(E)$ spectrum, but can also be set interactively. ATHENA provides utilities for most common chores involved in the preparation of EXAFS data for analysis such as energy calibration, alignment of data, use of reference spectra, deglitching and merging of data etc. ATHENA provides tools for the analysis of near-edge spectra as well. There are utilities for calculation of difference spectra, for fitting line shapes (arctangent, Gaussian, Lorentzian) to spectra, and for fitting linear combinations of standard spectra to unknown spectra. ATHENA can also import and display the results of FEFF8 calculations [33] for comparison with measured data. A significant feature of ATHENA is that processing and displaying many data sets simultaneously is as simple as for a single data set. The parameters controlling background removal and Fourier transforms can be adjusted for each data set individually or constrained in a flexible manner between data sets. Additional features include principle component analysis and self-absorption corrections for fluorescence data.

2.4.3 ARTEMIS

ARTEMIS works within the framework of FEFF’s multiple-scattering path expansion [15], [32]. In ARTEMIS the values of the parametric terms in the EXAFS equation, $N$, $\xi$, $E_0$, $\Delta R$ and $\sigma^2$ must be specified for each path included in the fit. The path expansion and how it is parameterized and used in a fit is described elsewhere [36], [37]. EXAFS analysis can be
quite subtle and complicated. By providing a graphical forms-based mechanism ARTEMIS makes basic analysis chores simple and sophisticated analysis problems easy to handle. Shown in Fig. 2.19 is the ARTEMIS window in its data view.

![Figure 2.19 Main window of ARTEMIS program.](image)

The data processing parameters, including the range of the Fourier transform from k-space and the fitting range in R-space, are set in the main window. The far right panel is used to control how plots are displayed. The middle panel is a list of all data sets, FEFF calculations and paths used in the fit. ARTEMIS includes access to the functionality of the ATOMS program, which converts crystallographic data into a format suitable for FEFF. These data are then converted into a FEFF input file or can be converted into a form suitable for export to a molecule viewer. For materials that are not crystalline or do not have a crystalline analogue,
FEFF input files prepared in some other way can be imported directly into ARTEMIS. A simple interface to FEFF is included in ARTEMIS for altering the contents of the input file as needed and a button for launching an external instance of FEFF. After the FEFF run, ARTEMIS displays a page containing a concise interpretation of the paths computed by FEFF including the path distances, degeneracy, atomic species in the path, whether the path is single or multiple-scattering, and estimated importance of the path. ARTEMIS has tools for organizing and plotting the results of the calculation, including plotting the individual contributions of each path in both k- and R-space. ARTEMIS has several features which facilitate the creation and examination of fitting models. One such is the automated generation of parameters appropriate for a first-shell fit. On conducting or importing a FEFF calculation, a set of fitting parameters are automatically generated. In many cases, a fit can be run immediately which will give a physically reasonable result. Because all fitting problems are unique, this fully automated fit is usually inadequate, but it provides a sensible starting point for almost any fitting problem from which the fitting model can be further refined. ARTEMIS provides convenient plotting in k-, R- or back-transformed k-space of the data, the fit and any number of the individual paths used in the fit. Numerous tools are available to check the consistency and sensibility of the parameters used in the fit and to evaluate the results of the fit. An extensive log file is presented upon completion of the fit, allowing the user to evaluate the quality of the fit, the reasonableness of the fitting parameters and the effects of the fitting parameters on the FEFF paths used in the fit. The major fitting statistics, including the reduced $\chi^2$ fitting metric and the R-factor are displayed along with uncertainties and correlations between all fitting parameters. ARTEMIS is equally well suited to simple first-shell analysis of single data sets as well as the most challenging fitting models. Among its advanced features are:

(i) Simultaneous refinement of multiple data sets.
(ii) Refinement using multiple k-weightings for any data set.

(iii) Use of multiple FEFF calculations in a single fit.

(iv) Co-refinement of a background spline to reveal correlations between the spline and the fitting parameters.

(v) Arbitrary constraints between and restraints on parameters.

2.4.4 Goodness of Fit

The experimental data fitting process based on some theoretical modelling invariably includes some presumably known or determinable experimental uncertainties from random noise and other influences. These can be divided into random noise (such as photon counting) and non-random (systematic) errors. It is important to track and eliminate the systematic errors, but they cannot be completely eliminated. While fitting data we systematically vary the hypothetical values of the “unknown” (i.e. only partially known) parameters to give the best agreement with the experimental data. We will not achieve perfect agreement with the data, because of the noise and other uncertainties (“errors”), but we can determine how far we can vary the parameters around the best-fit values while still getting an acceptable fit to within the experimental (and theoretical) errors. The quality of a fit can be quantified by a comparison between the experimental data and the theoretical fit. The simplest approach is to calculate the squared deviation between the data and theory. The deviation (“residual”) is squared so that both positive and negative deviations contribute positively to the error statistic. If there are many data points the squared deviations are summed:

$$\chi^2 = \sum_{i=1}^{n} \left( \frac{\chi_d(r_i) - \chi_t(r_i)}{\sigma(r_i)} \right)^2$$

where $\chi_d(r_i)$ is the $i$th measured data point, $\chi_t(r_i)$ represents the theory function, which depends on the independent variable $r_i$. For EXAFS fitting the goodness of fit can be determined by the following quantities:
Chi-square:

\[ \chi^2 = \frac{N_{\text{data}}}{N_{\text{dof}}} \sum_{\text{freq}} [\text{Re}(\chi_d(r_i) - \chi_t(r_i))^2 + \text{Im}(\chi_d(r_i) - \chi_t(r_i))^2] \]

Where \( \chi(r) \) is the FT EXAFS data (which is a complex quantity) and the subscripts \( d \) and \( t \) denote data and theory respectively and \( \epsilon \) = measurement uncertainty.

Reduced chi-square:

\[ \chi_v^2 = \frac{\chi^2}{v} \]

where

\[ v = N_{\text{dof}} - N_{\text{var}} \]

The values of \( \chi_v^2 \approx 10 \) or higher typically for good quality EXAFS data.

R-factor:

It is the fractional misfit between experimental data and the theoretical fit.

\[ R \text{ factor} = \frac{\sum_{\text{freq}} [\text{Re}(\chi_d(r_i) - \chi_t(r_i))^2 + \text{Im}(\chi_d(r_i) - \chi_t(r_i))^2]}{\sum_{\text{freq}} [\text{Re}(\chi_d(r_i))^2 + \text{Im}(\chi_d(r_i))^2]} \]

In all the EXAFS fittings presented in this thesis, uncertainties in the fitting parameters have been estimated and typical values are ±0.05 Å in R, ± 10% in CN and ±0.001 in DW factor (\( \sigma^2 \)).