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GNXAS. I. Phase shifts and signal calculations

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Fundamental aspects related to the calculation of phase shifts and XAFS signals in the PHAGEN and GNXAS programs in the GNXAS package are reviewed. The strategies behind multiple-scattering series and decomposition into irreducible n-body signals are illustrated. The main strengths of the codes and the input/output data flow facilitated by the CRYMOL and GNPEAK programs are described.

1. Introduction

The GNXAS package has been under development since 1990 and its theoretical background has been thoroughly described in two main articles (Filipponi et al., 1995; Filipponi & Di Cicco, 1995). The suite of programs implements state-of-the-art approaches for computation of the XAFS signal in the framework of the multiple-scattering theory in a complex effective potential for the photoelectron within the muffin-tin approximation. A flow chart of the input/output information through the main and ancillary programs of the suite is shown in Fig. 1.

A specific feature of this code is that the signals are directly associated with a list of specific relevant pair, triplet,... atomic configurations involving the photoabsorbing atomic species in the model structure. The related multiple-scattering expansions or the cumulative irreducible n-body signal can be directly computed using a continued fraction algorithm (Filipponi, 1991). The output signals are tabulated in a suitable energy mesh with separate amplitude and phase information, together with the derivative with respect to all geometrical parameters. This approach allows efficient energy interpolation, and accounts for possible displacements from the reference structures and thermal or structural disorder in the subsequent comparison with experimental data, which is performed using the FITHEO program, without the need to recompute the signals. The reliability of the underlying approximations for the XAFS range has been validated by numerous successful applications of the method to solid, liquid and molecular structures. Applications to the XANES range are possible, especially for systems where the muffin-tin approximation is still a reasonable model.

2. Muffin-tin potential and phase generation

The aim of the GNXAS package (Filipponi et al., 1995; Filipponi & Di Cicco, 1995, 2000) is to generate an accurate multiple-scattering simulation of the EXAFS signal χ(k) related to a model cluster of atoms relevant to the structure under investigation that can be used for structural refinement (fitting) of the raw experimental data. The experimental
EXAFS signal $\chi(k)$ is defined as the relative oscillation of the absorption cross section $\sigma(E)$ with respect to a smooth total atomic cross section $\sigma_0(E)$ normalized to the atomic cross section of the edge under consideration $\sigma_0(E)$, i.e., $\chi(k) = \frac{[\sigma(E) - \sigma_0(E)]}{\sigma_0(E)}$, where $k = \frac{[2m(E - E_0)]}{\hbar}^{1/2}$ is the modulus of the photoelectron wavevector and $E_0$ is the threshold energy of the edge.

The procedure can be divided into the following steps: (i) construction of the model potential for the final-state photoelectron, (ii) calculation of the atomic phase shifts, (iii) signal calculation and (iv) configurational averaging. The program PHAGEN takes care of steps (i) and (ii), while the model cluster can be generated using the CRYMOL program.

The absorption cross section for a cluster of atoms as a function of the incoming photon energy $\omega$ is given in terms of the full Green’s function (GF) of the system by

$$\sigma_{abs}(\omega) = -\frac{\Delta \alpha h \omega}{\pi} \times \sum_{\alpha,\beta} \int \left( \varphi_{\alpha}^* (r) \cdot \varphi (r', E) \right) \cdot \varphi (r', \omega) \, dr \, dr',$$

where $\alpha$ is the fine-structure constant, $\varphi_{\alpha}^* (r)$ is the wavefunction of the excited core electron with angular momentum $L_\alpha \equiv l_\alpha m_\alpha$ and spin $\sigma$, $E = \hbar \omega - E_c$ is the photoelectron energy, and $G(r, r'; E)$ is the solution of the equation

$$[\nabla^2 + E - V_{opt}(r)] G^+(r - r'; E) = \delta(r - r').$$

Here, $V_{opt}(r)$ is the (complex) potential obtained from the reduction of the photoabsorption many-body problem to an effective one-electron problem moving in an effective optical potential. In nonmagnetic materials $V_{opt}(r)$ is spin-independent, so that in equation (1) we can drop the spin summation and multiply the cross section by 2.

In multiple-scattering theory (MST) one divides the space into non-overlapping domains $\Omega_i$ (cells) and introduces a partition of the potential $V_{opt}(r) = \sum v_i(r)$, where $v_i(r)$ coincides with $V_{opt}(r)$ within the cell $\Omega_i$ and is zero outside. The Schrödinger equation (SE) is then solved in each cell and these local solutions are assembled together into the desired global solution.

One of the advantages of MST is that one can write an explicit form of the GF as

$$G(r, r'; E) = \sum_{LL'} \Phi_{LL'}(r; k) [\delta_{LL'} - \delta_{ll'} T_{LL'}] \Phi_{LL'}(r'; k)$$

in terms of the scattering-path operator $T_{LL'}$, and the local and regular and irregular solutions $\Phi_{LL'}(r; E)$ and $\Psi_{LL'}(r, E)$ of the SE at energy $E$ inside the cell located at $i$. $\Psi_{LL'}(r, E)$ smoothly matches the Hankel function $H(r; E) = -i k u_{LL'}(r) Y_{LL'}(r)$ at the boundary of the cell ($k = E^{1/2}$ in atomic units), whereas $\Phi_{LL'}(r, E)$ is regular at the origin. Here, $Y_{LL'}(r)$ are spherical harmonics, the origin, the cell $i$ and $r$, respectively.

Moreover, introducing the matrix $T = T_{LL'} \delta_{ll'}$, which is diagonal in the site indices, and the site-off-diagonal matrix $G = G_{LL'}(1 - \delta_{ll'})$, we have

$$\tau = (T^{-1} - G)^{-1} = \sum_{n} (TG)n^T T = \sum_{n} T (GT)^n.$$

The series expansion in equation (4) is absolutely convergent if the spectral radius (maximum eigenvalue of $TG$) $\rho(TG) < 1$, otherwise it is only conditionally (or asymptotically) convergent. Usually, for small clusters of ($\sim$10–15) atoms there is absolute convergence. In all other cases it is not difficult to find the order $n$ that gives meaningful results (Sébilleau & Natoli, 2009).

The quantity $T_{LL'}$ describes the scattering amplitude due to the potential $v_i(r)$ of cell $i$ for an impinging spherical wave of angular momentum $L$ into a spherical wave of angular momentum $L'$, whereas $G_{LL'}$ gives the amplitude of free propagation from site $i$ to site $j$ for spherical waves. Its expression is given in terms of 3-J symbols by

$$G_{LL'}^{ii} = \frac{-i [4\pi(2l + 1)(2l' + 1)]^{1/2} \sum_r (2l'' + 1)^{1/2} \begin{pmatrix} l & l' & l'' \\ m & m' & m'' \end{pmatrix} (1)^{m+m'} h_{m}^{l''} (kr_{ij}) Y_{m''}^{l''} (\vec{R}_{ij})}{2(2l + 1)^{1/2} \sum_r (2l'' + 1)^{1/2} \begin{pmatrix} l & l' & l'' \\ m & m' & m'' \end{pmatrix} (1)^{m+m'} h_{m}^{l''} (kr_{ij}) Y_{m''}^{l''} (\vec{R}_{ij}).$$

where $R_{ij} = R_i - R_j$ is the vector joining site $j$ to site $i$. For further details, refer to Natoli et al. (2020) and references therein.

With the aim of coping in a simple way with the wide variety of systems that are usually encountered in practical applications, one makes the ansatz that the optical potential is a function of the local density $\rho(r)$ of the system under consideration. Experience has shown that a potential made

![Figure 1](image_url)

A flow chart of the main input/output information (dashed rectangles) through the PHAGEN and GNXAS codes is shown, together with the roles of the auxiliary CRYMOL and GNPEAK programs that are useful for preparing the required input files.
up of the sum of the Hartree Coulomb potential and the complex Hedin–Lundqvist (HL) exchange and correlation energy (Natoli et al., 2003), satisfying this requirement, constitutes a very good approximation to this kind of ‘universal’ optical potential with satisfactory results.

Moreover, partitioning the space into non-overlapping domains in an automatic way is not straightforward for arbitrary atomic locations. This difficulty motivated the introduction of the muffin-tin (MT) approximation, whereby one draws a sphere around each atomic position, inside which the potential \( v(r) \) is spherically averaged, whereas it is approximated by a suitably chosen constant in the interstitial region between the spheres.

In this approximation, the atomic \( T \) matrix \( T_{LL'} \) is diagonal in the angular momentum indices and is independent of \( m \), so that \( T_{LL'} = \delta_{LL'} \delta^L \). In turn, \( \Phi_j(r; E) = R_l(r)Y_l^m(\hat{R}) \) and \( \Psi_j(r; E) = R^*_l(r) Y^m_{L}(\hat{R}) \), where \( R_l(r) \) and \( R^*_l(r) \) are regular and irregular solutions of the radial SE with angular momentum \( l \). Then,

\[
\ell' = \left[ \frac{[R_l(r)j_l^\ell(kr) - R^*_l(r)j^\ell_l(kr)]}{[R^*_l(r)h^{\ell^*}_j(kr) - R_l(r)h^\ell_j(kr)]} \right]_{r = R'_c},
\]

where the functions are calculated at the sphere radius \( R'_c \). Here, \( j^\ell_\ell(kr) \) is the Bessel function of order \( l \) and \( f^\ell(r) = d(f^\ell)/dr \). Notice that if the potential is complex, then the phase shifts \( \delta^\ell \) are also complex.

Within this approach, the total density \( \rho(r) \) of the cluster of atoms is constructed by superimposing the self-consistent charge densities of the neighbouring atoms on the atomic charge density present in each sphere, and then spherically averaging the anisotropic charge thus obtained. Moreover, since the Poisson equation is linear in charge density, we can overlap atomic Hartree potentials in the same way to obtain the total Coulomb potential of the cluster. This procedure makes it possible to calculate an average charge density and an average potential in the interstitial region. Finally, from the knowledge of the total density at each point in space, one can add the complex HL exchange and correlation energy to the Hartree potential to obtain the total optical potential. Once this latter is known in each sphere, one can integrate the radial SE by the Numerov procedure to obtain \( R_l(r) \) and \( R^*_l(r) \) and calculate \( t^\ell \) via equation (6). As a result of the MT approximation, these latter are the same for all atoms that are equivalent under the symmetry operation of the cluster. Further details of this whole procedure are given in Natoli et al. (2003).

3. Photoabsorption cross section

By inserting equation (3) into equation (1), we obtain the absorption cross section as the sum of an atomic absorption originating from the photoabsorber located at site 0 [the second term in equation (3)] and a contribution due to scattering from the environment,

\[
\sigma(\omega) = \sigma_{\text{sc}}(\omega) + \sigma_{\text{c}}(\omega),
\]

owing to the fact that \( \sigma_{\text{sc}}(\omega) \) becomes zero in the absence of a neighbourhood of the photoabsorber. From the expansion in equation (4), taking into account that \( G_{LL'}^{\text{LL}} = 0 \), we obtain

\[
\sigma_{\text{sc}}(\omega) = -8\pi a_0 \omega \sum_{m} \sum_{m'} (E_{LL'} + E_{m'm'}) \sum_{n=2}^{\infty} \frac{[\mathbf{T}_{n}^{\text{LL}}]^{0}_{m'm'} G_{LL'}^{n}\mathbf{M}_{LL'}^{n}(E),}
\]

where

\[
M_{LL'}(E) = \int d^3r \, R_l(r)Y^m_\ell(\hat{R}) (\mathbf{e} \cdot \mathbf{r}) R_{l'}(r; E) Y_{L'}^m(\hat{R})
\]

and the sum over \( L, L' \) is over the final angular momenta selected by the dipole selection rule.

If we average over the polarizations of the incoming photon, then equation (8) becomes

\[
\sigma_{\text{sc}}(\omega) = -8\pi a_0 \omega \sum_{l} \sum_{m} \frac{1}{2l+1} [\delta_{l,l-1} + (l+1)\delta_{l,l+1}] M_{ll}(E) \sum_{n=2}^{\infty} \frac{[\mathbf{T}_{n}^{\text{LL}}]^{0}_{m'm'} G_{LL'}^{n} M_{LL'}^{n}(E),}
\]

where now \( M_{ll}(E) = \int d^3r \, R_l(r)R_{l}(r; E) dr \) is the radial integral. For \( s \) core states (1s, 2s, 3s, ...) only the second term \((l+1)\) survives, which usually is much stronger than the \((l-1)\) term.

The separation of the total cross section into a scattering part \( \sigma_{\text{sc}}(\omega) \) and a core absorption \( \sigma_{\text{c}}(\omega) \) corresponds exactly to what is performed in the definition of the experimental structural signal \( \chi(k) \), so that the theoretical signal to compare with \( \chi(k) \) is \( \sigma_{\text{sc}}(\omega)/\sigma_{\text{c}}(\omega) \).

Writing down the MS series for \( s \) core states, we obtain

\[
\sigma(\omega) = \sigma_0 \left[ 1 + \sum_{l \neq 0} \chi_{2l}^{(0)} + \sum_{l \geq 3} \chi_{2l}^{(0)} + \sum_{l \geq 3} \chi_{2l}^{(0)} \right],
\]

where

\[
\chi_{2l}^{(0)} = \sum_{\ell = 0}^{2l-1} \frac{M_{\ell}^{(0)} t_{\ell}^{(1)}}{2l+1} \frac{1}{\sigma_0} \sum_{n=2}^{\infty} \left[ \sum_{m} \zeta_{2l-m}^{(0)} \right]_{n},
\]

where \( \sigma_0 = 8\pi a_0 \omega \) and specifically \( \zeta_{2l}^{(0)} = G_{0l}^{(0)} G_{1l}^{(0)} \) for \( \chi_{2l}^{(0)} \), \( \zeta_{2l}^{(0)} = G_{0l}^{(0)} G_{1l}^{(0)} G_{2l}^{(0)} \) for \( \chi_{2l}^{(0)} \), \( \zeta_{2l}^{(0)} = G_{0l}^{(0)} G_{1l}^{(0)} G_{2l}^{(0)} G_{3l}^{(0)} \) for \( \chi_{2l}^{(0)} \). In this notation, it is understood that the internal angular momentum indices have been saturated.

Notice that in the case of complex potentials the atomic absorption \( \sigma_{\text{c}}(\omega) \) does not factor out from \( \sigma_{\text{sc}}(\omega) \) as it does in the case of a real potential. \textit{PHAGEN} takes this peculiarity of the complex potentials into account.

4. Irreducible \( n \)-body signals

The analysis of MS paths based on equation (8), although useful, is not very efficient and versatile. One can, however, reorder the MS series in such a way as to obtain a faster convergence rate and to relate each order \( n \) to an \( n \)-body distribution function. Indeed, on the basis of equation (7) it is possible to calculate cross sections \( \sigma(0, i, j, \ldots) \) and the

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related XAFS signals \( \sigma(0, i, j, \ldots) / \sigma_0 - 1 \) associated with a photoabsorber 0 surrounded by an arbitrary number of atoms \( i, j, \ldots \), and this approach can be used to define and calculate the irreducible \( n \)-body contributions to the XAFS signal (Filipponi et al., 1995). The pair contribution due to atom \( i \) surrounding the photoabsorber is given by

\[
y^{(2)}(0, i) = \frac{\sigma(0, i)}{\sigma_0} - 1 = \chi^{00}_{2} + \chi^{0000}_0 + O(x^4),
\]

which is an oscillating function of \( k \) with a leading phase equal to \( 2 \mathbf{R}_0 \). It can be calculated directly using the full-matrix inversions of equation (4) for two atoms, or expanded into the corresponding multiple-scattering series, as indicated explicitly in equation (13).

The triplet contribution associated with the simultaneous presence of atoms \( i, j \) around the photoabsorber is given by

\[
y^{(3)}(0, i, j) = \frac{\sigma(0, i, j)}{\sigma_0} - \frac{\sigma(0, i)}{\sigma_0} - \frac{\sigma(0, j)}{\sigma_0} + 1,
\]

which is the XAFS signal due to atoms \( i, j \) minus the irreducible XAFS signals associated with the independent presence of atoms \( i \) and \( j \). \( y^{(3)}(0, i, j) \) is also an oscillating function of \( k \) with a leading phase \( R_0 + R_i + R_j \) determined by the shortest multiple-scattering path involving all sites. The multiple-scattering expansion for \( y^{(3)}(0, i, j) \) contains many terms and its direct calculation is computationally convenient if its amplitude and phase are well behaved.

The four-body contribution associated with the simultaneous presence of atoms \( i, j, k \) around the photoabsorber is given by

\[
y^{(4)}(0, i, j, k) = \frac{\sigma(0, i, j, k)}{\sigma_0} - \frac{\sigma(0, i, j)}{\sigma_0} - \frac{\sigma(0, i, k)}{\sigma_0} - \frac{\sigma(0, j, k)}{\sigma_0} + \frac{\sigma(0, i)}{\sigma_0} + \frac{\sigma(0, j)}{\sigma_0} + \frac{\sigma(0, k)}{\sigma_0} - 1,
\]

which is an oscillating function of \( k \) with a leading phase determined by the shortest multiple-scattering path involving all sites. The multiple-scattering expansions for the \( y^{(n)}(0, i, j, \ldots) \) signals become progressively cumbersome.

The total XAFS signal for a generic fixed atomic configuration surrounding the photoabsorber can therefore be expanded in a series of irreducible contributions of increasing order,

\[
\chi(k) = \sum_i y^{(i)}(0, i) + \sum_{(i,j)} y^{(j)}(0, i, j) + \sum_{(i,j,k)} y^{(k)}(0, i, j, k) + \ldots,
\]

that are expected to become progressively weaker and contribute with progressively higher frequencies to the spectrum. This series has improved convergence properties with respect to the multiple-scattering series since it combines in each term an infinite number of terms in the latter. The irreducible \( y^{(n)}(0, i, j, \ldots) \) signals can be computed by combining a finite number of total cross section calculations for finite-size clusters according to equations (13), (14) and (15), and this task can be conveniently and efficiently accomplished using the continued fraction algorithm (Filipponi, 1991). An example of signal decomposition into the main irreducible two-, three- and four-body signals is illustrated for the face-centred cubic (f.c.c.) structure of solid nickel in Fig. 2.

In particular cases each \( y^{(n)}(0, i, j, \ldots) \) signal can be approximated/computed using the leading terms of the corresponding multiple-scattering series. For \( y^{(3)} \) such a term corresponds to the well known single-scattering contribution given by Schaich (1984):

\[
\chi^{00}_{3}(k) = \exp(2i\mathbf{R}_0) \sum_{l'} (2l' + 1) [ \sum_{l''} (2l'' + 1) \left( \begin{array}{ccc} l & l' & l'' \\ 0 & 0 & 0 \end{array} \right) ]^2 \times [h^+_{l'}(kR_0)]^2.
\]

This is an exact curved wave expression which is at the basis of any modern single-scattering EXAFS calculation. Efficient equations for higher multiple-scattering paths were first introduced by Gurman et al. (1984) and other authors (Brouder et al., 1989).

References

