FEFF 5 - AN *ab initio* MULTIPLE SCATTERING XAFS CODE

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ABSTRACT

FEFF5 is an efficient automated code which calculates multiple scattering (MS) curved wave XAFS spectra for molecules and solids. We review the theoretical ingredients and approximations contained in the code, with the aim of describing the how XAFS spectra are efficiently simulated. The FEFF5 code consists of 4 independent modules: a scattering potential and phase shift module, a path finder module, a scattering amplitude module and an XAFS module. Multiple scattering Debye-Waller factors are built in using a correlated Debye model.[3]

1. Introduction

1.1. Theoretical Model

FEFF5 is an efficient code which calculates multiple scattering (MS) curved wave XAFS spectra for molecules and solids. In this brief article, we review the theoretical ingredients and approximations contained in the code,[1,2] with the aim of describing the how XAFS spectra are simulated. Many of the considerations dealt with here are common to other *ab initio* XAFS codes; others, such as our method for speeding up the MS calculation, are unique to FEFF5. Applications will be discussed elsewhere.[3]

The theoretical model upon which FEFF5 is based[1] is as follows: We consider a model system consisting of an absorbing atom of atomic number Z_c and an arbitrary cluster of atoms at sites $\vec{R}$ with atomic numbers Z. The XAFS photoabsorption spectrum χ_l for a given core level, *i.e.*, K, L_I, L_{III}, *etc.*, is then calculated using curved wave MS theory.[2] The molecular potential is constructed using an overlapped relativistic atom muffin-tin potential. Our potential includes inelastic losses automatically through the imaginary part of the electron self-energy. The code is automated to require as few user adjustable

parameters as possible. For example, core-hole lifetimes and mean free paths are built in, and MS Debye-Waller factors are calculated using a correlated Debye model.

1.2. Calculation Strategy

In brief, FEFF reads a single input file, feff.inp, which specifies the model system and then runs one or more of four program modules which correspond to the sequential steps in the simulation of XAFS. The output simulates experimental data over the range $k = 0 - 20$ Å^{-1}. Although highly automated, users must give FEFF5 enough input data to do its first two jobs of calculating the potentials and a sufficient number of paths for the XAFS calculation. For example, users must generally know or have some hypothetical estimate of the geometrical structure of the system for MS calculations to make sense. The number of MS paths can quickly proliferate, and although FEFF5 has provisions for limiting the output to the most important contributions, some analysis and experimentation by the user may be required. FEFF5 is written in ANSI standard FORTRAN 77 and is portable to any machine with a FORTRAN 77 compiler and at least 3 Mbytes of memory.

2. Code Modules

2.1. Atomic Potential and Phase Shift Code

The purpose of this part of the code is to calculate scattering potentials, scattering phase shifts, muffin-tin radii and other parameters for each atom. First, the relativistic Dirac equation is solved for each free atom type as if the atom were isolated in space. Then chemical effects are simulated by overlapping these free atomic potentials and densities based on the user-specified geometry of the cluster to form the scattering potentials, phase shifts, etc. The potential and phase shift data are stored in a binary file (phase.bin). This part of the code is similar to that of our single-scattering codes FEFF3 and FEFF4. Full details of the approximations underlying these potentials and phase shifts are given in Ref. 1.

For computational efficiency the code uses the same scattering potential for every atom in a similar chemical environment. Each such distinguishable potential is called a "unique potential." This is a good approximation as small differences in chemical environments are hardly noticeable in practice. The assignment of unique potentials is not automated in FEFF5 and requires some care on the part of a user.

2.2. Path Code

Deciding which MS paths to include for a particular system is the key problem in

MS XAFS simulations. In addition to the difficulty of visualizing and enumerating paths, the sheer number of paths quickly becomes overwhelming, growing exponentially with total path length. We have found, however, that most MS paths have small amplitudes and can simply be neglected, although exactly which paths will have significant amplitudes is usually not obvious. Moreover, the folklore that single scattering and shadowing paths dominate is not reliable. Our hope is that FEFF5 will enable users to answer this question on a case by case basis. The path code automatically determines which MS paths to consider, based on atomic position data in the input file and a quantitative estimate of the path amplitude.

The pathfinder constructs all scattering paths in order of increasing total path length up to some R_{max}. As a path is found, it is modified and considered again by putting it into a heap (a partially ordered data structure). These two modifications are guaranteed to find all paths in order of increasing path length. After all paths have been found, the list is checked for degeneracy, so that paths that are geometrically identical are counted and eliminated.

The quantity used to measure a path's importance is the mean scattering amplitude $|f|$ averaged over the full k-range, ie, the area under the curve of $|f|$ vs k. The filters, which eliminate the unimportant paths, are based on a comparison of the mean amplitude of the path being considered to that of the largest path encountered so far. The first three filters eliminate paths based on partial (and very fast) approximations to this amplitude, and are applied as early as possible in the calculation. The final filter is the result of the full curved wave calculation, including degeneracies.

2.3. Scattering Amplitude Module

The module GENFMT (generalized f-matrix formalism) calculates the XAFS parameters for each path based on the fast, accurate scattering matrix formalism of Rehr and Albers,[2] yielding the matrix product Tr $MF^N \cdots F^2 F^1$ needed in the calculation of the XAFS [Eq. (1) below]. Note that, unlike the plane wave approximation (PWA), this is a matrix product and is therefore not commutative (except in in the zero order limit of 1×1 matrices, which is only accurate to about 25%). That is, if two paths have the same angles and leg lengths but in different orders, the XAFS will in general not be the same. The only exception to this is when the paths are exactly backwards (or time-reversed) in which case the XAFS will be identical. The pathfinder sees these paths as degenerate. These XAFS parameters are represented in terms of the quantities in the standard XAFS equation. GENFMT calculates these parameters for each path in the path list (paths.dat) using the phase shifts, etc., from phase.bin. The results are written to files feffnnnn.dat. A

separate file, files.dat, contains a list of all the feffnnnn.dat files that were made, including data on the path amplitudes.

2.4. XAFS module FF2CHI

The contribution to the XAFS spectrum from a given path $\chi_\Gamma(k)$ is calculated from the XAFS parameters for each path. This module is called FF2CHI (i.e., feff to chi). FF2CHI reads the feffnnnn.dat files listed in files.dat and makes chi.dat, using the exact curved wave XAFS formula,[1]

$$\chi_\Gamma(p) = \text{Im} \, S_0^2 \, \frac{e^{i(\rho_1 + \rho_2 + \cdots \rho_N + 2\delta_1)}}{\rho_1 \rho_2 \cdots \rho_N} e^{-\sigma_\Gamma^2 p^2/2} \text{Tr} \, M F^N \cdots F^2 F^1. \tag{1}$$

The correlated Debye model Debye-Waller factors[3] are also calculated in this module.

2.5. Options and Control

Though highly automated, the code does have provisions for a number of options. These include several self-energy models [Hedin-Lundqvist (default), Dirac-Hara, ground state], overlapped muffin-tins, and ionized atomic configurations. Additional parameters can be specified in the path search, e.g., the maximum path length. Which of the modules are executed in a given run are set by control parameters. For example, it is possible to refine the path search by running only the PATH module.

2.6. Output Files

The code produces a number of output files. Our strategy is to print out enough information to complete a calculation and to permit successive calculations and refinements without the need for recalculating potentials and phase shifts. The potential and phase shift data is stored in a single binary file, phase.bin, and the path data is in a path list, paths.dat. The complete XAFS data for each path is stored in a short file feffnnnn.dat, where nnnn is the path index. The FF2CHI module produces a single XAFS file chi.dat from a given set of feffnnnn.dat files. Additional diagnostic files are printed at high print levels.
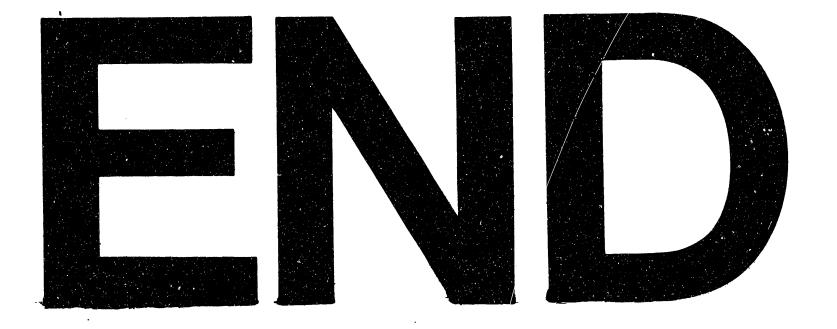
3. Acknowledgment

4. References

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