XFIT – an Interactive EXAFS Analysis Program

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XFIT is an interactive and user-friendly program for the analysis of X-ray absorption fine structure (XAFS, EXAFS) curves. *XFIT* incorporates in a single package a number of features available in other existing programs: *ab initio* EXAFS calculation (using *FEFF*4.06/6.01), empirical EXAFS calculation (as in *XFPAKG*), allowance for polarization, use of Fourier filtering, and the application of constraints and restraints. Additional features not previously available are: simultaneous refinement with respect to several data sets, simultaneous refinement of several absorber sites, and Monte-Carlo error analysis. Applications including the analysis of EXAFS data from mixtures and the analysis of DAFS (diffraction anomalous fine structure) data are indicated.

1. Introduction

The analysis of X-ray absorption fine structure (XAFS, EXAFS) is an important technique for determining the immediate environment of an atomic species (the absorber) in a compound. Above an X-ray absorption edge, the interaction of the absorbing atom with photoelectron waves backscattered by neighbouring atoms leads to an oscillatory modulation in the X-ray absorption coefficient, the EXAFS (see Lee, Citrin, Eisenberger & Kincaid, 1981; Gurman, 1995). Analysis of the EXAFS can yield the numbers and types of backscattering atoms, and accurate absorber–backscatterer distances. Applications include the determination of the structure of metal sites in proteins and catalysts.

Software packages available for the analysis of EXAFS data include *XFPAKG* (Cramer, Hodgson, Stiefel & Newton, 1978; Cramer & Hodgson, 1979; Scott, 1985), *EXCURVE* (Binsted, Campbell, Gurman & Stephenson, 1991; Binsted, Strange & Hasnain, 1992), *UWXAFS* (Stern, Newville, Ravel, Yacoby & Haskel, 1994), and *GNXAS* (Filipponi, Di Cicco, Tyson & Natoli, 1991; Westre *et al.*, 1995). In a typical analysis, the dimensions of a model are adjusted so as to optimize the agreement between the calculated and experimental EXAFS. *XFPAKG* calculates EXAFS using either tabulated amplitude and phase functions obtained by *ab initio* calculation, or empirical functions derived from the EXAFS of compounds with known structure. *EXCURVE*, *UWXAFS* and *GNXAS* exclusively use functions calculated *ab initio*. All of the cited packages include Fourier filtering of the experimental EXAFS. *EXCURVE* makes provision for several types of parameter restraint and constraint.

Experience in the use of *XFPAKG* and *EXCURVE* suggested to the authors that substantial improvements in EXAFS analysis could be achieved if a single program offered all of the following options:

(*a*) a choice between *ab initio* and empirical calculations of EXAFS,

(*b*) Fourier filtering of both experimental and calculated EXAFS,

(*c*) a generalized formalism for parameter constraints and restraints,

(*d*) the ability to fit a model simultaneously to several EXAFS data sets,

(*e*) the ability to fit a model with more than one absorption site,

(*f*) a user-friendly interface.

The program *XFIT* incorporates these features.

2. The model

The aim of an EXAFS analysis is to minimize the difference between an observed EXAFS spectrum and the theoretical EXAFS calculated from a *model* of the absorber site.

The model is described in terms of *shells*, each comprising identical atoms at the same distance from the absorber. In *XFIT*, a shell has the following parameters: Z, the atomic number of the atoms in the shell; N, the number of atoms in the shell; R_{as}, the distance of the atoms from the absorber; (x, y, z), the coordinates of an atom representing the shell;* and σ^2, the Debye–Waller temperature factor.

If the amplitude and phase parameters for the EXAFS calculation have been derived empirically (see below), then they are included as additional parameters for each shell.

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* $R_{as} = |(x, y, z)_a - (x, y, z)|$ where $(x, y, z)_a$ is the position of the absorber. In a single-scattering calculation it is usually convenient to fix the absorber at (0, 0, 0), equate R_{as} with one of the atomic coordinates, and set the other two atomic coordinates to zero.

3. Calculation of the theoretical EXAFS

The expression commonly used in the calculation of theoretical EXAFS is:

$$\chi(k) = \sum_s N_s[f_{as}(k)/kR_{as}^2]\exp(-2\sigma_{as}^2k^2)$$

$$\times \exp(-2R_{as}/\lambda)\sin[2kR_{as} + \alpha_{as}(k)] \qquad (1)$$

where N_s is the number of backscattering atoms in shell s; R_{as} is the distance of the atoms in shell s from the absorbing atom; σ_{as}^2 is the mean-square deviation in R_{as};* λ is the photoelectron mean-free path; $f_{as}(k)$ is the effective scattering amplitude function; and $\alpha_{as}(k)$ is the phase function.

k is the magnitude of the photoelectron wavevector and is related to the X-ray energy by the expression:

$$k = \hbar^{-1}[2m_e(E - E_0)]^{1/2} \qquad (2)$$

where E is the energy of the incident X-ray photon and E_0 is the threshold energy for the removal of the core electron.

The parameters $f_{as}(k)$ and $\alpha_{as}(k)$ depend on the nature of the absorber and scatterer atoms and can be derived either empirically by analysing the EXAFS of compounds with known structure, or *ab initio* by quantum-mechanical calculation.

4. Empirical EXAFS calculation

In empirical EXAFS calculations, $f_{as}(k)$ and $\alpha_{as}(k)$ are conveniently parameterized by a procedure introduced in *XFPAKG* (Cramer, Hodgson, Stiefel & Newton, 1978; Cramer & Hodgson, 1979; Scott, 1985). Eight coefficients are introduced for each shell:

$$f_{as}(k) = c_0[\exp(c_1k + c_2k^2)]k^{c_3} \qquad (3)$$

$$\alpha_{as}(k) = a_{-1}k^{-1} + a_0 + a_1k + a_2k^2. \qquad (4)$$

The coefficients c_0, c_1, ... , a_2 are derived from the EXAFS of a compound whose structure is accurately known. The values of the atomic number Z, population N and distance R_{as} in equation (1) are taken from the known structure. The eight coefficients in $f_{as}(k)$ and $\alpha_{as}(k)$ are varied until the fit between the observed and calculated EXAFS is optimized.

5. *Ab initio* EXAFS calculation

Alternatively, the EXAFS may be calculated *ab initio* using the single-scattering EXAFS program *FEFF*4.06 or the multiple-scattering program *FEFF*6.01 (Rehr & Albers, 1990; Rehr, Mustre de Leon, Zabinsky & Albers, 1991; Mustre de Leon, Rehr, Zabinsky & Albers, 1991). These

programs may be obtained as stand-alone versions (see *Program availability*, below). Their function is restricted to the calculation of EXAFS. *FEFF*6.01 has previously been used for this purpose in *UWXAFS* (Stern, Newville, Ravel, Yacoby & Haskel, 1994).

The expression used by both programs to calculate EXAFS is:

$$\chi(k) = \sum_\Gamma N_\Gamma A(k)\frac{|f_{\mathrm{eff}\Gamma}(\pi,k,R)|}{kR_\Gamma^2}\sin\{2kR_\Gamma + 2\mathrm{Re}[\delta_\Gamma^c(k)]$$

$$+ \Phi_{\mathrm{eff}\Gamma}(k)\}\exp(-2\sigma_\Gamma^2k^2)\exp[-2R_\Gamma/\lambda_\Gamma(k)] \qquad (5)$$

$$A(k) = S_0^2\exp\{-\mathrm{Im}[\delta_\Gamma^c(k)]\} \qquad (6)$$

where Γ designates a scattering path; N_Γ is the multiplicity of the scattering path and depends on the number of atoms in each shell on the path; R_Γ is the effective path length; σ_Γ^2 is the mean-square deviation in R_Γ; $\delta_\Gamma^c(k)$ is the final-state central-atom phase shift; $f_{\mathrm{eff}\Gamma}(\pi,k,R) = |f_{\mathrm{eff}\Gamma}(\pi,k,R)|\exp[i\Phi_{\mathrm{eff}\Gamma}(k)]$ is the effective curved-wave backscattering amplitude; $\lambda_\Gamma(k)$ is the mean free path of the photoelectron; $A(k)$ is a factor combining intrinsic losses, final-state interference effects, and central-atom losses; S_0^2 is a many-body amplitude reduction factor; and Re and Im represent the real and imaginary parts of a number.

All the parameters in the EXAFS equation are calculated *ab initio* by *FEFF*4.06 or *FEFF*6.01 from the model parameters $\{Z_{\mathrm{shell}}, N_{\mathrm{shell}}, (x, y, z)_{\mathrm{shell}}\}$, except the following: S_0^2 is included as an additional variable; N_Γ is calculated by *XFIT* from the number of atoms, N, in each shell on the path; and σ_Γ^2 is calculated by *XFIT* from the σ^2 parameters and the geometry of the path, using an isotropic uncorrelated vibration model.*

For single-scattering, $N_\Gamma = N$, and $\sigma_\Gamma^2 = \sigma^2$. In the multiple-scattering case, the values of σ^2 estimated by *XFIT* are accurate for linear paths and become less reliable as the paths deviate from linearity. More sophisticated models exist [*e.g.*, in *GNXAS* (Filipponi, Di Cicco, Tyson & Natoli, 1991)]. They are not used in *XFIT* because (i) they add an excessive number of parameters in systems of even moderate complexity, and (ii) the multiple-scattering effects are generally strongest for near-linear paths, and the effects of small errors in calculating them become unimportant rapidly as the deviation from linearity increases.

Changes from *ab initio* to empirical EXAFS calculation and *vice versa* can be programmed or made interactively. The parameters which the two modes of calculation have in common are retained if there is a change from one mode to the other.

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* Following common practice (see, *e.g.*, Gurman, 1995), R_{as} is assumed to have a Gaussian distribution. This allows the disorder to be quantified using a single parameter for each atom.

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* The model is based on the assumptions that (i) the atomic vibrations are isotropic, and (ii) the vibrations of any pair of atoms are uncorrelated. For paths in which no atom appears more than once, these assumptions yield the expression:

$$\sigma_\Gamma^2 = \sum_i \sigma_i^2(1 - \cos\theta_i)/2$$

where σ_i^2 is the single-scattering σ^2 factor for atom i on the path and θ_i is the internal angle between the incoming and outgoing legs at atom i.

6. Polarized EXAFS

The program *FEFF*6.01 calculates the plane-polarized or elliptically polarized EXAFS for K, L_1, L_2 and L_3 edges accurately. A more rapid but less accurate method, applicable only to K and L_1 edges, is to use *FEFF*4.06 or empirical calculations. In this case the plane-polarized EXAFS is obtained by multiplying the unpolarized EXAFS by an approximate polarization factor. The polarization factor is (Lee, Citrin, Eisenberger & Kincaid, 1981):

$$p_{\Gamma} = 3(\hat{e}.\hat{R}_{as})^2 = 3\cos^2\theta \qquad (7)$$

where $\hat{e}$ is the electric field polarization vector; $\hat{R}_{as}$ is the absorber–scatterer vector; and θ is the angle between $\hat{e}$ and $\hat{R}_{as}$.

7. Fourier filtering

The observed and calculated EXAFS are usually multiplied by a factor k^n to compensate for the rapid attenuation of the EXAFS with increasing k. The arbitrary exponent n is called the k-weighting and is typically 2 or 3.

The Fourier transform of a k-weighted EXAFS spectrum is a complex function of the distance, and can be treated as a type of radial distribution function. If the phase function $\alpha(k)$ were uniformly 0, the magnitude of the Fourier transform would peak near the distances of the backscattering atoms. In practice, a 'phase' correction relating the peak positions to the true interatomic distances is required (Lee, Citrin, Eisenberger & Kincaid, 1981).

The inverse transform of the Fourier transform is the original EXAFS. Noisy or otherwise unwanted parts of the EXAFS or its Fourier transform may be given lower weights ('filtered') by applying a window function prior to the forward or inverse Fourier transformation. In *XFIT*, Fourier filtering involves the following operations:

(i) The original spectrum is multiplied by k^n.

(ii) The k^n-weighted spectrum is multiplied by a window function.

(iii) The windowed spectrum is Fourier transformed.

(iv) The Fourier transform is multiplied by a window function.

(v) The windowed Fourier transform is inverse Fourier transformed.

The Fourier-filtered EXAFS is given by the equation:

$$\chi_{\text{filtered}} = \mathfrak{F}^{-1}[\Lambda_R(\mathfrak{F}\Lambda_k\,k^n\,\chi_{\text{original}})] \qquad (8)$$

where $\mathfrak{F}$ is the Fourier transform, $\mathfrak{F}^{-1}$ is the inverse Fourier transform, n is the k-weighting, Λ_k is the EXAFS window, and Λ_R is the Fourier-transform window.

The window functions in *XFIT* consist of an edge rising from 0 to 1, a region of magnitude 1, and an edge falling from 1 to 0. The edge regions avoid abrupt truncation of the curves and minimize the distortion of the transforms. The width, position and functional form of each edge can be varied.

Although Fourier filtering is an almost universal feature of EXAFS analysis, many investigators apply the filter only to the observed EXAFS and not to the calculated EXAFS. This makes comparisons between the observed and calculated EXAFS formally incorrect, since the use of a filter may distort the EXAFS contribution of one or more scatterers. A valid comparison between the observed and calculated EXAFS is possible only if the two functions have been modified (*i.e.* distorted) in the same way.

8. Refinement algorithm

XFIT varies the structural parameters of the model so as to optimize the match between the calculated EXAFS χ_{calc} and the observed EXAFS χ_{obs}. The optimization is achieved by minimizing X^2 which is defined as follows:

$$X^2_{\text{exafs}} = \int_{k=0}^{\infty} \{w[\chi_{\text{obs}}(k) - \chi_{\text{calc}}(k)]\}^2 dk \qquad (9)$$

where w is the weighting factor; $\chi_{\text{obs}}(k)$ is the filtered observed EXAFS curve; and $\chi_{\text{calc}}(k)$ is the filtered calculated EXAFS curve.

Most of the parameters, including the E_0 value, the filter parameters, the weighting factors as well as the model and empirical parameters, may be refined. The refinement uses the Levenberg–Marquardt method (Marquardt, 1963). The integral is calculated numerically.

9. Constraints and restraints

Constraints and restraints are used to incorporate prior information into an analysis, or to reduce the degrees of freedom of the model. Constraints specify precise relationships between parameters, restraints specify targets for relationships between parameters.

Although constraints and restraints have been included in other software packages, notably *EXCURVE* (Binsted, Campbell, Gurman & Stephenson, 1991; Binsted, Strange & Hasnain, 1992), a distinctive feature of *XFIT* is that the treatment of constraints and restraints has been generalized. In *XFIT* any relation that can be written as a mathematical expression, using vector or scalar arithmetic, trigonometric and other operations, equalities or inequalities, can be used as a restraint. Similarly, any expression of equality can be used as a constraint, with the restriction that it must be linear in any parameters being refined. Examples of constraints and restraints are given in a later section.

A restraint expression may be followed in braces by a value analogous to an estimated standard deviation, $\{\sigma\}$. Inclusion of this value is optional. The default value is 1.

Restraints are applied by adding an extra term to X^2 so that the quantity minimized is

$$X^2 = X^2_{\text{exafs}} + \sum_{\text{restraints}} X^2_{\text{restraint}} \qquad (10)$$

where

$$X^2_{restraint} = (\Delta_{restraint}/\sigma_{restraint})^2 \qquad (11)$$

and $\Delta_{restraint} = 0$ if the expression is satisfied; $\Delta_{restraint}$ is the difference between the two sides of the restraint expression otherwise; and $\sigma_{restraint}$ is the σ value given for the restraint (default value = 1).

10. Refinement using more than one EXAFS data set

XFIT has the capacity to use several experimental EXAFS spectra (data sets) simultaneously. The X^2_{exafs} value minimized is then the sum of the individual X^2 values:

$$X^2_{exafs} = \sum_{sets} X^2_{set}. \qquad (12)$$

The filter parameters, the weighting factor w in (9), the energy E_0 and the polarization for each data set are independent of the other data sets.

Potential applications of this feature of *XFIT* include the use of polarized EXAFS data recorded for several orientations of a crystal specimen, or the use of EXAFS data recorded at different absorption edges for a specimen containing more than one type of absorber. For example, it would be possible to refine the structure of a Cu–Fe cluster in a metalloprotein simultaneously with respect to the Cu and Fe EXAFS spectra. The ability to produce a single structure that is optimized with respect to all the data would be particularly advantageous for determining Cu$\cdots$Fe or Cu$\cdots$X$\cdots$Fe interactions which contribute to both the Cu and the Fe EXAFS.

11. Multiple absorbing atom sites

Another feature of *XFIT* is the capacity to refine models containing a single absorber in more than one environment. In such cases, the observed EXAFS is the weighted mean of contributions from the individual absorber sites. *XFIT* permits (i) the simultaneous refinement of several absorber sites, and (ii) the simultaneous use of several data sets in which the absorber sites have different occupancies. In the case of polarized EXAFS data from oriented single crystals, there is provision for (iii) the simultaneous use of several data sets in which the absorber sites have different orientations with respect to the polarization vector. Thus it is possible to analyse the EXAFS of virtually any mixture in which an absorber is present in several environments. The mixture may be a frozen solution containing an equilibrium mixture of two components, or a mixture of several phases. An important potential application is the analysis of DAFS (diffraction anomalous fine structure) data where the contributions of symmetry-related absorbers to the EXAFS profile of a reflection may have different polarizations. All these applications are subject to the normal restrictions on the number of variables that can be refined with respect to the data.

12. Goodness-of-fit (residual)

The progress of the refinement is monitored (as in an X-ray crystal structure analysis) by means of a residual R, defined as:

$$R = (X^2/X^2_{calculated \equiv 0})^{1/2} \qquad (13)$$

where X^2 is the quantity minimized during the refinement, and $X^2_{calculated \equiv 0}$ is the value of X^2 when the calculated EXAFS is uniformly 0.

At the end of the refinement, the R factor is reported with and without the contribution from the restraints. The correlation matrix and the estimated standard deviations for the refined parameters are also reported. The estimated standard deviation of a parameter is defined as the change which causes X^2 to increase by 1 when all the other parameters are refined.

It is to be noted that the residual R takes no account of the degrees of freedom in the data or the model. These are generally unknown and may be hard to estimate. The estimated standard deviation, though routinely used, can be misleading unless X^2 is a 'true' value, *i.e.* $\sum\{[\chi(k)_{calc} - \chi(k)_{obs}]/\sigma(k)_{obs}\}^2$. This condition cannot be satisfied when k-weighting or Fourier filtering is used.

13. Monte-Carlo error analysis

More objective estimates of the standard deviations may be obtained by means of a Monte-Carlo calculation (see, *e.g.*, Hammersley & Handscomb, 1965). In order to derive e.s.d.'s by this method, *XFIT* requires (i) a smoothed EXAFS data set in which the noise in the observed EXAFS has been suppressed, and (ii) a 'noise curve' representing the magnitude of the noise as a function of k. A program to smooth the EXAFS data and to calculate the noise curve is supplied.* *XFIT* first generates a series of simulated EXAFS data sets by adding random noise to the smoothed EXAFS. At each value of k, the noise is assumed to have a Gaussian distribution and an r.m.s. value equal to the amplitude of the noise curve. The model is then refined with respect to each of the simulated data sets. Thus a series of values is obtained for each refined parameter. A linear regression analysis of these values yields the correlation

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* Smoothing the EXAFS is achieved by applying a low-pass filter (double Fourier transformation). The absolute value of the difference between the smoothed EXAFS and the observed EXAFS is defined as the noise at each data point. A low-pass filter is applied either to the values of the noise or to their squares, resulting in a smooth function. If the function is derived from the values of the noise, its amplitude at each data point is multiplied by $(\pi/2)^{1/2}$, the ratio between the average and r.m.s magnitudes of a Gaussian distribution. If the function is derived from the squared values of the noise, its amplitude at each data point is converted to the square root. The decision whether to use noise or noise-squared values, the k-weighting, and the choice of parameters for the low-pass filters, are under the investigator's control.

matrix, the estimated standard deviations, and estimates of the uncertainty in the estimated standard deviations (Spiegel, 1975a,b).

The number of refinements performed during the Monte-Carlo analysis can be varied. The default value is 16. If this is used, the e.s.d.'s have e.s.d.'s equivalent to approximately 17% of their own value (Spiegel, 1975a).

The Monte-Carlo analysis in *XFIT* also permits the user to calculate the estimated standard deviation in any function of the parameters. The functions included in the analysis are evaluated after each refinement. The resulting series of values are analysed in the same way as those obtained for the refined parameters. This feature is useful, for example, when a model is refined in terms of Cartesian coordinates but the e.s.d.'s in the polar coordinates are required.

To the best of our knowledge, this is the first time a Monte-Carlo error analysis has been applied to EXAFS.

14. User-friendly interface

XFIT is command-driven. Only the following set of simple commands is required:

(a) EXAFS (read in an EXAFS data set).

(b) THEORY (set the theory to use in calculating EXAFS).

(c) PRINT (save the observed and calculated EXAFS, Fourier transforms and windows).

(d) DELETE (remove constraints, restraints or EXAFS data sets).

(e) REFINE (refine a set of parameters).

(f) RESTORE (restore all parameters to their original values).

(g) MONTECARLO (do a Monte-Carlo error analysis on a set of parameters).

(h) LIST (display constraints, restraints or EXAFS data sets).

(i) SAVE (save the current constraints, restraints, model or data sets).

The three-dimensional model is displayed depth-cued in a separate window. The orientation from which the model is viewed can be manipulated using the mouse. For each data set, windows display the experimental and calculated EXAFS, Fourier transforms, window functions and filtered EXAFS. The curves to be displayed are selected by means of buttons in the windows.

A feature of *XFIT* which is particularly helpful when specifying restraints and constraints is the capacity to write expressions using vector and scalar arithmetic, normalization, absolute value, dot- and cross-products, and trigonometric and other functions. The expressions can be evaluated and reported at any time.

15. Examples

(1) *Use of an XFIT command.* The command to refine the position and number of the atoms in shell 1 is `refine v1 N1`.

(2) *Manipulation of parameters.* The command `x1 = 2` sets the value of the x coordinate of shell 1 to 2.0. The command to access the value is `? x1`.

(3) *Application of a numerical constraint.* The expression `N1 + N2 == N3 + N4` constrains the number of atoms in shells 3 and 4 to be equal to the number in shells 1 and 2.

(4) *Application of a symmetry constraint.* A mirror plane perpendicular to x is created by the constraint expressions `x1 == -x2, y1 == y2, z1 == z2`.

(5) *A restraint on the number of atoms in a shell.* The number of atoms in shell 1 can be restrained to be less than 2.0 by using the expression `N1 < 2 { 0.5 }`. The value in braces is optional and is analogous to an estimated standard deviation (σ). Its default value is 1.

(6) *A restraint on a bond length.* Bond 1—2 is restrained to a value near 1.54 Å by the expression `|v1-v2|~=1.54{0.01}`.

(7) *A restraint on a bond angle.* The expression

`acos (|(v1-v2)^.(v3-v2)^|)*180/pi ~= 120 {5}`

restrains the angle 1—2—3 to 120°, with a σ value 5°. The symbol '^' is the normalization operator.

(8) *Restraining atoms to be coplanar.* The expression

`((v1 - v2) x (v3 - v2))^.(v4 - v2) ~= 0 {0.01}`

restrains the atoms 1, 2, 3 and 4 to be coplanar. Here 'x' and '.' are the vector cross- and dot-products.

16. Data

The EXAFS files used by the program are plain text files to facilitate manipulation and transfer. The data are arranged as columns of numbers in free format. The type of data stored in any column is determined by a heading at the top of the column, allowing arbitrary column order. Each data point consists of an energy or k value and the corresponding EXAFS value. There is provision to include the edge at which the data were collected and the E_0 value for the scan. Energies may be stated in eV, Hartree or Rydberg units. For polarized EXAFS data, the direction of the polarization vector of the X-ray beam in relation to the model coordinates may be indicated; if this is done, it automatically triggers the calculation of polarized EXAFS when the data set is used. Other information relating to the data may be stored in the file as comments.

17. Some recent *XFIT* analyses

(1) An unconstrained and unrestrained single-scattering refinement based on transmission EXAFS data showed that the Cu site in (3-chloroanilinium)$_8$(CuCl$_6$)Cl$_4$ has the expected elongated tetragonal geometry (Ellis, Freeman, Hitchman, Reinen & Wagner, 1994). In a published X-ray crystal structure analysis, the Cu site had been described as having a compressed tetragonal geometry. This geometry

was seen to be the average of two components of a disordered structure.

(2) A constrained and restrained multiple-scattering refinement based on transmission EXAFS data showed that the Cu site in $[Cu(py_3CH)_2](NO_3)_2$ also has an elongated tetragonal geometry (Astley *et al.*, 1995). In this case, an X-ray crystallographic analysis had yielded a trigonally symmetrical Cu site geometry, again reflecting disorder in the crystals. In the EXAFS refinement, constraints were used to apply a plane of symmetry to the model and to make the pattern of Debye–Waller factors around all the pyridine rings identical. The dimensions of the ligand were restrained to values taken from a related compound. Additional restraints ensured that the Debye–Waller factors increased with increasing distance from the Cu atom.

(3) The Cu^I–ligand bond lengths in the reduced forms of the copper protein plastocyanin at high and low pH were re-determined by means of a multiple-scattering analysis (Ellis, Hedman, Hodgson & Freeman, 1995). Models for the *two forms* of the Cu site were refined *simultaneously* with respect to unpolarized EXAFS data recorded from frozen solutions at 10 K, and polarized EXAFS data recorded from single crystals at high and low pH at 295 K. The models obtained are consistent with all *eight* EXAFS data sets. Constraints were applied to force the Cu site dimensions at 10 and 295 K to be identical whilst permitting the Debye–Waller factors to differ. The dimensions of the ligand groups were restrained to ideal values, and additional restraints were applied to the Debye–Waller factors as in (2) above.

18. Program availability

The program is implemented in C on the Silicon Graphics Iris 4D/20, Indigo xs24 and Indigo 2 computers running IRIX Release 4.0.5 and 5.3 System V. Versions running under X-Windows, OS/2 and Win32 are in preparation. The programs *FEFF*4.06 and *FEFF*6.01 used in the *ab initio* calculations were developed at the University of Washington. *XFIT* users are required to have a licence for these programs from the *FEFF* Project, Department of Physics, University of Washington, Seattle WA 98195, USA.

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