Chemical transferability of single- and multiple-scattering EXAFS Debye–Waller factors

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Single- and multiple-scattering EXAFS Debye-Waller factors are amplitude reduction parameters that appear in the EXAFS $\chi(k)$ equation accounting for the structural and thermal disorder of a given sample. These parameters must be known accurately in order to obtain quantitative agreement between theory and experiment. Since experimental data can only support a limited number of fitted parameters these factors must be known from another source. Although various approaches have been considered in the past with a variety of results, the self-consistent *ab initio* Density functional theory stands for the most accurate and reliable method regardless of molecular symmetry or other specific sample requirements. Since DFT scales as N^3 where N is the number of atomic basis set, an *ab initio* calculation on a large structure is not feasible due to enormous CPU demand and in many cases due to hard energy/geometry convergence. In this paper we present two ways of overcoming this problem. Both they use the idea that by reducing the structure, the DWFs are still chemically transferable. In order to test this we use the Zn tetraimidazole. This molecule represents typical metal-organic ring samples that can be seen in active sites of metaloproteins. Results are compared to experimental EXAFS spectra.

Keywords: EXAFS; Density Functional Theory; Debye-Waller factors.

1. Introduction

The X-Ray Absorption Fine Structure (XAFS)(Stern, E.A., 1988 & Lee, P. A., and Pendry, J. B., 1975) Debye-Waller factor is an important term that appears in the XAFS $\chi(k)$ equation as an exponential of the form $e^{-2k^2\sigma^2}$ accounting for disorder, thermal and structural, of a given sample. Since experimental data can only support a limited number of fitted parameters these factors must be known from another source. In the past *ab initio* calculation in small molecules using the Density Functional Theory (DFT) (Dimakis, N., and Bunker, G., 1998), semi-empirical in the Zn-tetraimidazole (Dimakis, N., and Bunker, G., 1999) and the equation of motion approach have been presented (Poiarkova, A.V., and Rehr, J.J., 1999) as an alternative to the one parameter Einstein or Debye model that clearly fails to describe either single scattering (SS) heterogeneous bonds and/or multiple-scattering (MS) paths. Although previous investigators agree that self-consistent, fully *ab initio* calculation is the most desirable approach, great CPU demand and also hard energy and/or geometry convergence make it not always feasible. In order to overcome this problem we present a dual-path alternative way to the full *ab initio* calculation in the case of metal-organic ring structures that appear as active sites in metaloproteins. Our approach is based on the idea that the DWFs will not be affected much, maybe with an exception of the first shell one, if we start reducing the structure by removing rings around the metal absorbing atom and either maintaing the symmetry and the first neighboring atoms or removing these at all.

In the first approach cluster symmetry and first shell atoms are maintained in the test structure whereas empty lobes are filled with hydrogen atoms. This is to maintain molecular charge and spin multiplicity of the cluster. Also there are no constrains in any of the reduced structures. In the second case only one imidazole, the Zn metal, and one hydrogen for the empty lobe is present. In this case the Zn-N interatomic distance is constrained to the value found by either by fitting experimental EXAFS data with FEFF[1] or from *ab initio* calculation on the full structure. Maintaining molecular symmetry and the inclusion of first shell atoms make the first accurate than second but at a cost of higher CPU demand. The second is much faster will almost none of the typical convergence problems that might arise in the first but less accurate.

Calculations were performed using Unichem/DGAUSS 4.1 by Oxford Molecular Group at a Silicon Graphics ORIGIN 200 dual tower server. The method used was DFT under local spin density approximation (LDA) with double zeta basis set (DZ). Spin multiplicity was not chosen at random. It was found that the high spin multiplicity (spin one in this case) corresponds to lower energy i.e. to the ground state.

2. The first approach: Maintaing Molecular Symmetry

As it was mentioned before, in the first case we start reducing the Zn tetraimidazole structure by removing imidazole rings from the cluster. By using Debye program [2] we calculate SS and MS DWFs for various Zn-ring paths (Fig. 1). The DWFs for the most important of these paths at 150° K can be seen in Table 1. By carefully examining Table 1 it can be seen that the variation on the DWFs among the various reduced structures and from the all-ring case is less 8%. We then used these DWFs as input parameters in FEFF file where the amplitudes and phases correspond to the *all*-rings case. As it can be easily seen there is almost no variation on the magnitude of the Fourier transform beyond the first shell. Therefore this first approach could predict very accurately SS and MS DWFs with the possible exception of the first shell SS DWF that

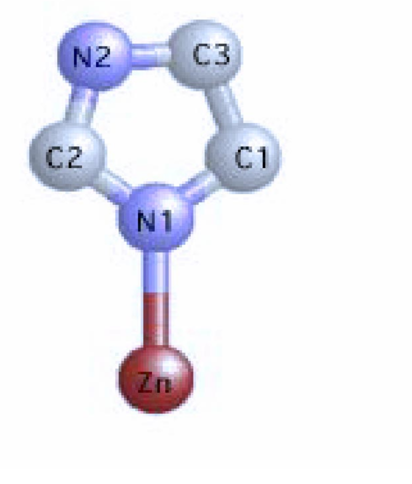

Figure 1
Zn and one imidasole ring.

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[1] In typical active sites of metaloprotens first shell radial distance is well resolved from the rest of the shells.

[2] First written by N. Dimakis at 1997.

Table 1
Calculated SS and MS DWFs of Zn tetraimidazole for multiplicity 3 and $T = 150K$. Empty lobes are filled by NH_2.

Path	*Arrangement*			
	1 Ring	*2 Rings*	*3 Rings*	*All Rings*
	$\sigma^2(\times 10^{-3}\AA^2)$			
Zn-N(1)	3.25	3.158	3.083	2.987
Zn-N(2)	4.374	4.613	4.578	4.532
Zn-C(1)	6.13	6.174	6.07	5.755
Zn-C(2)	6.44	6.957	6.763	6.595
Zn-C(3)	4.297	4.19	4.100	3.967
Zn-N(1)-N(2)-Zn	3.90	3.912	3.855	3.824
Zn-N(1)-C(3)-Zn	4.010	3.944	3.877	3.778
Zn-C(2)-N(1)-Zn	4.490	4.570	4.446	4.386
Zn-C(1)-N(1)-Zn	4.135	4.089	4.049	3.914
Zn-C_2-N_2-N_1-Zn	4.290	4.416	4.353	4.215

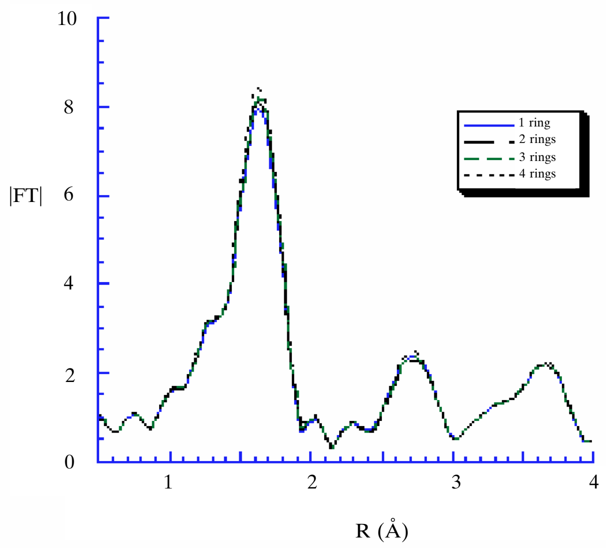

Figure 2
Magnitude of the Fourier Transform of the Zn tetraimidasol using DWFs from one, two, three and *all* ring configuration.

could well determined by RATIO and/or non-linear LSQ fitting with experimental EXAFS data.

During DFT calculation no particular geometry/energy optimization convergence problems appeared in the procedure if the high spin (low energy in this case) was used. In a arbitrary cluster reducing adjacent rings might induce convergence problems and constaints especialy to maintain the particular molecular symmetry might be nessasary.

3. The second approach: Breaking the Molecular symmetry

In the second case only one ring, the absorbing metal Zn and a hydrogen atom for the empty lobe is present in the test structure. By using Debye program again we re-calculate SS and the MS for this arrangment and we are comparing the magnitude of the corresponding Fourier transform with the one-ring case and all ring case of the preveious techniquie (Fig. 2). Although this approach is not as accurate as the one it it faster and has no convergence difficulties that might arise in more complicated structures. Results are finally compared to experimental EXAFS data and a very good agreement is obtained (Fig. 3). In this case the first shell radial distance distance is fixed to 1.99$\AA$ as predicted by RATIO.

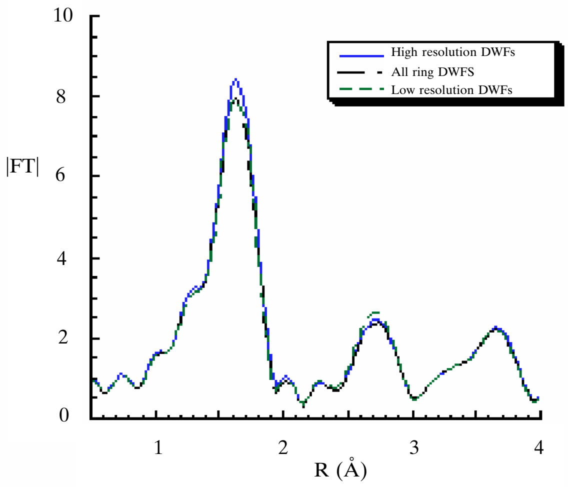

Figure 3
Magnitude of the Fourier Transform of the Zn tetraimidasol using DWFs from 1 (with and without molecular symmetry) and all ring configuration.

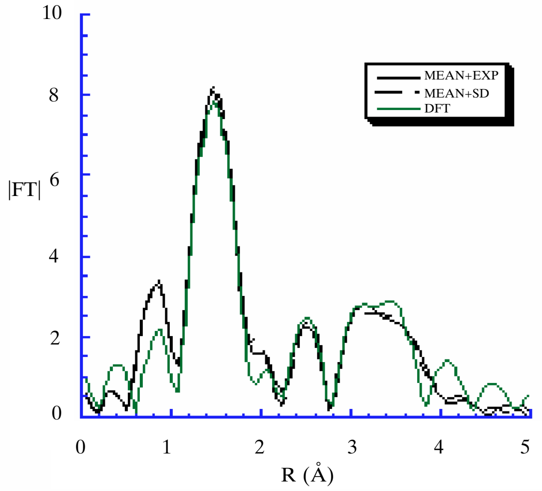

Figure 4
Magnitude of the Fourier Transform of the Zn tetraimidasol using DWFs from ring-one without molecular symmetry (first shell r_{Zn-N} is constrained to 1.99$\AA$) vs experimental EXAFS spectra at $T = 120°K$.

4. Conclusion

Chemical transferability on SS and MS DWFs, using two simmilar approaches wasproved using the Zn tetraimidasole. Generalization to asymmetric active protein sites as Cu(II) bisimidazole phenole is under investigation.

This project is supported by NIH-RR08630.

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Received 31 July 2000 • Accepted 30 November 2000