

## Treatment of disorder effects in X-ray absorption spectra beyond conventional approach

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X-ray absorption spectroscopy (XAS) is an excellent tool to probe the local environment in crystalline, nanocrystalline and disordered solids, liquids and gases in a wide range of external conditions. The theoretical description of the X-ray absorption fine structure (XAFS) relies on the multiple-scattering (MS) formalism. The size of the region probed by XAS depends on the degree of thermal and static disorder present in a material and is limited by the mean-free path of the excited photoelectron. Typically, the information reach region extends up to 3-10 Å around the absorbing atom. The conventional analysis of XAFS based on the fitting procedure becomes challenging, when it extends beyond a few nearest coordination shells around the absorber, due to (i) the number of structural parameters increases exponentially with the probed region size and (ii) strong correlation exists between parameters of distant scattering paths caused by their overlap. Moreover, the conventional analysis assumes some shape (often Gaussian) for a distribution of interatomic distances that can be inaccurate in the case of strongly distorted environment.

To address these issues, we employ atomistic simulation methods such as molecular dynamics (MD) and reverse Monte Carlo (RMC), which are implemented in two codes – EDACA (<http://www.dragon.lv/edaca/>) and EvAX (<http://www.dragon.lv/evax/>). The EDACA code allows one to calculate configuration-averaged EXAFS or XANES spectra using the results of MD simulations performed by one of the external codes such as LAMMPS, GULP, DL\_POLY and CP2K. For each atomic configuration (“snapshot”) obtained during the MD simulation, EXAFS is calculated using ab initio real-space multiple-scattering FEFF code, whereas XANES is evaluated by ab initio FDMNES code. The obtained configuration-averaged EXAFS or XANES spectrum can be directly compared with the experimental one. The EvAX code allows one to reconstruct the local structural and thermal disorder in crystalline and nanocrystalline materials by analyzing EXAFS. The structure optimization process in our RMC is based on the evolutionary algorithm which significantly reduced the computation time. Moreover, we employ the comparison between the experimental and calculated EXAFS spectra in k- and R-spaces simultaneously using Morlet wavelet transform that stabilizes the obtained model. In this study, we will demonstrate the use of both methods on an example of several materials such as W, FeF<sub>3</sub>, Cu<sub>3</sub>N and aqueous solutions of 3d ions.

Molecular dynamics and reverse Monte Carlo methods provide a natural way to include disorder effects into EXAFS and XANES simulations. Both approaches allow one to interpret EXAFS spectra based on the MS formalism far beyond the first coordination shell and to extract structural information on the distribution functions and related parameters. Note that the MD-EXAFS method relies on the accuracy of the interatomic potential model, but the structural model is uniquely defined from the results of the MD simulation, and no structural fitting

parameters are used. Therefore, the MD-EXAFS method is well suited for a validation of theoretical MD models.