EDACA software demonstration for Molecular Dynamics simulations of EXAFS spectra

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EXAFS Spectroscopy Laboratory

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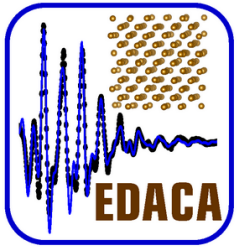

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Preface

X-ray absorption spectroscopy (XAS) at synchrotron radiation sources is a structural tool providing information on the local atomic and electronic structure around an atom of a particular type. Today XAS is successfully applied to a study of crystalline, nanocrystalline and disordered solids, liquids and gases in a wide range of external conditions defined by temperature, pressure, etc. 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 extended up to 3-10 A around the absorbing atom.

An advantage of the XAS method is its sensitivity to many-atom distribution functions, giving rise to multiple-scattering (MS) contributions, and to correlation effects in atom dynamics. Note that accurate account of both effects is still challenging.

The time-scale (about 10^{-15}-10^{-16} s) of the X-ray absorption process is much shorter than the characteristic time (about 10^{-13}-10^{-14} s) of thermal vibrations. Therefore, the atoms may be considered as frozen at their instantaneous positions during a single photoabsorption process, and the total experimentally measured X-ray absorption spectrum corresponds to the configurational average of all atomic positions over the time of the experiment. This situation can be straightforwardly modelled combining the molecular dynamics (MD) simulation with the extended X-ray absorption fine structure (EXAFS) calculations, known as the MD-EXAFS approach.

Finally, the agreement between the experimental and configuration-averaged EXAFS spectra can be used to validate the accuracy of the interatomic potential (force-field) models employed in the MD simulations.

MD-EXAFS method

The general scheme of the MD-EXAFS method is shown in figure below.

The order of elements in the command line is important and should correspond to that in the pot.dat file (see below), the first atom is always the absorber.
After running edamd.exe, XYZ file produced by MD simulation will be split into a set of smaller XYZ files. Each small XYZ file corresponds to individual atomic configuration and is centred at proper absorbing atom ('0' number) surrounded by other atoms ('1', '2', ...) located within a sphere with the radius Rmax. The full list of small XYZ file names is written in a **conf.dat** file.

The edaca.exe code uses the results produced by the edamd.exe code plus a number of additional files, which should be located in the same directory.

A set of files required by the edaca.exe includes:
1) a set of small **XYZ** files and **conf.dat** file produced by edamd.exe.
2) **feff.exe** - an executable of the FEFF8x or FEFF9x code.
3) ***.bin** and other files required by the FEFF code (output files after FEFF8 & FEFF9 calculation for static configuration), if cluster potential is supplied by the user (recommended).
4) **feff.dat** - an input file in ASCII format for the FEFF8x or FEFF9x code with the *.dat extension: it can be produced from the feff.inp file simply by deleting all atomic coordinates after ATOM command.
5) **pot.dat** - a file in ASCII format which describes correspondence between elements (potentials) in the MD simulation and FEFF calculation. The order of elements (potentials) is important and should be checked by the user!

The edaca.exe code calculates EXAFS spectrum for each XYZ file specified in the conf.dat file. These spectra are saved under the names xt.001, xt.002, ... The main result is saved under the name **xt_tot.txt** and contains the configuration-averaged EXAFS spectrum.

Downloads

Download EDACA User's Manual in PDF format.

Download the current version of the EDACA package.
The ZIP archive includes code, manual and examples.

References

Please cite these works in your publications based on the results of the EDACA simulations:

A. Kuzmin, R.A. Evarestov, *Quantum mechanics-molecular dynamics approach to the interpretation of X-ray absorption spectra*, J. Phys.: Condens. Matter 21 (2009) 055401 (6 pp). DOI: 10.1088/0953-8984/21/5/055401

A. Kuzmin, A. Anspoks, A. Kalinko, J. Timoshenko, *The use of x-ray absorption spectra for validation of classical force-field models*, Z. Phys. Chem. 230 (2016) 537-549. DOI: 10.1515/zpch-2015-0664

This page is maintained by Alexei Kuzmin (a.kuzmin@cfi.lu.lv).

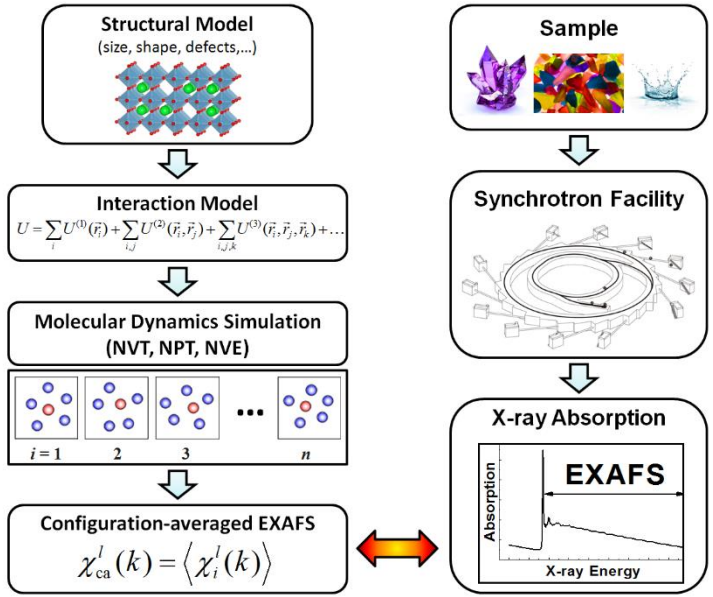
MD-EXAFS approach: Concept

VESTA

Databases

Molecular Dynamics
(LAMMPS, GULP, …)

EDACA
(EDAMD+EDACA+STDEV)
+
FEFF8-Lite
(feff.exe)



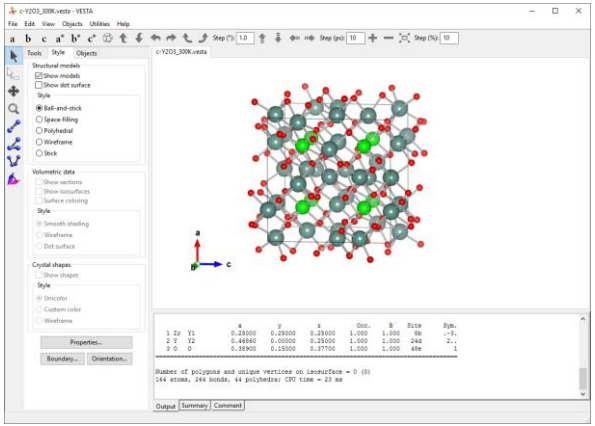
EDACA code:

A. Kuzmin and R.A. Evarestov, J. Phys.: Condens. Matter 21 (2009) 055401.
A. Kuzmin, A. Anspoks, A. Kalinko, J. Timoshenko, Z. Phys. Chem. 230 (2016) 537-549.

Structure visualization

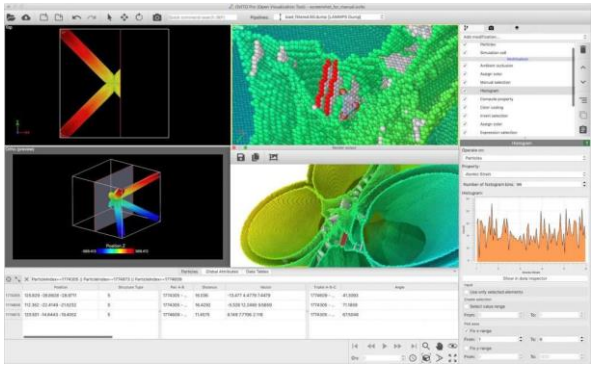
VESTA a 3D visualization program for structural models, volumetric data such as electron or nuclear densities, and crystal morphologies.

http://jp-minerals.org/vesta/en/



OVITO is a scientific visualization and data analysis solution for atomistic and other particle-based models.

https://www.ovito.org/



Databases of interatomic potentials

Curtin University GULP https://gulp.curtin.edu.au/gulp/models.cfm

https://www.ucl.ac.uk/klmc/Potentials/

IPR Interatomic Potentials Repository https://www.ctcms.nist.gov/potentials/

OpenKIM https://openkim.org/

Molecular Dynamics Programs

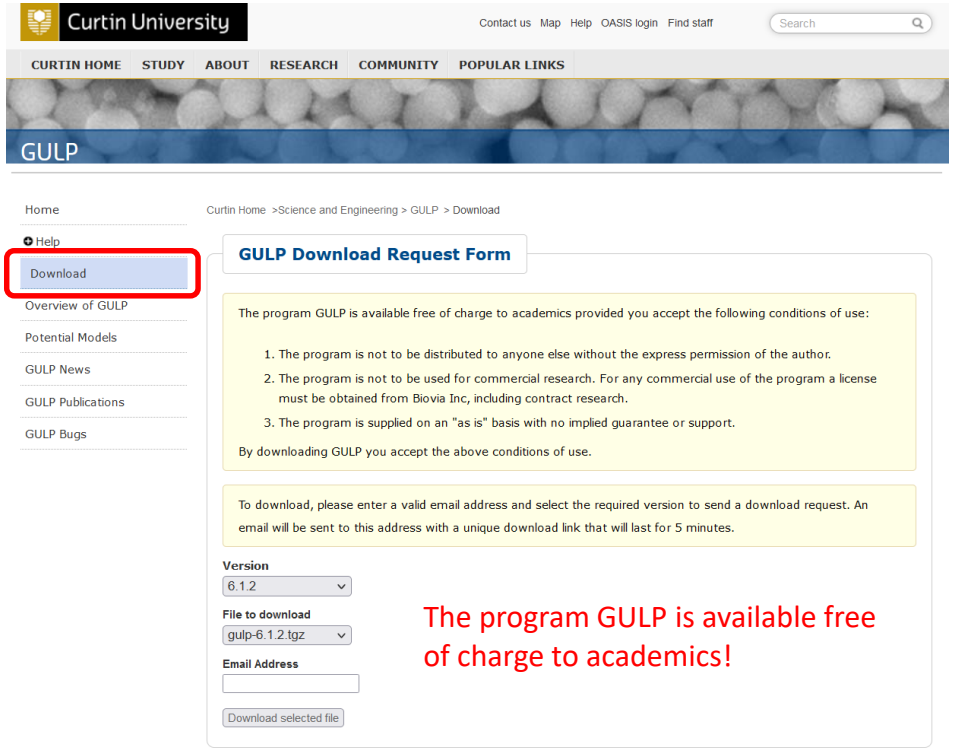
https://en.wikipedia.org/wiki/Comparison_of_software_for_molecular_mechanics_modeling

GULP	- the General Utility Lattice Program. https://gulp.curtin.edu.au/gulp/
LAMMPS	- a Large-scale Atomic/Molecular Massively Parallel Simulator. https://www.lammps.org/
DL_POLY	- a general purpose serial and parallel molecular dynamics simulation package. https://www.scd.stfc.ac.uk/Pages/DL_POLY.aspx
CP2K	- a program to perform atomistic and molecular simulations of solid state, liquid, molecular, and biological systems. (also ab initio) https://www.cp2k.org/

Important: MD trajectory must be saved as *.XYZ file with a specific structure.

Molecular Dynamics Program - GULP

https://gulp.curtin.edu.au/gulp/



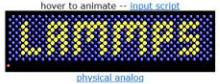
Molecular Dynamics Program - LAMMPS

https://www.lammps.org/

LAMMPS Molecular Dynamics Simulator

lamp: a device that generates light, heat, or therapeutic radiation; something that illumines the mind or soul -- www.dictionary.com

hover to animate -- input script



physical analog

lammps-stable.tar.gz

2023 LAMMPS Workshop & Symposium, held virtually from Aug 8-11, 2023. Visit workshop website.

There is a new LAMMPS overview paper which you can cite in your publications. See citation details here and cool images here.

Big Picture	Code	Documentation	Results	Related Software	Context	User Support
Features	Download	Manual	Publications	Pre/Post processing	Authors	MatSci forum
Non-features	Git mirror	Programmer guide	Picture gallery	External packages & tools	History	Slack channel
Packages	SourceForge	Tutorials	Movie gallery	Pizza.py toolkit	Funding	IRC channel
FAQ	Latest features & bug fixes	MD to LAMMPS glossary	Benchmarks	Visualization	Open source	Workshops
Wish list	Report bugs & request features	Commands	Citing LAMMPS	Other MD codes	Contribute to LAMMPS	Books about MD

LAMMPS is a classical molecular dynamics code with a focus on materials modeling. It's an acronym for Large-scale Atomic/Molecular Massively Parallel Simulator.

LAMMPS has potentials for solid-state materials (metals, semiconductors) and soft matter (biomolecules, polymers) and coarse-grained or mesoscopic systems. It can be used to model atoms or, more generically, as a parallel particle simulator at the atomic, meso, or continuum scale.

LAMMPS runs on single processors or in parallel using message-passing techniques and a spatial-decomposition of the simulation domain. Many of its models have versions that provide accelerated performance on CPUs, GPUs, and Intel Xeon Phis. The code is designed to be easy to modify or extend with new functionality.

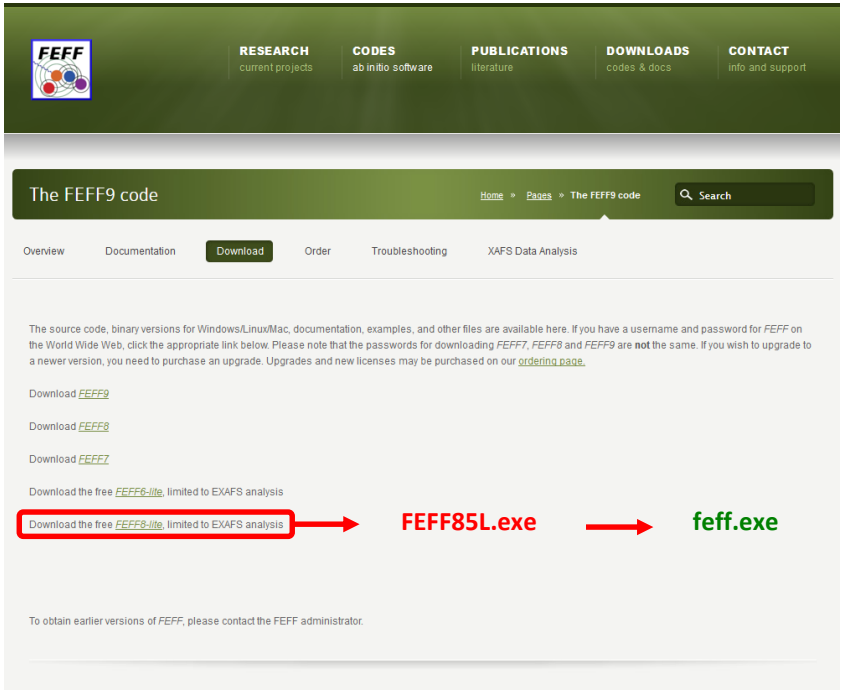
LAMMPS is distributed as an open source code under the terms of the GPLv2. The current version can be downloaded here. Links are also included to older versions. All LAMMPS development is done via GitHub, so all versions can also be accessed there.

The main authors of LAMMPS can be contacted via email to "developers at lammps.org" and are listed individually on this page along with contact info and other contributors. Funding for LAMMPS development has come primarily from the US Deparment of Energy (OASCR, OBER, ASCI, LDRD, Genomes-to-Life) and is acknowledged here.

https://packages.lammps.org/windows.html → **LAMMPS-64bit-latest.exe**

EXAFS engine: FEFF8-Lite

https://feff.phys.washington.edu/feffproject-feff-download.html



FEFF8-Lite is a free version of the FEFF8 code, restricted to EXAFS calculations.

Minimum requirements for EDACA run

runedaca.bat
edaca.exe
edamd.exe
stdev.exe
feff.exe

} EDACA + FEFF

***.xyz** — Coordinates of atoms from the MD simulation

feff.dat
pot.dat — Files required to create FEFF.inp

feff.bin
phase.bin
pot.bin
xsect.bin

} Results of potential calculations by FEFF

MD-EXAFS simulation related parameters

MD simulation

- Equilibration time
- Proper averaging (number of configurations (>1000) & time step)
- The simulation box size must be large enough to avoid boundary condition artifacts such as, for example, artificial correlations (simulation box size > $2R_{max}$)

EXAFS calculation

- Multiple-scattering series truncation problem in **FEFF8.5L**:

  NLEG = 8 default 8 order × (bond length 2-3 Å) / 2 = 8-12 Å

- Criteria to limit the number of paths:

  CRITERIA 4.0 2.5 default critcw=4.0% critpw=2.5%

  CRITERIA 0 0 use all paths, if possible (cw and pw criteria turned off)

- A “configuration” average over the spectra of multiple absorbing atoms (for nanoparticles)

  CFAVERAGE iphabs nabs rclabs

  iphabs potential index for the type of absorbing atoms over which to make the configuration average
  nabs the configuration average is made over the first nabs absorbers in the `feff.inp' file of type iphabs
  rclabs radius to make a small atom list from a bigger one allowed in `feff.inp'

How many configurations to average?

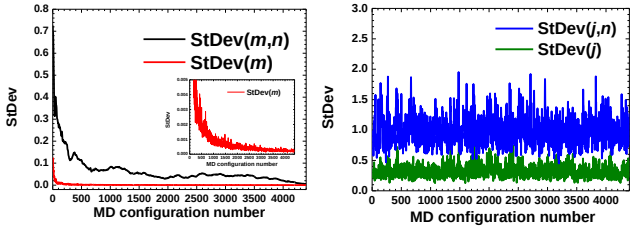
$$\chi^l_{\text{ca}}(k) = \langle \chi^l_i(k) \rangle$$

The configuration-averaged EXAFS signal over ***n*** MD configurations:

$$\chi^l_{\text{ca}}(k) \equiv \chi^l_{\text{ca}}(n,k) = \frac{1}{n}\sum_{i=1}^{n} \chi^l_i(k)$$

The configuration-averaged EXAFS signal over ***m*** MD configurations:

$$\chi^l_{\text{ca}}(m,k) = \frac{1}{m}\sum_{i=1}^{m} \chi^l_i(k)$$



The standard deviation of $\chi^l_{\text{ca}}(m,k)$ from $\chi^l_{\text{ca}}(m-1,k)$:

File: **stdevm.txt**

$$\mathbf{StDev}(m) = \sqrt{\frac{1}{nk}\sum_{k=1}^{nk}[\chi^l_{\text{ca}}(m,k) - \chi^l_{\text{ca}}(m-1,k)]^2}$$

The standard deviation of $\chi^l_{\text{ca}}(m,k)$ from $\chi^l_{\text{ca}}(n,k)$

File: **stdevav.txt**

$$\mathbf{StDev}(m,n) = \sqrt{\frac{1}{nk}\sum_{k=1}^{nk}[\chi^l_{\text{ca}}(m,k) - \chi^l_{\text{ca}}(n,k)]^2}$$

The standard deviation of **two consecutive** EXAFS spectra:

File: **stdevx.txt**

$$\mathbf{StDev}(j) = \sqrt{\frac{1}{nk}\sum_{k=1}^{nk}\left[\chi^l_{\text{j}}(k) - \chi^l_{\text{j}-1}(k)\right]^2}$$

The standard deviation from the **mean** EXAFS spectrum:

File: **stdevxav.txt**

$$\mathbf{StDev}(j,n) = \sqrt{\frac{1}{nk}\sum_{k=1}^{nk}\left[\chi^l_{\text{j}}(k) - \chi^l_{\text{ca}}(n,k)\right]^2}$$

List of EDACA applications to different materials

Material	Reference
$SrTiO_3$	A. Kuzmin, R.A. Evarestov, Quantum mechanics-molecular dynamics approach to the interpretation of X-ray absorption spectra, J. Phys.: Condens. Matter **21** (2009) 055401 (6 pp).
$SrTiO_3$	A. Kuzmin, R.A. Evarestov, Quantum mechanics-classical molecular dynamics approach to EXAFS, J. Phys.: Conf. Ser. **190** (2009) 012024 (6pp).
ReO_3	A. Kalinko, R.A. Evarestov, A. Kuzmin, J. Purans, Interpretation of EXAFS in ReO_3 using molecular dynamics simulations, J. Phys.: Conf. Ser. **190** (2009) 012080 (4pp).
NiO	A. Anspoks, A. Kuzmin, A. Kalinko, J. Timoshenko, Probing NiO nanocrystals by EXAFS spectroscopy, Solid State Commun. **150** (2010) 2270-2274.
Ge	J. Timoshenko, A. Kuzmin, J. Purans, Molecular dynamics simulations of EXAFS in germanium, Centr. Eur. J. Phys. **9** (2011) 710-715.
$LaCoO_3$	A. Kuzmin, V. Efimov, E. Efimova, V. Sikolenko, S. Pascarelli, I. O. Troyanchuk, Interpretation of the Co K-edge EXAFS in $LaCoO_3$ using molecular dynamics simulations, Solid State Ionics **188** (2011) 21-24.
NiO	A. Anspoks, A. Kuzmin, Interpretation of the Ni K-edge EXAFS in nanocrystalline nickel oxide using molecular dynamics simulations, J. Non-Cryst. Solids **357** (2011) 2604-2610.
NiO	A. Anspoks, A. Kalinko, R. Kalendarev, A. Kuzmin, Atomic structure relaxation in nanocrystalline NiO studied by EXAFS spectroscopy: Role of nickel vacancies, Phys. Rev. B **86** (2012) 174114:1-11.
NiO	A. Anspoks, A. Kalinko, R. Kalendarev, A. Kuzmin, Probing vacancies in NiO nanoparticles by EXAFS and molecular dynamics simulations, J. Phys.: Conf. Ser. **430** (2013) 012027:1-4.
$CaWO_4$ $SrWO_4$ $BaWO_4$	A. Kalinko and A. Kuzmin, Interpretation of EXAFS in scheelite-type AWO_4 (A= Ca, Sr, Ba) compounds using molecular dynamics simulations, J. Phys.: Conf. Ser. **430** (2013) 012075:1-4.
NiO	A. Anspoks, A. Kalinko, R. Kalendarev, A. Kuzmin, Local structure relaxation in nanocrystalline $Ni_{1-x}O$ thin films, Thin Solid Films **553** (2014) 58-62.
ZnO	J. Timoshenko, A. Anspoks, A. Kalinko, A. Kuzmin, Temperature dependence of the local structure and lattice dynamics of wurtzite-type ZnO, Acta Mater. **79** (2014) 194-202.
ZnO	J. Timoshenko, A. Anspoks, A. Kalinko, A. Kuzmin, Local structure and dynamics of wurtzite-type ZnO from simulation-based EXAFS analysis, Phys. Status Solidi (c) **11** (2014) 1472-1475.
Y_2O_3	K. Lazdins, A. Kuzmin, Local structure and lattice dynamics of cubic Y_2O_3: an x-ray absorption spectroscopy study, IOP Conf. Ser.: Mater. Sci. Eng. **77** (2015) 012031:1-5.
MoS_2	I. Pudza, D. Bocharov, A. Anspoks, M. Krack, A. Kalinko, E. Welter, A. Kuzmin, Unraveling the interlayer and intralayer coupling in two-dimensional layered MoS_2 by X-ray absorption spectroscopy and ab initio molecular dynamics simulations, Mater. Today Commun. **35** (2023) 106359.
$SrTiO_3$ ZnO	A. Kuzmin, A. Anspoks, A. Kalinko, J. Timoshenko, The use of x-ray absorption spectra for validation of classical force-field models, Z. Phys. Chem. **230** (2016) 537-549.
ScF_3	D. Bocharov, M. Krack, A. Kalinko, J. Purans, F. Rocca, S. E. Ali, A. Kuzmin, Ab initio molecular dynamics simulations of the Sc K-edge EXAFS of scandium trifluoride, J. Phys.: Conf. Ser. **712** (2016) 012009:1-4.
UO_2	D. Bocharov, M. Chollet, M. Krack, J. Bertsch, D. Grolimund, M. Martin, A. Kuzmin, J. Purans, E. Kotomin, Interpretation of the U L_3-edge EXAFS in uranium dioxide using molecular dynamics and density functional theory simulations, J. Phys.: Conf. Ser. **712** (2016) 012091:1-4.
Y_2O_3	I. Jonane, K. Lazdins, J. Timoshenko, A. Kuzmin, J. Purans, P. Vladimirov, T. Gräning, J. Hoffmann, Temperature-dependent EXAFS study of the local structure and lattice dynamics in cubic Y_2O_3, J. Synchrotron Rad. **23** (2016) 510-518.
Cu_3N	J. Timoshenko, A. Anspoks, A. Kalinko, A. Kuzmin, Local structure of copper nitride revealed by EXAFS spectroscopy and reverse Monte Carlo/evolutionary algorithm approach, Phys. Scr. **91** (2016) 054003 (11pp).
FeF_3	I. Jonane, J. Timoshenko, A. Kuzmin, Atomistic simulations of the Fe K-edge EXAFS in FeF_3 using molecular dynamics and reverse Monte Carlo methods, Phys. Scr. **91** (2016) 104001 (6pp).
$CaWO_4$ $SrWO_4$ $BaWO_4$	A. Kalinko, A. Bauer, J. Timoshenko, A. Kuzmin, Molecular dynamics and reverse Monte Carlo modeling of scheelite-type AWO_4 (A=Ca, Sr, Ba) W L_3-edge EXAFS spectra, Phys. Scr. **91** (2016) 114001 (9pp).
UO_2	D. Bocharov, M. Chollet, M. Krack, J. Bertsch, D. Grolimund, M. Martin, A. Kuzmin, J. Purans, E. Kotomin, Analysis of the U L_3-edge X-ray absorption spectra in UO_2 using molecular dynamics simulations, Prog. Nucl. Energy **94** (2017) 187-193.
W	I. Jonane, A. Anspoks, A. Kuzmin, Advanced approach to the local structure reconstruction and theory validation on the example of the W L_3-edge extended X-ray absorption fine structure of tungsten, Modelling Simul. Mater. Sci. Eng. **26** (2018) 025004 (11 pp).
Cu_3N	D. Bocharov, A. Anspoks, J. Timoshenko, A. Kalinko, M. Krack, A. Kuzmin, Interpretation of the Cu K-edge EXAFS spectra of Cu_3N using ab initio molecular dynamics, Rad. Phys. Chem. **175** (2020) 108100.
ScF_3	D. Bocharov, M. Krack, Yu. Rafalskij, A. Kuzmin, J. Purans, Ab initio molecular dynamics simulations of negative thermal expansion in ScF_3: the effect of the supercell size, Comp. Mater. Sci. **171** (2020) 109198.
ZnO	D. Bocharov, I. Pudza, K. Klementiev, M. Krack, A. Kuzmin, Study of high-temperature behaviour of ZnO by ab initio molecular dynamics simulations and X-ray absorption spectroscopy, Materials **14** (2021) 5206.
W *Mo* *Cu* *Ni*	A. V. Shapeev, D. Bocharov, A. Kuzmin, Validation of moment tensor potentials for fcc and bcc metals using EXAFS spectra, Comput. Mater. Sci. **210** (2022) 111028.

LAMMPS simulation of bcc Fe

Prerequisites:

in_Fe	LAMMPS input file with all commands for MD
Fe_2.eam.fs	EAM potential for Fe
	M.I. Mendelev, S. Han, D.J. Srolovitz, G.J. Ackland, D.Y. Sun, M. Asta, Phil. Mag. A, 83, 3977-3994 (2003).
lmp.exe	LAMMPS code

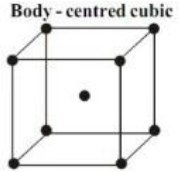
MD run:

```
set OMP_NUM_THREADS=2
lmp.exe  -sf omp -in in_Fe > in_Fe.out
```

optional

Result:

in_Fe.out	Run-time information
log.lammps	Run-time information
Fe_bcc_300K_MD.xyz	Main result with atomic coordinates

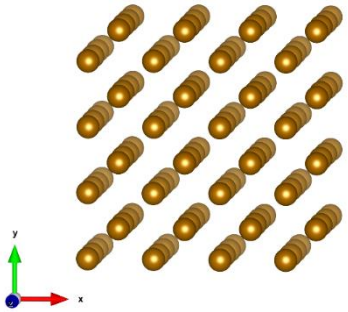


Format of *.XYZ file with all atomic configurations

https://en.wikipedia.org/wiki/XYZ_file_format

bcc Fe (Im-3m)

a_0=2.87 Å



Fe (0,0,0)

Supercell 5×5×5

	X (Å)	Y (Å)	Z (Å)
250			
bcc-Fe			
Fe	-0.003171981	-0.006046713	0.005888966
Fe	-0.011223222	0.012783375	2.871724065
Fe	-0.006298499	0.004336602	5.734868344
Fe	0.000943344	0.009443672	8.593349402
Fe	-0.001532700	2.870304695	-0.000738247
Fe	-0.000804552	2.867348425	2.880470514
Fe	0.006914872	2.882055839	5.755811660
Fe	0.003875439	2.880648336	8.594442865
Fe	0.000164260	5.746693888	-0.004734108
Fe	0.004873029	5.751540760	2.857146517
Fe	0.015511055	5.755458620	5.745901262
Fe	0.016529552	5.733253295	8.614467435
Fe	0.005988304	8.601091974	0.003687874
Fe	0.001261002	8.623239717	2.864929427
Fe	0.009947805	8.595233783	5.731019979
Fe	0.008693730	8.592584189	8.610273059
Fe	2.856966745	-0.009030214	0.007767937
Fe	2.871853523	0.011577101	2.871955369
Fe	2.865793288	-0.008288564	5.756744263
Fe	2.866463241	0.003235423	8.600038492
Fe	2.866765098	2.859385056	-0.010228880
Fe	2.859892361	2.866509006	2.867922683
Fe	2.880929537	2.884695489	5.740121875
Fe	2.853719466	2.860682618	8.608663985
Fe	2.858700691	5.756342390	0.005668939
		...	

```
<number of atoms>
comment line
<element> <X> <Y> <Z>
...

<number of atoms>
comment line
<element> <X> <Y> <Z>
...

<number of atoms>
comment line
<element> <X> <Y> <Z>
...
```

EDACA simulation of bcc Fe

edamd.exe Fe_bcc_300K_MD.xyz 0 12 8.0 Fe 0
edaca.exe
stdev.exe

} **runedaca.bat**

Additional required codes:

1) feff.exe — EXAFS engine (FEFF8x, FEFF9x)

Input files:

1) Fe_bcc_300K_MD.xyz — XYZ file with coordinates of atoms after MD simulation
2) pot.dat — File describing the correspondence between MD and FEFF potentials
3) feff.dat — FEFF input file with ALL required commands but without coordinates (up to ATOMS)
4) *.bin and other files — required by FEFFx (output files after FEFF8 & FEFF9 calculation for static configuration), if potentials will not be recalculated for each configuration (recommended)

Output files:

edamd
1) conf.dat — Includes a list of filenames of all atomic configurations produced by **edamd**
2) **g2_tot.txt, g2_FE-FE.txt** — Total and partial radial distribution functions (RDFs) g(R) (atoms/Å), N=∫g(r)dr

edaca
3) **xt_tot.txt**, mu_tot.txt — Configuration averaged EXAFS $\chi^{l}_{ca}(k)$ and $\mu^{l}_{ca}(E)$

stdev
4) **stdevav.txt**, **stdevm.txt**, stdevx.txt, stdevxav.txt — Different standard deviations (see slide 12)
5) xt_av.txt — Configuration averaged EXAFS $\chi^{l}_{ca}(k)\boldsymbol{k^2}$

EDACA simulation of bcc Fe

edamd.exe Fe_bcc_300K_MD.xyz 0 12 8.0 Fe 0
edaca.exe
stdev.exe

} **runedaca.bat**

edamd.exe ***filename_xyz SkipFirst Skip Rmax atom1 absorber_number atom2 atom3 ...***
edamd.exe Fe_bcc_300K_MD.xyz 0 12 8.0 Fe 0

filename_xyz	The name of XYZ file with atomic coordinates from GULP (DL_POLY, LAMMPS, ...)
SkipFirst	A number of configurations to skip from the beginning, default *SkipFirst*=0
Skip	A number of configurations to skip (e.g., skip=0 means to read all configurations, *Skip*=1 means to read each second configuration, *Skip*=1 means to read each third configuration, etc).
Rmax	The radius (in Å) of the small cluster around the absorber used in the EDACA calculations and generated from the large XYZ file. Rmax must be larger than the maximum distance (RPATH) specified in the feff.dat file.
atom1	the absorber
absorber_number	**= 0** default automatic mode: the absorber located at the MD box center, **>0** equals to the absorber number in the list of atoms, **<0** then |*Absorber_number*| is equal to a number of possible absorbers from the beginning of the XYZ file: this option is required to calculate configuration averaged EXAFS for a part of atoms, e.g. in the central box of MD or RMC simulation.
atomX	next atom in the compound (if present), those potential is mentioned in the pot.dat file.

EDACA simulation of bcc Fe

edamd.exe Fe_bcc_300K_MD.xyz 0 12 8.0 Fe 0
edaca.exe
stdev.exe

} **runedaca.bat**

conf.dat file:

```
Fe_bcc_300K_MD_13.xyz
Fe_bcc_300K_MD_26.xyz
Fe_bcc_300K_MD_39.xyz
Fe_bcc_300K_MD_52.xyz
....
Fe_bcc_300K_MD_49998.xyz
```

pot.dat file:

```
# potential      potential
#  in XYZ        in feff.inp (0=Fe*, 1=Fe)
     0      0
     1      1
```

feff.dat file (created from feff.inp):

```
TITLE   Fe  metal  bcc a=2.866 Å
EDGE     K
S02      1.0

*            pot    xsph  fms   paths genfmt ff2chi
CONTROL  0     0    0     1     1     1
PRINT    1     0    0     0     0     0
*         r_scf   [ l_scf  n_scf  ca ]
SCF      3.0  0     30     0.1
*              ixc  [ Vr  Vi ]
EXCHANGE 0     0  0

EXAFS  20.0
RPATH    6.5

CRITERIA  0.0 1.5

POTENTIALS
*   ipot   z [ label   l_scmt  l_fms  stoichiometry ]
    0  26   Fe    -1     -1      0
    1  26   Fe    -1     -1      1

ATOMS
```

EDACA simulation of bcc Fe

Fe_bcc_300K_MD_13.xyz file:

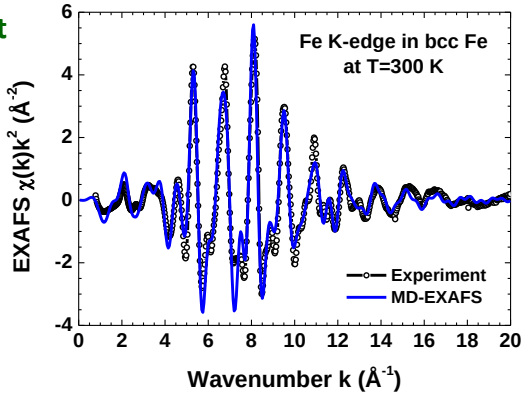
```
# Cluster: 13. Atoms. Timestep: 12
1  8.43699999999998E-0002 -5.61688000000000E+0000 -5.61410000000000E+0000
1 -2.80043000000000E+0000 -2.83183000000000E+0000 -5.75195000000000E+0000
1 -2.92000000000048E-0003 -2.79186000000000E+0000 -5.62604000000000E+0000
…
1 -1.35530000000000E+0000 -1.45886000000000E+0000 -1.58075000000000E+0000
0  0.00000000000000E+0000  0.00000000000000E+0000  0.00000000000000E+0000
1  1.49455000000000E+0000 -1.33926000000000E+0000 -1.35191000000000E+0000
…
```

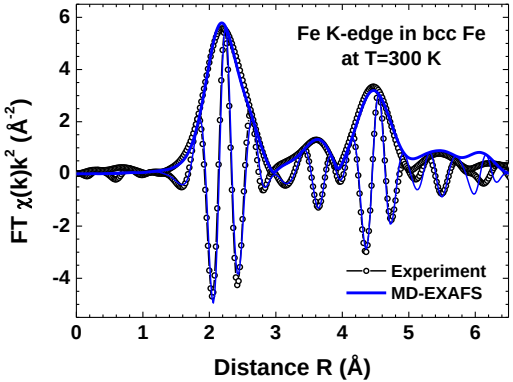
pot.dat file:

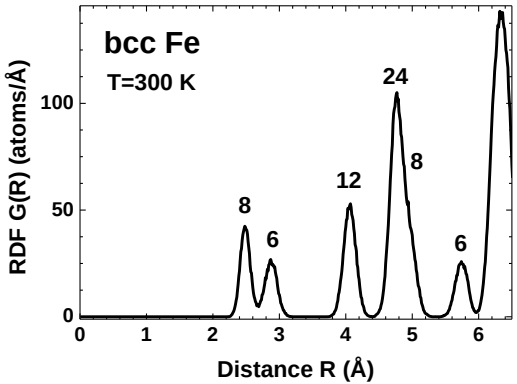
```
# potential      potential
#  in XYZ        in feff.inp (0=Fe*, 1=Fe)
     0     0
     1     1
```

MD-EXAFS results for bcc Fe

xt_tot.txt

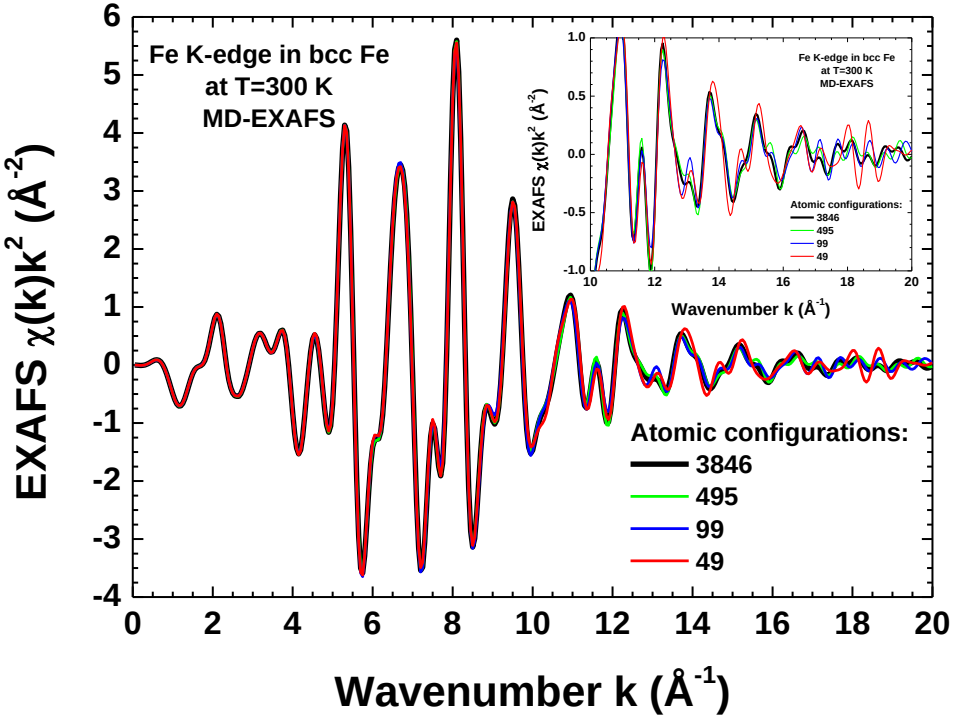






g2_tot.txt, g2_FE-FE.txt

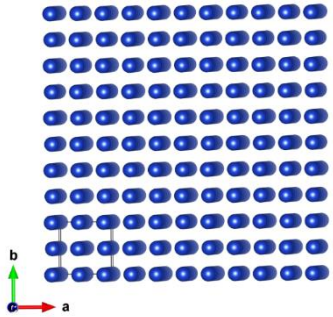
Dependence of MD-EXAFS results on the number of atomic configurations for bcc Fe



Metallic fcc Cu

fcc Cu (Fm-3m)

a_0=3.615 Å



Cu (0,0,0)

Supercell 5×5×5

Prerequisites:

in_Cu	LAMMPS input file with all commands for MD
Cu1.eam.fs	EAM potential for Cu
	M.I. Mendelev, M.J. Kramer, C.A. Becker, M. Asta, Phil. Mag. 88, 1723 - 1750 (2008).
lmp.exe	LAMMPS code

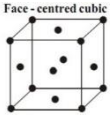
MD run:

optional

lmp.exe -pk omp 2 -sf gpu -in in_Cu > in_Cu.out

Result:

in_Cu.out	Run-time information
log.lammps	Run-time information
Cu_fcc_300K_MD.xyz	Main result with atomic coordinates



EDACA simulation of fcc Cu

edamd.exe Cu_fcc_300K_MD.xyz 0 10 8.0 Cu 0
edaca.exe
stdev.exe

} **runedaca.bat**

conf.dat file:

```
Cu_fcc_300K_MD_11.xyz
Cu_fcc_300K_MD_22.xyz
Cu_fcc_300K_MD_33.xyz
Cu_fcc_300K_MD_44.xyz
....
Cu_fcc_300K_MD_39996.xyz
```

pot.dat file:

```
# potential      potential
#  in XYZ        in feff.inp (0=Cu*, 1=Cu)
     0      0
     1      1
```

feff.dat file (created from feff.inp):

```
TITLE   Cu  metal  fcc a=3.61 Å
EDGE     K
S02      1.0

*            pot    xsph  fms   paths genfmt ff2chi
CONTROL  0    0    0    1    1    1
PRINT    1    0    0    0    0    0
*         r_scf   [ l_scf  n_scf  ca ]
SCF      4.0  0    30    0.1
*              ixc  [ Vr  Vi ]
EXCHANGE 0     0  0

EXAFS  20.0
RPATH    6.5

CRITERIA  0.0 1.5

POTENTIALS
*   ipot   z [ label   l_scmt  l_fms  stoichiometry ]
    0  29   Cu    -1     -1     0
    1  29   Cu    -1     -1     1

ATOMS
```

EDACA simulation of fcc Cu

Cu_fcc_300K_MD_11.xyz file:

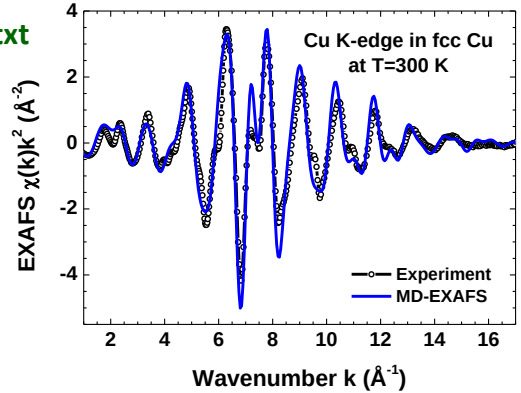
```
# Cluster: 11. Atoms. Timestep: 10
1 -1.722070000000000E+0000 -1.972020000000000E+0000 -7.313280000000000E+0000
1  1.824200000000000E+0000 -1.985650000000000E+0000 -7.259880000000000E+0000
1 -1.179899999999998E-0001 -1.282800000000000E-0001 -7.220410000000000E+0000
…
1 -2.957999999999993E-0002  1.773080000000000E+0000 -1.854810000000000E+0000
0  0.000000000000000E+0000  0.000000000000000E+0000  0.000000000000000E+0000
1 -1.874840000000000E+0000  1.791320000000000E+0000 -4.600999999999990E-0002
…
```

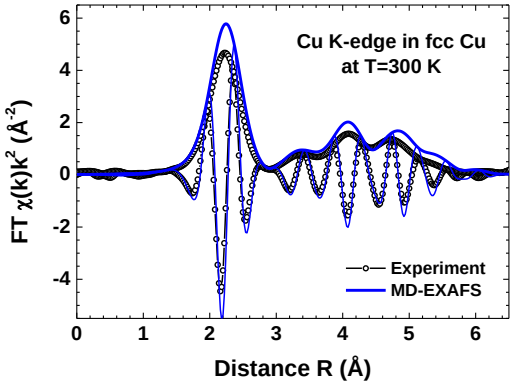
pot.dat file:

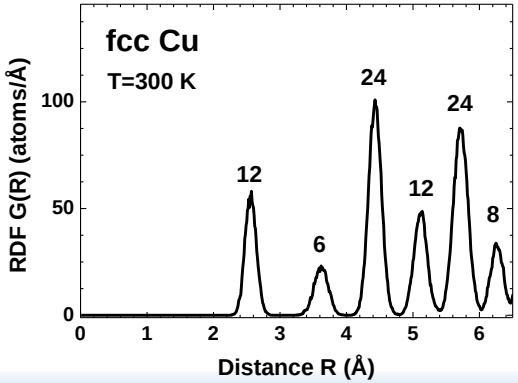
```
# potential      potential
#  in XYZ        in feff.inp (0=Cu*, 1=Cu)
     0      0
     1      1
```

MD-EXAFS results for fcc Cu

xt_tot.txt





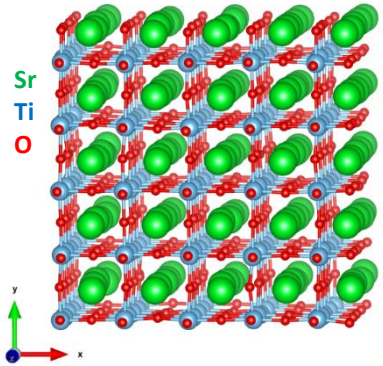


g2_tot.txt, g2_CU-CU.txt

MD-EXAFS results for cubic perovskite $SrTiO_3$

Cubic $SrTiO_3$ (Pm-3m)

a_0=3.905 Å



Sr (0,0,0)
Ti (0.5,0.5,0.5)
O (0,0.5,0.5)

Supercell 5×5×5

Prerequisites:

srtio3_555_TMB_md.gin	GULP input file with all commands for MD and potentials from **B. S. Thomas, N. A. Marks, B.D. Begg, Nucl. Instrum. Meth. B 228 (2005) 288.**

Result:

output	Run-time information
SrTiO3_555_TMB_300K.xyz	Main result with atomic coordinates

EDACA simulation of cubic perovskite $SrTiO_3$

edamd.exe SrTiO3_555_TMB_300K.xyz 0 0 8.0 Ti 0 Sr O
edaca.exe
stdev.exe

} **runedaca.bat**

conf.dat file:

SrTiO3_555_TMB_300K_1.xyz
SrTiO3_555_TMB_300K_2.xyz
SrTiO3_555_TMB_300K_3.xyz
SrTiO3_555_TMB_300K_4.xyz
....
SrTiO3_555_TMB_300K_2000.xyz

pot.dat file:

# potential in XYZ	potential in feff.inp (0=Ti*, 1=O, 2=Sr 3=Ti)
0	**0**
2	**2**
1	**3**
3	**1**

feff.dat file (created from feff.inp):

```
TITLE cubic SrTiO3 a=3.905 Å
EDGE     K
S02      1.0

*            pot    xsph  fms   paths genfmt ff2chi
CONTROL  0    0    0    1    1     1
PRINT    1    0    0    0    0     0
*         r_scf   [ l_scf  n_scf  ca ]
SCF      4.0  0    30    0.1
*              ixc  [ Vr  Vi ]
EXCHANGE 0     0  0

EXAFS  20.0
RPATH    6.5
CRITERIA   2.0  2.5

POTENTIALS
*   ipot   z [ label   l_scmt  l_fms  stoichiometry ]
 0  22   Ti    -1     -1      0
 1   8   O     -1     -1      3
 2  38   Sr    -1     -1      1
 3  22   Ti    -1     -1      1

ATOMS
```

EDACA simulation of cubic perovskite $SrTiO_3$

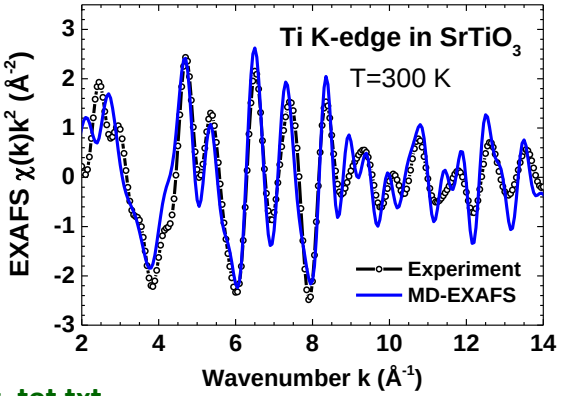
SrTiO3_555_TMB_300K_1.xyz file:

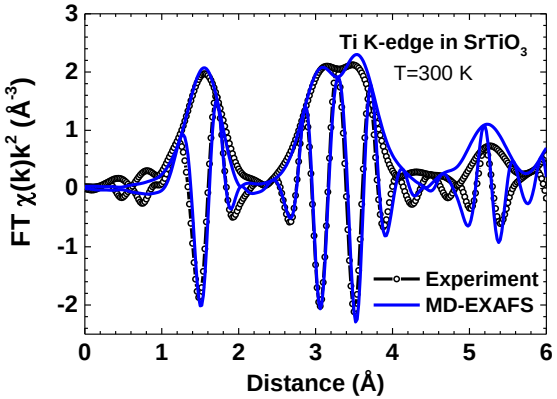
```
# Cluster: 1. SCF Done          -9251.24551535
2 -5.6638366219999998E+000 -1.9345635749999994E+000 -1.8965811260000001E+000
2 -5.8161227160000006E+000 -1.9902422660000001E+000  2.0225423609999993E+000
2 -5.8223570030000005E+000  1.7646858830000003E+000 -1.9921332800000000E+000
…
2  5.9074305330000003E+000  2.0739280749999995E+000  1.9143412239999993E+000
1 -7.7015225640000002E+000  9.8370500000006800E-003 -7.4649180000001536E-003
1 -3.8341469420000003E+000 -3.8993493439999996E+000 -3.9374565160000001E+000
1 -3.8725798060000005E+000 -3.9208021269999995E+000 -3.0967081000000007E-002
…
1  6.5886389000000101E-002  2.7292039000000656E-002 -3.9367556619999999E+000
0  0.0000000000000000E+000  0.0000000000000000E+000  0.0000000000000000E+000
1 -4.0397950000006233E-003  1.0309552800000077E-001  3.7966132160000008E+000
…
3 -5.7877681580000004E+000 -3.8631761129999997E+000  1.2871437000000263E-002
3 -5.8439203129999999E+000  2.2320960000001833E-003 -3.9290554370000002E+000
3 -5.8210508980000002E+000 -4.3372319999999576E-002 -3.8712526000000302E-002
…
```

pot.dat file:

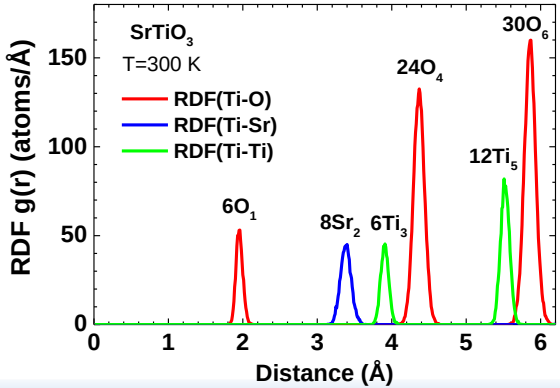
```
# potential      potential
#  in XYZ        in feff.inp (0=Ti*, 1=O, 2=Sr 3=Ti)
   0      0
   2      2
   1      3
   3      1
```

MD-EXAFS results for cubic perovskite $SrTiO_3$





xt_tot.txt



g2_tot.txt

g2_TI-O.txt

g2_TI-SR.txt

g2_TI-TI.txt

MD-EXAFS simulations of XANES

EDACA code can use two ab initio real-space full-multiple-scattering codes

- **FEFF8x/9x** code [1-3] and
- **FDMNES** [4,5]

to calculate XANES for each atomic configuration (“snapshot”).

Files required:
1) feff.exe + feff.dat
or
2) fdmnes.exe + fdmnes.dat

The FEFF8x/FEFF9x code can be obtained from

https://feff.phys.washington.edu/feffproject-feff-download.html.

The FDMNES code is available from

https://fdmnes.neel.cnrs.fr/.

1. J. J. Rehr and R. C. Albers, *Rev. Mod. Phys.* 72 (2000) 621.
2. A. L. Ankudinov, B. Ravel, J. J. Rehr, S. D. Conradson, *Phys. Rev. B* 58 (1998) 7565.
3. J.J. Rehr, J.J. Kas, F.D. Vila, M.P. Prange, K. Jorissen, *Phys. Chem. Chem. Phys.* 12 (2010) 5503.
4. Y. Joly, *Phys. Rev. B* 63 (2001) 125120.
5. O. Bunau and Y. Joly, *J. Phys.: Condens. Matter* 21 (2009) 345501.

MD-EXAFS simulations of XANES with the FEFF code

Note that since the calculation of cluster potential is a time-consuming part of the calculation, one can perform it only once at the beginning for some average atomic structure.

The minimum set of FEFF commands in the **feff.dat file** relevant to the MD-XANES simulations are:

- XANES calculations up to k_{max}=4.0 Å^{-1} with the steps Δk=0.05 Å^{-1} and ΔE=0.2 eV:
  XANES 4.0 0.05 0.2

- Compute full multiple scattering within a sphere of radius 8.0 Å:
  FMS 8.0

- A “configuration” average over the spectra of multiple absorbing atoms (for nanoparticles):
  CFAVERAGE iphabs nabs rclabs
  iphabs potential index for the type of absorbing atoms over which to make the configuration average
  nabs the configuration average is made over the first nabs absorbers in the `feff.inp' file of type iphabs
  rclabs radius to make a small atom list from a bigger one allowed in `feff.inp'

MD-EXAFS simulations of XANES with the FDMNES code (I)

FDMNES code calculates XANES using two techniques:

(i) the Green function formalism (multiple-scattering) on a muffin-tin potential and
(ii) the Finite Difference Method (FDM) to solve the Schrödinger equation.

The first approach is much faster but less accurate.

Besides, the calculations can be performed using self-consistent (SCF) and non-self-consistent potential as well as different multipolar expansions (dipole, quadrupole, etc).

There are many advanced possibilities implemented in the FDMNES code, so please consult the documentation.

MD-EXAFS simulations of XANES with the FDMNES code (II)

The minimum set of FDMNES commands in the **fdmnes.dat** file relevant to the MD-XANES simulations are:

- The energy range (in eV) relative to the Fermi level (E_{min}, step, E_{max}, …):

  Range

  -20.0 1.0 -10.0 0.2 0.0 0.2 15.0 0.5 20.0 1.0 40.0 2.0 100.0
- The Green function formalism (multiple-scattering) on a muffin-tin potential:

  Green
- The absorption edge (K, L1, L2, L3, M1, …):

  Edge

  K
- Cluster radius for XANES calculations:

  Radius

  8.0
- Cluster structure followed by the unit cell parameters (the atom positions will be automatically added from XYZ file below these lines) :

  Molecule

  1.0 1.0 1.0 90. 90. 90. = a, b, c, alpha, beta, gamma

Summary

The accuracy of configuration-averaged EXAFS calculations (MD-EXAFS approach) is limited mainly by the accuracy of molecular dynamics simulations (interatomic potentials).

Good choice of equilibration time, proper averaging (number of configurations (>1000) & time step) and simulation box size in MD simulations is crucial.

EXAFS calculations for each atomic configuration are based on the FEFF code, therefore all possible problems related to it should be taken into account.

EDACA code is under continuous development, so check for new possibilities at

http://www.dragon.lv/edaca

Thank you for your attention!