Multiple Scattering EXAFS Analysis

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Theoretical EXAFS Equation:

Single scattering path:

$$\chi_{\Gamma}(k) = \frac{NS_0^2}{kR^2} \left| f^{\text{eff}}(k) \right| e^{-2\sigma^2 k^2} e^{\frac{-2R}{\lambda}} \sin\left[2kR - \frac{4}{3}C_3k^3 + \delta(k)\right]$$

Multiple-scattering path:



J. Rehr, S. Zabinsky, R. Albers, PRL 69, 3397 (1992)





Easy and transparent parameterization of structural models for EXAFS data fitting
FEFF theory
Error analysis

FEFF

FEFF6,8, 9: Spherically symmetric potentials (muffin tin approximation) Input: (xyz) coordinates and atomic numbers Mean free path Imaginary part of interstitial potential and life time broadening Self Energy Metals – Hedin-Lundqvist Insulators – Hedin-Lundqvist or Dirac-Hara Molecules – Dirac-Hara or ground state Multiple scattering expansion Each photoelectron path with its f(k), $\delta(k)$, $\lambda(k)$ is saved as a file

Data analysis using MS contributions

Remove background: $\mu(E) \rightarrow \chi(k)$.

Fourier transform data: $\chi(k) \rightarrow \widetilde{\chi}(r)$

Pick a model

Calculate f(k), $\delta(k)$ and $\lambda(k)$: FEFF

Fit theory to data

Error analysis $\{x_i \pm \delta x_i\}$

Information content in EXAFS is limited (P < N) → we need to limit the number of variables.
Which paths are most important? Often, collinear paths dominate EXAFS spectrum



FIG. 5. Scattering amplitude $f(\theta)$ for energy E=2,8, 15,25 hartree (1 hartree=27,2 eV).

P. Lee, J. Pendry, Phys. Rev. **B** 11, 2795 (1975). Debye Waller Factors of Collinear Multiple-Scattering Paths



$$\sigma_{j}^{2} \equiv \left\langle \left(r_{j} - R_{j}\right)^{2} \right\rangle = \left\langle \left(\frac{1}{2} \sum_{i=1}^{n_{j}} \left(\vec{u}_{i} - \vec{u}_{i+}\right) \hat{R}_{ii+}\right)^{2} \right\rangle = \frac{1}{4} \left\langle \left(\sum_{i=1}^{n_{j}} \left(\vec{u}_{i} - \vec{u}_{i+}\right) \hat{R}_{ii+}\right)^{2} \right\rangle$$
$$\sigma_{ss}^{2} = \frac{1}{4} \left\langle \left[\left(\vec{u}_{a} - \vec{u}_{c}\right) \hat{R}_{0} + \left(\vec{u}_{c} - \vec{u}_{a}\right) \left(-\hat{R}_{0}\right)\right]^{2} \right\rangle = \frac{1}{4} \left\langle \left[2\left(\vec{u}_{a} - \vec{u}_{c}\right) \hat{R}_{0}\right]^{2} \right\rangle$$



$$\sigma_{\rm SS}^2 = \frac{1}{4} \left\langle \left[\left(\vec{u}_a - \vec{u}_c \right) \hat{R}_0 + \left(\vec{u}_c - \vec{u}_a \right) \left(- \hat{R}_0 \right) \right]^2 \right\rangle = \frac{1}{4} \left\langle \left[2 \left(\vec{u}_a - \vec{u}_c \right) \hat{R}_0 \right]^2 \right\rangle \\ = \left\langle \left[\left(\vec{u}_a - \vec{u}_c \right) \hat{R}_0 \right]^2 \right\rangle = \left\langle \left(\vec{u}_a \hat{R}_0 \right)^2 \right\rangle + \left\langle \left(\vec{u}_c \hat{R}_0 \right)^2 \right\rangle - 2 \left\langle \left(\vec{u}_a \hat{R}_0 \right) \left(\vec{u}_c \hat{R}_0 \right) \right\rangle \\ = \left\langle u_{ax}^2 \right\rangle + \left\langle u_{cx}^2 \right\rangle - 2 \left\langle u_{ax} u_{cx} \right\rangle,$$

$$\hat{R}_{ab} = \hat{R}_{bc} = -\hat{R}_{ca} \equiv \hat{R}_0$$

₩ _b







$$\hat{R}_{D} \qquad \hat{R}_{D} \qquad \hat{R}_{D} \qquad \hat{R}_{SS1} = \langle u_{ax}^{2} \rangle + \langle u_{cx}^{2} \rangle - 2 \langle u_{ax} u_{cx} \rangle,$$

$$\hat{R}_{D} \qquad \hat{R}_{SS1} = \frac{1}{4} \langle [(\vec{u}_{a} - \vec{u}_{c})\hat{R}_{0} + (\vec{u}_{c} - \vec{u}_{b})(-\hat{R}_{0}) + (\vec{u}_{b} - \vec{u}_{a})\hat{R}_{0}]^{2} \rangle$$

$$= \frac{1}{4} \langle [2(\vec{u}_{b} - \vec{u}_{c})\hat{R}_{0}]^{2} \rangle = \langle [(\vec{u}_{b} - \vec{u}_{c})\hat{R}_{0}]^{2} \rangle = \langle u_{bx}^{2} \rangle + \langle u_{cx}^{2} \rangle - 2 \langle u_{bx} u_{cx} \rangle$$

$$\hat{R}_{D} \qquad \hat{R}_{D} \qquad$$

$$\sigma_{\rm TS}^2 = \frac{1}{4} \left\langle 2 \left[(\vec{u}_a - \vec{u}_c) \hat{R}_0 + 2 (\vec{u}_c - \vec{u}_a) (-\hat{R}_0) \right]^2 \right\rangle$$
$$= \frac{1}{4} \left\langle \left[4 (\vec{u}_a - \vec{u}_c) \hat{R}_0 \right]^2 \right\rangle = 4 \left\langle \left[(\vec{u}_a - \vec{u}_c) \hat{R}_0 \right]^2 \right\rangle = 4 \left[\left\langle u_{ax}^2 \right\rangle + \left\langle u_{cx}^2 \right\rangle - 2 \left\langle u_{ax} u_{cx} \right\rangle \right] = 4 \sigma_{\rm SS1}^2$$

P. Shanthakumar, M. Balasubramanian, D. Pease, A. I. Frenkel, D. Potrepka, J. Budnick, W. A. Hines, V. Kraizman Phys. Rev. B **74**, 174103 (2006).

Practical applications of MS analysis

Example 1: Rock Salt Structure

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Multiple-scattering x-ray-absorption fine-structure analysis and thermal expansion of alkali halides

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X-ray-absorption fine-structure (XAFS) data of RbBr, RbCl, and KBr at 30 K and 125 K were measured and analyzed. An ionized-atom multiple-scattering calculation and a correlated Debye model were used for fitting the theory used in the FEFF5 computer code to data. The modifications of FEFF5 necessary to obtain good fits to the data are discussed. The results demonstrate the domination of single-scattering and focusing paths in XAFS and the determination of vibrational information through at least 10 Å around the center atom. Numerical calculations were performed to analyze the cause of the difference found between the forward-scattering amplitudes of Rb⁺ and Br⁻ focusing atoms. The second and third cumulants were determined of the first and second neighbors and were used to calculate the temperature. Agreement with macroscopic thermal-expansion measurements was found.

TABLE VII. Path parameters of KBr (Br edge, 30 K) $\chi_{\rm th}(k)$ for correlated Debye model (CDM) calculation and final fit; two left columns indicate path and half path length. Subscripts f and v indicate whether the given value was fixed in fitting process or allowed to vary, respectively.

Path		ΔE_{Γ} (eV)		$\sigma^2 (10^{-2} \text{ Å}^2)$	
Type	R (Å)	\mathbf{CDM}	Final fit	CDM	Final fit
SS	3.27	2.0_{v}	2.0_{f}	0.64	$0.61_{v} \pm 0.05$
SS	4.62	1.6_{v}	1.6_{f}	0.54	$0.51_{v} \pm 0.05$
SS	5.66	1.6_v	1.6_{f}	0.87	$0.87_v \pm 0.05$
SS	6.53	1.6_v	1.6_{f}	0.56	$0.57_v \pm 0.05$
DS(Foc.: c)	6.53	1.6_v	1.6_{f}	1.15	$1.2_v \pm 0.1$
TS(Foc.: c)	6.53	1.6_{v}	1.6_{f}	1.15	$1.2_v\pm 0.1$
DS(Foc.: 1NN)	6.53	2.3_v	2.3_{f}	0.56	$0.57_v \pm 0.05$
TS(Foc.: 1NN)	6.53	1.2_{v}	1.2_{f}	0.56	$0.57_v \pm 0.05$
SS	7.30	1.6_{v}	1.6_{f}	0.85	$0.85_v \pm 0.05$
SS	8.00	1.6_{v}	1.6_{f}	0.55	$0.55_v \pm 0.05$



FIG. 3. Fourier transformed Br edge XAFS functions of KBr at 30 K: fitting of theory (correlated Debye model, solid line) to data (dashed line) by (a) adjusting ΔE_0 overall and (b) using ΔE_{Γ} for every path containing nearest neighbors; (c) final fit of FEFF5 theory to data by varying σ_i^2 .



FIG. 5. Collinear scattering amplitude of DS focusing paths Rb-Br-Rb (solid line) and Br-Rb-Br (dashed line).

Example 2: Using MS contributions to measure bond buckling angles in random alloys





A. Frenkel, V. Machavariani, A. Rubshtein, Y. Rosenberg, A. Voronel, E. Stern PRB 62, 9364 (2000)

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Buckled Crystalline Structure of Mixed Ionic Salts

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X-ray absorption fine structure (XAFS) measurements of mixed salts $Rb_x K_{1-x}Br$ and $RbBr_y Cl_{1-y}$ at their congruent melting points compositions reveal that their actual structure buckles about the NaCl average structure with an rms angular deviation from collinearity of 7°-9°. XAFS measures the buckling directly through three-body correlations, and verifies the homogeneity and randomness of the mixtures. The characteristic ionic sizes are found to be dependent on concentration, causing changes to 0.1 Å in interatom bond distances. A computer simulation based on the information from XAFS and diffraction displays the actual structure of the salts.



FIG. 3. Fit of the magnitude of the theoretical $\chi(R)$ (dashed line) to Rb_{0.76}K_{0.24}Br, Br edge data (solid line).

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Solving the structure of disordered mixed salts

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FIG. 3. Schematic of photoelectron SS(1), SS(2), SS(4), and SS(5) paths in the (100) plane of a NaCl structure to the 1NN, 2NN, 4NN, and 5NN, respectively, and DS (and its time reversed path DS) and TS paths to the 4NN. In all the cases the center atom is a positive ion denoted by c. SS paths to 3NN and 6NN are out of the plane.

Obtaining bond angles from the MS fit:

 $\langle F(k,\Theta) \rangle \approx F(k,0)[1-b(k)\langle \Theta^2 \rangle],$



FIG. 4. $F(k, \Theta)$ $(k = 8 \text{ Å}^{-1})$ of nearly collinear DS paths: (1) Br-Rb¹-Br⁴-Br; (2) Rb-Br¹-Rb⁴-Rb; (3) Br-K¹-Br⁴-Br; (4) Rb-Cl¹-Rb⁴-Rb. Superscripts indicate the coordination shell.

How to model XAFS data in nanoparticles?

A priori knowledge or a working hypothesis must exist (the "zero" approximation) otherwise: the transferability of amplitude/phase will not work!)



- I) Hemispherical
- 2) Crystal order
- 3) Size: about 20 Å

What information can be obtained from 1st shell EXAFS analysis?

- 1) Size of the particle (via N)
- 2) Distances, thermal vibration, expansion
- 3) Static disorder (icosahedral? surface tension?)



First shell analysis is not adequate for full structural studies of small clusters



Coordination numbers in CO, IH and TO clusters

EXAFS data analysis and modeling





Coordination numbers for the first 5 shells:

i	10% Pt/C	40% Pt/C	60% Pt/C	Pt foil	Bulk fcc
1	8.3(5)	10.5(5)	11.4(6)	12.6(7)	12
2	2.3(1.1)	4.0(1.3)	4.7(1.7)	5.9(2.0)	6
3	10.9(3.2)	16.8(3.5)	19(4)	23(5)	24
4	5.5(1.4)	7.6(1.4)	8.5(1.6)	11(2)	12
5	5.4(3.4)	10(4)	11(4)	14(5)	24



Bimetallic Pt-Ru/C nanoparticles:



monoatomic Pt/C nanoparticles:



Structure:

- -Atomic packing: face center cubic.
- -Cluster shape: hemispherical cuboctahedron.
- -Texture: basal plane is (111)
- -Composition: Core/shell or random

-Surface disorder. Surface layers relaxed inward (surface tension)

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M. Nashner, A. Frenkel, D. Adler, J. Shapley, R. Nuzzo J. Am. Chem. Soc. 119, 7760 (1997)
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Summary

- Multiple scattering contributions help uncover 3D information (size, shape, structure, morphology of nanoparticles)
- MS contributions are structural indicators (e.g., fcc or not, large nanoparticles present or not, etc.)
- Data analysis that includes multiple scatterings and single scatterings:

Constrain the fitting variables;

Make physical sense;

Interpret the results;

Calibrate analysis on standard compounds first.