Introduction of X-ray Absorption Near Edge Structure (XANES)

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Outline

1. Introduction of XANES
2. Structural and chemical properties from XANES
3. Fingerprint Analysis of XANES
4. FEFF8. and FDMNES Codes for XANES calculation
5. Modules and cards in FEFF8. and FDMNES
6. Theoretical XANES calculations by using FEFF8. and FDMNES
XANES is the range of the X-ray absorption spectrum from absorption edge to ~50eV.
**XANES and EXAFS**

EXAFS is broken at the range of $k < k_c = \frac{2\pi}{d}$, $\sim 3$ Å$^{-1}$.
What is XANES?

XANES = Pre-edge + Edge + XANES

X-ray absorption spectrum of Ti K-edge of TiO$_2$
**Structural and Chemical Properties from XANES**

XANES is considerably sensitive to the chemistry (formal oxidation state and geometry) of the absorbing atom.

<table>
<thead>
<tr>
<th>Region</th>
<th>Features</th>
<th>Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-edge</td>
<td>Pre-edge is formed by electronic transitions to empty bound states. Transition probability controlled by dipolar selection rules.</td>
<td>Local geometry around absorbing atom. Oxidation state Bonding characteristics</td>
</tr>
<tr>
<td>Edge</td>
<td>Defines ionization threshold to continuum states.</td>
<td>Oxidation state (chemical shift) - Main edge shifts to higher energy with increased oxidation state.</td>
</tr>
<tr>
<td>XANES</td>
<td>XANES is formed by multiple-scattering resonances of the photoelectrons ejected at low kinetic energy. Large scattering cross section</td>
<td>Atomic position of neighbors Inter-atomic distances and bond angles. Geometric structure</td>
</tr>
</tbody>
</table>
X-ray Absorption Edges

- XANES directly probes the angular momentum of unoccupied electronic states

- Dipole selection rules: \( \Delta l = \pm 1 \), \( \Delta j = \pm 1 \), \( \Delta s = 0 \)

- Primary transition will be:
  
  s \rightarrow p \text{ for K (1s core electron) and L}_1(2s \text{ core electron initial state}) \text{ edges.}
  
  p \rightarrow d \text{ for L}_2(2p_{1/2}) \text{ and L}_3(2p_{3/2}) \text{ edges}

- But s-p and p-d hybridization is often the interesting part of the XANES
K and L – edge XANES Spectra

1. K-edge XANES spectra (1s → np)
   - Pre-edge peak: Oh/Td, metal valence
   - Main-edge peak: Crystal structure & oxidation state
     : Useful for determination of the oxidation state and local symmetry of 3d transition metal

2. L₁-edge XANES spectra (2s → np)
   - White line peak: hole density in final np state & oxidation state
     : Useful for the exact calculation of the valence state of halogen/chalcogen ions

3. L₂/L₃-edge XANES spectra (2p → ns, nd)
   - Main-edge peak: crystal field strength around metal & hole density in final ns and nd states
     : Useful for the examination of the crystal field and valence state of post-transition metal ions
Crystal Field theory
Pre-edge Peak of Transition Metal K-edge

**Pure Octahedral case**
Centro-symmetric: no p-d mixing allowed:
Only quadrupolar transitions – very low intensity ($1s \rightarrow 4p$)

**Distortion from Octahedral**
P-d mixing allowed: dipole transition in pre-edge
- increasingly larger intensity ($1s \rightarrow 3d$)

**Pure tetrahedral (4p-3d hybridization)**
Largest pre-edge intensity ($1s \rightarrow 3d$)
\textbf{K-edge XANES of octahedral structure}

- Intense edge absorption due to dipole selection rule allowed $s \rightarrow p$ transition
- Weaker pre-edge feature results from mixing of $3d-4p$ orbitals of suitable symmetry
- Symmetry around absorbing atoms strongly affects pre-edge transition
Pre-edge Peak of Ti K-edge as depending on coordination
Transition Metal K-edge XANES

- Pre-edge peak much larger for tetrahedral coordination
- Edge of Cr shifts to high energy with increasing oxidation state
- Pre-edge peak made by transition from 1s to 3d generally for Td structure is sharp and intense from Ti → Mn, while it decreases from Fe → Cu and is absent for Zn due to filling of the 3d band
The XANES is affected by the geometric structure around a probe atom.
**EXAMPLE  ZnO Growth mechanism**

Zn(NO$_3$)$_2$ powder

\[ \Downarrow \quad 6(\text{H}_2\text{O}) \]

Zn(NO$_3$)$_2$·6(H$_2$O) solution

\[ \Downarrow \quad 6(\text{CH}_2\text{N}_4 \text{ at } 80 \degree \text{C} \]

Zn-hexamine complex (ZNHC)

\[ \Downarrow \quad \text{Precipitate at } 95 \degree \text{C} \]

ZnO nanorods
1. The shape of XANES for the precipitated ZnO is similar to that of nanorods.
2. The edge energies of precipitated ZnO and Zn(NO3)2 powder are 9659.5eV and 9662eV, respectively.
Experiment XANES of ZnCoO film
Linear Combination Fit (LCF) Using Athena
Linear Fit of Ce\textsubscript{0.7}Zr\textsubscript{0.3} oxide
Advantages and Difficulty of XANES

- Faster to measure than full spectrum like EXAFS
- Sensitive to chemical information: valence, charge transfer.
- Probes unoccupied electronic states.
- Fingerprint to identify presence of a particular chemical species.
- XANES depends on the potential of neighboring atoms, electronic density of state, self-energy, Hole life time and so on.
- XANES is easier to crudely interpret than EXAFS, but the exact physical and chemical interpretation of all spectral features is difficult to do accurately, precisely, and reliably.

The Schrodinger equation in final state:

$$\left[ -\frac{1}{2} \nabla^2 + V(E) \right] \Psi = E \Psi \quad V(E) = V_{coul} + \sum (E)$$
Ab initio XANES calculation with FEFF8 and FDMNES codes

If I don’t calculate it, I don’t understand it

FEFF8. :
1. It is developed by J. J. Rehr group and based on cluster calculations of the single particle Green’s function.
2. It is presented a SCF real-space multiple-scattering(RSMS) theory for arbitrary systems without any requirement of symmetry or periodicity.
3. Potential used in FEFF8 is muffin-tin potential.


FDMNES:
1. Schrodinger Equation is solved by using Finite-difference Method(FDM).
2. The potential is calculated by using local density approximation. Self–consistent way for periodical system, Superposition of atomic densities for complex system

EXAMPLE 1

Comparison of distortion effects calculated by FEFF

Rutile TiO2, Ti K-edge

EXAMPLE 2

Polarization-dependent XANES calculated by FDMNES

Rutile TiO2, Ti K-edge

**XANES Calculation with FEFF8.0**

1. **Free atom potentials** are calculated by using relativistic Dirac-Fock atom code

2. **Scattering potentials** are calculated by overlapping the free atom densities in muffin-tin approximation and Fermi energy is determined with SCF (self-consistent field, Hartree-Fock code)

3. **Phase shifts** are determined by matching at the muffin-tin radius

4. The calculation of **Cross-section (EXAFS, XANES) and LDOS** (local density of states) of electron

5. **Full multiple-scattering XANES**
The calculation Related to XAFS in FEFF

1. Extended x-ray absorption fine structure (EXAFS)
2. X-ray absorption near edge structure (XANES)
3. X-ray natural circular dichroism (XNCD)
4. Spin polarized x-ray absorption (SPXAS)
5. Nonresonant x-ray emission (XES)
6. Electronic structure including local densities of states (LDOS)
TITLE  Zinc oxcide  Zn  K-edge

EDGE    K
S02     1.0

*p  pot  xsph  fms  paths genfmt ff2chi

CONTROL 1  1  1  1  1  1
PRINT    1  0  0  0  0  0  3

*r_scf  [ l_scf  n_scf  ca ]

SCF    2.4  0  15  0.1

*  ixc  [ Vr  Vi ]

EXCHANGE 2  0  0

*EXAFS

*RPATH  7.93408

*kmax  [ delta_k  delta_e ]

XANES  4.0  0.07  0.5

*r_fms  [ l_fms ]

FMS    2.45  0

*

RPATH  0.10000

*  emin  emax  resolution

LDOS  -10  30  0.1

* continued ----->

POTENTIALS

*  ipot  z  [ label  l_scmt  l_fms  stoichiometry ]

0  30  Zn  -1  -1  0
1  8  O  -1  -1  1
2  30  Zn  -1  -1  1

ATOMS

0.00000  0.00000  0.00000  0  Zn1  0.00000
0.00000  0.00000  1.80320  1  O1  1.80320
-1.86482  0.00000  -0.64680  1  O1  1.97381
0.93244  -1.61500  -0.64680  1  O1  1.97383
0.93244  1.61500  -0.64680  1  O1  1.97383
0.93244  1.61500  -2.45000  2  Zn1  3.07899
0.93244  -1.61500  -2.45000  2  Zn1  3.07899
0.93244  -1.61500  2.45000  2  Zn1  3.07899
0.93244  1.61500  2.45000  2  Zn1  3.07899
-1.86482  0.00000  -2.45000  2  Zn1  3.07897
-1.86482  0.00000  2.45000  2  Zn1  3.07897

End
1. **Pot**: The calculation (self-consistent) scattering potentials and Fermi energy

2. **Xsph**: The calculation cross-section and phase shifts and LDOS

3. **Fms**: The calculation of full multiple scattering for XAS

4. **Path**: Path enumeration

5. **Genfmt**: The scattering amplitudes and other XAFS parameters

6. **Fff2chi**: The calculation of final output
<table>
<thead>
<tr>
<th>module</th>
<th>Print levels</th>
</tr>
</thead>
</table>
| pot    | 0  write ‘pot.bin’ only  
|        | 1  add ‘misc.dat’ |
| xsph   | 0  write ‘phase.bin’ and ‘xsect.bin’ only; with [LDOS](#) card add ‘rhoINN.dat’ and ‘logdos.dat’ |
| fms    | 0  ‘fms.bin’ |
| paths  | 0  write ‘paths.dat’ only  
|        | 1  add ‘crit.dat’  
|        | 5 write only ‘crit.dat’ and do not write ‘paths.dat’. (This is useful when exploring the importance of paths for large runs.) |
| genfmt | 0  write ‘list.dat’, and write ‘feff.bin’ with all paths with importance greater than or equal to two thirds of the curved wave importance criterion |
| ff2chi | 0  write ‘chi.dat’ and ‘xmu.dat’  
|        | 1  add ‘sig2.dat’ with Debye–Waller factors  
|        | 2  add ‘chipNNNN.dat’ (χ(κ) from each path individually, this can quickly fill up your disk if you’re doing a large run)  
|        | 3  add ‘feffNNNN.dat’ (input files for Matt Newville’s FEFFIT program) and ‘files.dat’, and do not add ‘chipNNNN.dat’ files. |
## Useful Cards for Calculation of EXAFS and XANES

<table>
<thead>
<tr>
<th>Module</th>
<th>card</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>POT</td>
<td>EXCHANGE Ixc [Vr Vi]</td>
<td>To specify the energy of exchange correlation potential. Ixc – potential model</td>
</tr>
<tr>
<td></td>
<td>SCF r_scf [l_scf n_scf ca]</td>
<td>Self-consistent potential calculation. r_scf – the radius of the cluster for scattering during the self-consistency loop</td>
</tr>
<tr>
<td></td>
<td>POTENTIAL lpot z [l_scmt l_fms]</td>
<td>The list for the calculation of unique potential to each atom lpot – potential index, z – atomic number l_scmt and l_fms – the limitation of the angular momentum SCF and FMS for each atoms</td>
</tr>
<tr>
<td>XSPH</td>
<td>EXAFS, XANES</td>
<td>To calculate EXAFS and XANES</td>
</tr>
<tr>
<td></td>
<td>LDOS</td>
<td>To calculate the angular momentum projected density of states</td>
</tr>
<tr>
<td></td>
<td>POLARIZATION</td>
<td>To calculate the polarized XAFS</td>
</tr>
<tr>
<td>FMS</td>
<td>fms</td>
<td>To compute full multiple scattering within a sphere of radius rfms centered on the absorbing atoms</td>
</tr>
<tr>
<td>PATHS</td>
<td>RPATH</td>
<td>To determine the maximum effective distance</td>
</tr>
<tr>
<td>GENFMT</td>
<td>CRITERIA</td>
<td>To determine the amplitude of curved and plane wave.</td>
</tr>
<tr>
<td>FF2CHI</td>
<td>DEBYE</td>
<td>To calculate Debye–Waller factor for each path</td>
</tr>
</tbody>
</table>
FEFF8 Code

TITLE Zinc oxide Zn K-edge

EDGE K
S02 1.0

* pot xsph fms paths genfmt ff2chi

CONTROL 1 1 1 1 1 1
PRINT 1 0 0 0 0 0

* r_scf [ l_scf n_scf ca ]
SCF 3.5 0 25 0.1

* ixc [ Vr Vi ]

EXCHANGE 2 0 0

* EXAFS
* RPATH 7.93408

* kmax [ delta_k delta_e ]
XANES 4.0 0.07 0.5
* r_fms [ l_fms ]
FMS 5.55 0

* RPATH 0.10000
* emin emax resolution
LDOS -10 30 0.1

* continued ----->
Comparison of Theoretical XANES with Experimental Data

ZnO

TiO₂
The XANES structure begins to take shape, but all the features are broad.
Adding a Ti shell causes the features to become a little distinct.
Adding an Oxygen shell causes the features to become much more distinct.

Coordination Shells of TiO₂ (anatase)

<table>
<thead>
<tr>
<th>Shell</th>
<th>Element</th>
<th>Radius(Å)</th>
<th>Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>O</td>
<td>1.937</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>O</td>
<td>1.966</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>Ti</td>
<td>3.040</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>Ti</td>
<td>3.785</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td>O</td>
<td>3.867</td>
<td>8</td>
</tr>
<tr>
<td>6</td>
<td>O</td>
<td>4.252</td>
<td>8</td>
</tr>
</tbody>
</table>

Adding an Oxygen shell cause the features to become much more distinct.
Filout
 TiO2/output/anatase/TiO2
Green !multiple scattering mode. a muffin-tin one

SCF
N_self
10
Density
state_all

Range ! Energy range of calculation (eV)
-10. 0.1 0. 0.3 10. 1. 50.

Absorber
1

Spgroup
I41/amd:2

Radius
3.8
Crystal !(unit cell)
 3.785 3.785 9.514 90. 90. 90.
22 0.0 0.250 -0.1250 ! Z, x, y, z (unit cell unit)
8 0.0 0.25 0.0816

Convolution
End

Molecule
1. 1. 1. 90. 90. 90.
22 0.000000 0.000000 0.000000
8 -1.338200 -1.338200 0.412908
8 -1.338200 1.338200 -0.412908
8 1.338200 -1.338200 -0.412908
8 1.338200 1.338200 0.412908
8 0.000000 0.000000 -1.965592
8 0.000000 0.000000 1.965592
XANES calculation at MT model in FDMNES

Fermi energy: $-5.475\,\text{eV}$

number of atom: 77,
6 Co around core atom

Normalized Absorption

E(eV)

Fermi energy: $-5.475\,\text{eV}$

number of atom: 77,
6 Co around core atom

- blue: calculation
- black: $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$