Theory and Calculation of X-Ray Spectra with FEFF9

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Outline

• Introduction to XAS
• Theory of EXAFS
• Theory of XANES
• Pitfalls of FEFF
• Calculating XANES
Introduction: What is XAS?
Fine Structure – EXAFS and XANES

XANES - X-ray absorption Near Edge Structure

EXAFS - Extended X-ray Absorption Fine Structure

Cu K-edge 10 keV x-rays
Qualitative Interpretation of EXAFS

Sayers, Stern, and Lytle 1970

EXAFS Fourier transform -> Shifted Radial distribution
Theory of EXAFS

1) \[ \mu \propto \sum_f \left| \langle i | d | f \rangle \right|^2 \delta (E_f - E_i - \hbar \omega) \]

| \( i \rangle \) = initial "core" state \( \langle f \rangle \) = final "photoelectron" state

Fermi's Golden Rule

2) \[ \langle i | d | f \rangle \approx \psi_f (0) \int_c d^3 r \psi_i (r) \hat{\mathbf{e}} \cdot \mathbf{r} \]

3) \[ \psi_f (r) \approx \frac{e^{ikr}}{kr} \left[ 1 + i f(\pi, k) \frac{e^{ikR}}{kR} \frac{e^{ik|r-R|}}{k|r-R|} \right] ; \quad k = \sqrt{2E} \]
Theory of EXAFS

4) \[ \left| \langle i | d | f \rangle \right|^2 \approx A_i \left[ 1 + i f(\pi, k) \frac{e^{ikR}}{kR} \frac{e^{ik|r-R|}}{k|r-R|} + c.c. \right] \]

\( \chi \) is defined as the oscillatory part of the signal

6) \( \chi = K f(\pi, k) \frac{\sin(2kR)}{(kR)^2} \)

Many Single Scattering events

\[ \Rightarrow \chi = \sum_i A_i f_i(\pi, k) \frac{\sin(2kR_i)}{(kR_i)^2} \]
The real EXAFS Equation

- Phase Shifts
- Debye Waller Factors
- Inelastic losses
- Many-Body $S_0^2$
- Curved Wave Scattering
- Multiple Scattering
\[ \chi = \sum_i A_i |f_i(\pi, k)| \frac{\sin(2kR_i + \delta_c(k) + \delta_i(k))}{(kR_i)^2} \]
Disorder: Debye-Waller Factors

\[ p(R) = \left(2\pi\sigma^2_i\right)^{-\frac{1}{2}} e^{-\frac{(R-R_i)^2}{2\sigma_i^2}} \]

\[ \chi = \sum_i A_i |f_i(\pi, k)| \frac{\sin(2kR_i + \delta_c(k) + \delta_i(k))}{(kR_i)^2} \exp(-2\sigma_i^2 k^2) \]
Inelastic losses

\[ E_{qp} = \frac{p^2}{2m} + \Sigma(E) + i \Gamma_{ch} \quad \quad p_{qp} = p' + i p'' = p' + \frac{i}{\lambda} \]

\[ \lambda \approx \frac{k}{|\text{Im} \Sigma| + \Gamma_{ch}} \]

\[ \Rightarrow \chi = \sum_i A_i |f_i(\pi, k)| \frac{\sin(2kR_i + \delta_c(k) + \delta_i(k))}{(kR_i)^2} \exp\left(\frac{-2R}{\lambda(k)}\right) \]
Many-Body Effects $S_0^2$

$$\Rightarrow \chi = \sum_i N_i S_0^2 |f_i(\pi, k)| \frac{\sin(2kR_i + \delta_c(k) + \delta_i(k))}{(kR_i)^2} e^{-\frac{R}{\lambda(k)}}$$
Multiple Scattering and Curved Wave Scattering Amplitudes

\[ \chi = \sum_i N_i S_0^2(k) |f_{\text{eff}}(\pi, k)| \frac{\sin(2kR_i + \delta_c(k) + \delta_i(k))}{(kR_i)^2} \frac{-R}{\lambda(k)} e^{-2k^2\sigma^2} \]

Phase corrected EXAFS Fourier transform – radial distribution function

\[ \chi(R) \]

R_{nn} = 2.769

fcc Pt

R (Å)
X-Ray Absorption

Principles, Applications, Techniques of EXAFS, SEXAFS and XANES

Edited by Koningsberger and Prins (1988)

Chapter 1 - Theory of EXAFS, E. A. Stern

Quantitative Theory of EXAFS

J. J. Rehr & R.C. Albers
Rev. Mod. Phys. 72, 621 (2000)
Theory of XANES

• Back to Fermi’s Golden Rule
  \[ \mu \propto \sum_f \left| \langle i | d | f \rangle \right|^2 \delta(E_f - E_i - \hbar \omega) \]

• |i>, |f> are Many-Body states
  – Effective Single Particle Theory, DFT, Quasiparticle, etc.
  – BSE, TDDFT, CI, CAS SCF, ...
  – Multiplet theory
DFT/Quasiparticle Methods

• Basis set methods
  – Periodic: Quantum Espresso, WIEN2K, ...
  – Localized: Stobe, ORCA, ...

• Real space grid
  – Real Space Grid: FDMNES

• Green’s function methods
  – RSMS: FEFF, SPRKKR, ...
DFT/Quasiparticle Methods

\[ r(i) \rightarrow V_{\text{eff}}^{(i)} \rightarrow (i+1)/G^{(i+1)} \rightarrow (i+1) \rightarrow \text{SCF} \]

Spectrum: Golden Rule

\[ r(i+1) = r(i) \]
Green’s Functions and Absorption

1) \[ \mu \propto \sum_f \left| \langle i|d|f \rangle \right|^2 \delta (E_f - E_i - \hbar \omega) \] Fermi's Golden Rule

2) \[ \sum_f \left| \langle i|d|f \rangle \right|^2 \delta (E_f - E_i - \hbar \omega) = \langle i|d \sum_f |f \rangle \langle f|\delta (E_f - E_i - \hbar \omega) d^\dagger |i \rangle \]

\[ - \frac{1}{\pi} \text{Im}[G(E_i + \hbar \omega)] \]

3) \[ \mu \propto -\frac{1}{\pi} \text{Im} \langle i|d G(\omega) d^\dagger |i \rangle \]

SCF: \[ \rho(r) = -\frac{1}{\pi} \int_{-\infty}^{E_{\text{Fermi}}} \text{Im}[G(r,r;E)]dE \]
Real-Space Multiple Scattering

\[ G = [E - H]^{-1} = G^0 + G^0VG^0 + G^0VG^0VG^0 + \cdots \]

\[ V = \sum_i V_i \]
Real-Space Multiple Scattering

- $G = [E - H]^{-1} = G^0 + G^0VG^0 + G^0VG^0VG^0 + \cdots$

- $V = \sum_i v_i$
Real-Space Multiple Scattering

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Real-Space Multiple Scattering

- $G = [E - H]^{-1} = G^0 + G^0 V G^0 + G^0 V G^0 V G^0 + \cdots$

- Scattering Matrix: $t^i = v^i + v^i G^0 t^i$

- Move to site and angular momentum basis
  Separates structural and chemical dependence

Structural dependence: $G_{iL,jL}'$
Chemical dependence: $t^i_L$
Path Expansion and Full Multiple Scattering

- Path Expansion – EXAFS Equation

\[ G = G_0 + G_0 T G_0 + G_0 T G_0 T G_0 + \ldots \]

- Full Multiple Scattering - XANES

\[ G(\omega) = G_0 + G_0 T G_0 + G_0 T G_0 T G_0 + \ldots = [1 - G_0 T]^{-1} G_0 \]
XANES and LDOS
Beyond DFT – Quasiparticle Self-Energy Effects

- \( G = (E - H - \Sigma)^{-1} \)
- \( \Sigma \): Self-Energy operator \( \rightarrow \) Quasi-particles
Core-Hole Interaction

- Photo-electron and hole interact
- Self-Consistent calculation without core electron: Final State Rule
- Linear response: \( W_{ch} = \epsilon^{-1} \nu_{ch} \)
FEFF: Key Approximations

- Spherical muffin-tin potentials
- Local Density approximation
- Quasi-particle approximation
- Core-hole treatment
When might approximations break down?

• Spherical potentials: non-symmetric systems, water, graphene, benzene, ...

• Treatment of the core hole

• Self-energy approximations

• Many-body effects
  – Charge transfer excitations: transition metal oxides, cuprates, ...
  – Multiplet effects: L-edges in transition metals, L/M edges in f-state systems
Muffin-Tin Approximation

\[ \text{Br}_2 \]

![Graph of Muffin-Tin Approximation](image)

The graph shows the comparison between FEFF-FP, Experiment, and Muffin-Tin approximations for \( \text{Br}_2 \). The x-axis represents energy (E in eV), and the y-axis represents \( m(E) \). The graph illustrates the differences in the approximations for the Br2 molecule.
Many-Body Effects: Charge Transfer

Calandra et al, PHYSICAL REVIEW B 86, 165102 (2012)
XANES is sensitive to ...

- Unoccupied local DOS
- Symmetry
- Charge transfer (oxidation state)
- Occupation (L-edges)
Eu$_2$O$_3$ L3 XANES
Eu$_2$O$_3$ L3 XANES
Symmetry and Pre/Near-Edge Features
Symmetry and Pre/Near-Edge Features

Ti K edge XANES
BaTiO₃
Edge Position and Charge Transfer

![Graph showing edge positions and charge transfer](image)
Edge Position and Charge Transfer

$E_{Core}$, $E_{Edge}$, $E_{Fermi}$

Graphs showing partial charge vs. distance to surface for different systems:
Simulation of XANES with FEFF

- Structure – coordinates, species, vibrational character
- Important options for XANES calculations
  - Self-consistent potentials
  - Core hole treatment
  - Self-energy
- Convergence: FMS/SCF radii, Maximum angular momentum
FMS Convergence

- Guess: Inelastic mean free path
SCF Convergence
$L_{\text{max}}$ Convergence
Potentials in FEFF

- Symmetry enforced using “unique potentials”
- Add unique potentials to relax restraints on symmetry
- Potential of absorbing atom is always unique
  - Must average spectrum over absorbers
Augmenting FEFF with DFT

- Find possible structures
- Check full potential effects
- Check accuracy of Fermi level
- Fine chemical shifts
- Find dynamical properties
Conclusions

• EXAFS
  – Quantitative MS path expansion -> Physical parameters, EXAFS equation
    • Bond lengths
    • Dynamic structure (Debye-Waller factors)
    • Chemical species

• XANES
  – Semi-quantitative, FMS calculations, sensitive to
    • Electronic structure (LDOS)
    • Symmetry
    • Oxidation or charge state

Thank You!