II. Real-space multiple-scattering theory of EXAFS and XANES & FEFF

J. J. Rehr, J. J. Kas and F. D. Vila
Talk:
- Real-space multiple-scattering (RSMS) Theory
  *aka* Real-space Green’s function (RSGF) theory
- Implementation of RSMS in FEFF

Key approximations and limitations
Effects of structure and disorder
Some advanced developments
Full spectrum XAS: Expt. Vs Theory

fcc Al

UV x-ray

μ (Ångstrom⁻¹)

ω (eV)
The devil is in the details: edges, fine-structure ...
Historical interpretation of EXAFS*
*Stern Sayers Lytle, UW 1971

Short range order theory → EXAFS Fourier Transform

→ X-ray Microscope!

BUT needed to calibrate experiment with “Standard”
Quantitative theory of EXAFS:

Theory behind FEFF6

J. J. Rehr & R.C. Albers
Rev. Mod. Phys. 72, 621 (2000)
Ab initio theory and calculations of X-ray spectra

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Available online 5 December 2008

Update of Rehr & Albers: Advanced techniques and ab initio treatment of many-body effects
Real-space multiple-scattering calculation and interpretation of x-ray-absorption near-edge structure

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(Received 26 September 1997; revised manuscript received 14 April 1998)

Parameter-free calculations of X-ray spectra with FEFF9

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DOI: 10.1039/b926434c
Atomic models:
e.g. de Groot. Atomic cross-sections, multiplet theory with fitted parameters, crystal field model Hamiltonians

DFT (Density Functional Theory):
WIEN2k, ABINIT, VASP, CASTEP, StoBe, Orca ..., Accurate for ground-state properties, not reliable for excited states, Delta-SCF “Final State Rule” with core-hole

Quasi-particle Green’s Function Theory: FEFF9
Appropriate for excited states, NOT full potential

BSE (Bethe-Salpeter Equation):
Exc!ting, OCEAN, Al2NBSE. Accurate but demanding. Less user friendly. Misses excitations & satellites

QC methods:
MRCI, MRCC, CASPT2, QMC, etc, highly accurate but mostly intractable except in small molecules

RSGF in the hierarchy of spectroscopy methods
"Pretty good" spectra

Advantages:
- Real-space
- Fully relativistic, all-electron
- Semi-automated, user-friendly, easy to use
- Built for EXAFS and related x-ray spectroscopies
- Applicable to materials throughout the periodic table

Disadvantages: Not always the best tool:
- Spherical potentials – can lose accuracy near edges
- Quasi-particle theory only – ignores multiplets, satellites
FEFF quantitative XANES theory in one Feynman diagram
“Can you write an equation for the theory?”

P.A.M. Dirac
Answer: Exact EXAFS Equation*

\[ \chi(k) = S_0^2 \sum_R \frac{|f_{\text{eff}}(k)|}{kR^2} \sin(2kR + \Phi_k) e^{-2R/\lambda_k} e^{-2\sigma^2 k^2} \]

Effective Scattering Amplitude \( f_{\text{eff}} \)

\( S_0^2 \) Many body amplitude factor

EXAFS measures local structure & disorder

Distance \( R \) Coordination \( N \) Disorder \( \sigma^2 \)

\( \lambda_k \) Mean free path

\( \sigma^2 \) Mean square vib amplitude

BUT: need many parameters!

**Question:** Can the EXAFS parameters $k, f_{\text{eff}}, \Phi_k, \sigma^2, \lambda_k, S_0^2$ be calculated theoretically?
**FEFF: Many-body → effective single particle**

**Many-body Fermi’s Golden Rule**

\[
\mu(\omega) \propto \sum_{F} |\langle I | \Delta | F \rangle|^2 \delta (E_F - E_I - \omega)
\]

**Effective Single particle Fermi’s Golden Rule**

\[
\mu(\omega) \propto \sum_{i,f} |\langle i | d | f \rangle|^2 \delta (E_f - E_i - \omega) S_0^2
\]

\[
H = -(1/2)\nabla^2 + V
\]

\[
H' = H + V_{ch} + \Sigma(E)
\]
Effective Single particle
Fermi’s Golden Rule

\[ \mu(\omega) \propto \sum_{ij} \langle i | d^\dagger | f \rangle \langle f | d | i \rangle \delta(E_f - E_i - \omega) \, S_0^2 \]
Effective Single particle
Fermi’s Golden Rule

\[\rho(r, r', E) = \sum_f |f\rangle \langle f| \delta(E_f - E)\]

Density Matrix

\[\mu(\omega) \propto \sum_{ij} \langle i | d^\dagger | f \rangle \langle f | d | i \rangle \delta(E_f - E_i - \omega) S_0^2\]
FEFF: From sum-over-states to Green’s function

Effective Single particle

Fermi’s Golden Rule

$$\mu(\omega) \propto \sum_{i,j} \langle i | d^\dagger | f \rangle \langle f | d | i \rangle \delta(E_f - E_i - \omega) S_0^2$$

$$\rho(r,r',E) = \sum_f \langle f | \langle f | \delta(E_f - E)$$

$$\text{Im} \left[ G(r,r',E) \right] = -\frac{1}{\pi} \rho(r,r',E)$$

$$G = [E - H + i\Gamma]^{-1}$$

Density matrix from Green’s function
Effective Single particle 
Fermi’s Golden Rule

\[ \rho(r, r', E) = \sum_f |f\rangle \langle f| \delta(E_f - E) \]

\[ \text{Im} \left[ G(r, r', E) \right] = -\frac{1}{\pi}\rho(r, r', E) \]

\[ G = [E - H + i\Gamma]^{-1} \]

Substitute sum over final states with Green’s function

\[ \mu(\omega) \propto \sum_{ij} \langle i|d^\dagger|f\rangle \langle f|d|i\rangle \delta(E_f - E_i - \omega) S_0^2 \]

\[ \mu(\omega) \propto \text{Im} \sum_{i} \langle i|d^\dagger G(\omega + E_i)d|i\rangle \theta_1(\omega + E_i - E_{Fermi}) S_0^2 \]
What’s a Green’s function?

Wave function in QM \[ H \Psi = E \Psi \]

\[ \Psi(r) = \text{Amplitude to find particle at } r \]

Green’s function \[ (H - E) G = - \delta(r-r') \]

\[ G(r,r',E) = \text{aka Propagator} \]

= Amplitude to go from \( r \) to \( r' \)
\[ \mu(\omega) \propto \text{Im} \sum_i \langle i | d^\dagger G(\omega + E_i) d | i \rangle \theta_{\Gamma}(\omega + E_i - E_{\text{Fermi}}) \quad S_0^2 \]

Insert complete set of states

\[ 1 = \sum_L |i, L \rangle \langle i, L| \]
FEFF: Local basis and matrix elements

\[ \mu(\omega) \propto \text{Im} \sum_i \langle i | d^\dagger G(\omega + E_i) d | i \rangle \theta_\Gamma(\omega + E_i - E_{\text{Fermi}}) S_0^2 \]

Insert complete set of states

\[ 1 = \sum_L |i, L\rangle \langle i, L| \]

\[ \mu(\omega) \propto \text{Im} \sum_{iLL'} \langle i | d^\dagger | i, L \rangle G_{LL'}(\omega + E_i) \langle i, L' | d | i \rangle \theta_\Gamma(\omega + E_i + E_{\text{Fermi}}) S_0^2 \]
FEFF: Local basis and matrix elements

\[ \mu(\omega) \propto \text{Im} \sum_i \langle i | d^\dagger G(\omega + E_i) d | i \rangle \theta(\omega + E_i - E_{\text{Fermi}}) S_0^2 \]

Insert complete set of states

\[ 1 = \sum_L |i, L\rangle \langle i, L| \]

Matrix elements

\[ \mu(\omega) \propto \text{Im} \sum_{iLL'} \langle i | d^\dagger | i, L \rangle G_{LL'}(\omega + E_i) \langle i, L' | d | i \rangle \theta(\omega + E_i + E_{\text{Fermi}}) S_0^2 \]

Green’s Function matrix
Getting $G$: Multiple Scattering Theory

Dyson’s equation:

\[ G = G^0 + G^0 V G \]

Iterating:

\[ G = G^0 + G^0 V G^0 + G^0 V G^0 V G^0 + \cdots \]
Dyson’s equation:  
\[ G = G^0 + G^0 V G \]

Iterating:  
\[ G = G^0 + G^0 V G^0 + G^0 V G^0 V G^0 + \cdots \]

\[ G(r, r') = G_0(r, r') + \int d^3 r'' G_0(r, r'') V(r'') G_0(r'', r') + \cdots \]
Getting $G$: Multiple Scattering

Dyson’s equation:  \[ G = G^0 + G^0VG \]

Iterating:  \[ G = G^0 + G^0VG^0 + G^0VG^0VG^0 + \cdots \]

Atomic pot. partition

\[ V = \sum_i v_i \]

\[ G = G^0 + \sum_i G^0 v_i G^0 + \sum_{i,j} G^0 v_i G^0 v_j G^0 + \cdots \]
Getting $G$: Multiple Scattering

Dyson’s equation:

$$ G = G^0 + G^0 V G $$

Iterating:

$$ G = G^0 + G^0 V G^0 + G^0 V G^0 V G^0 + \cdots $$

Atomic pot. partition

$$ V = \sum_i v_i $$

$$ G = G^0 + \sum_i G^0 v_i G^0 + \sum_{i,j} G^0 v_i G^0 v_j G^0 + \cdots $$

Site scatt. matrix

$$ t_i = v_i + v_i G_0 t_i $$

$$ G = G^0 + \sum_i G^0 t_i G^0 + \sum_{i \neq j} G^0 t_i G^0 t_j G^0 + \cdots $$
Getting $G$: Multiple Scattering

Dyson’s equation: $G = G^0 + G^0 V G$

Iterating: $G = G^0 + G^0 V G^0 + G^0 V G^0 V G^0 + \cdots$

Atomic pot. partition $V = \sum_i v_i$

$G = G^0 + \sum_i G^0 v_i G^0 + \sum_{ij} G^0 v_i G^0 v_j G^0 + \cdots$

Site scatt. matrix $t_i = v_i + v_i G_0 t_i$

$G = G^0 + \sum_i G^0 t_i G^0 + \sum_{i \neq j} G^0 t_i G^0 t_j G^0 + \cdots$

$G_0 V G_0$

$G_0 T G_0$
Getting $G$: Multiple Scattering

$$G = G^0 + \sum_i G^0 t_i G^0 + \sum_{i \neq j} G^0 t_i G^0 t_j G^0 + \ldots$$
Getting $G$: Multiple Scattering

\[
G = G^0 + \sum_i G^0 t_i G^0 + \sum_{i \neq j} G^0 t_i G^0 t_j G^0 + \ldots
\]

Central atom contrib.

\[
G_c = G_0 + G_0 t_c G_0
\]

EXAFS

\[
G = G_c + G_c \sum_{i \neq c} t_i G_c + G_c \sum_{i \neq c} \sum_{j \neq c} t_i G_0 t_j G_c + \ldots
\]
Getting $G$: Multiple Scattering

\[ G = G^0 + \sum_{i} G^0 t_i G^0 + \sum_{i \neq j} G^0 t_i G^0 t_j G^0 + \ldots \]

Central atom contrib.

\[ G_c = G_0 + G_0 t_c G_0 \]

EXAFS

\[ G = G_c + G_c \sum_{i \neq c} t_i G_c + G_c \sum_{i \neq c} \sum_{j \neq c} t_i G_0 t_j G_c + \ldots \]

Graphically: Path expansion

\[ G = G_c + G_c T G_c + G_c T G^0 T G_c + G_c T G^0 T G^0 T G_c + \ldots \]
Getting $G$: Full Multiple Scattering

\[ G = G^0 + \sum_i G^0 t_i G^0 + \sum_{i \neq j} G^0 t_i G^0 t_j G^0 + \ldots \]
Getting $G$: Full Multiple Scattering

$$G = G^0 + \sum_i G^0 t_i G^0 + \sum_{i \neq j} G^0 t_i G^0 t_j G^0 + \ldots$$

Total scatt. matrix

$$T_{LL'}^{ij} = t_{LL'}^i \delta_{ij}$$

$$G = G^0 + G^0 T G^0 + G^0 T G^0 T G^0 + \ldots$$
Getting $G$: **Full Multiple Scattering**

$$G = G^0 + \sum_i G^0 t_i G^0 + \sum_{i \neq j} G^0 t_i G^0 t_j G^0 + ...$$

**Total scatt. matrix**

$$T_{LL'}^{i,j} = t_{LL'}^i \delta_{ij}$$

**Sum and invert**

$$G = G^0 + G^0 T G^0 + G^0 T G^0 T G^0 + ...$$

**XANES**

$$G = [1 - G^0 T]^{-1} G^0$$
Implementation: FEFF Code

Real-space multiple-scattering calculation and interpretation of x-ray-absorption near-edge structure

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Core-hole, SCF potentials

Essential!
Example: Pt EXAFS – path expansion

Path Expansion 15 paths

R

\( \chi(R) \)

Path Expansion 15 paths

No peak shift!

\( R_{nn} = 2.769 \)

fcc Pt

*Theoretical phases accurate distances to < 0.01 Å
Example: Pt XANES full multiple-scattering

Pt L₃-edge

Pt L₂-edge (S. Bare, UOP)

- **Relativistic** FEFF8 code reproduces all spectral features, *including absence of white line at L₂-edge*.

- **Self-consistency essential**: position of Fermi level strongly affects white line intensity.
Green’s Functions and Parallel Computation

Parallel calculation of electron multiple scattering using Lanczos algorithms

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μ(E) \sim -\frac{1}{\pi} \text{Im} \langle i | \hat{\epsilon} \cdot r' G(r', r, E) \hat{\epsilon} \cdot r | i \rangle

Energy E is just a parameter!

“Natural parallelization”

Each CPU does one energy

FeffMPI Scaling with Cluster Size

Normalized time relative to single processor vs. Inverse number of nodes in cluster \frac{1}{N_{CPU}}
Self-consistent Densities and Potentials

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

\( \rho^{(0)} \)

\( V^{(i)}_{\text{eff}} \)

\( \psi^{(i+1)} / G^{(i+1)} \Rightarrow \rho^{(i+1)} \)

\( \rho^{(i)} \)

\( \rho^{(i+1)} = \rho^{(i)} ? \)

Spectrum: Golden Rule
Key approximations in FEFF

- Dirac-Fock relativistic atomic states; semi-relativistic scattering states
- Spherical overlapped muffin-tin potentials: Huge simplification of the problem
- Quasi-particle approximation: Electron propagates in lossy medium described by Approximate self-energy
- Core-hole treatment: RPA or DFT-Screened core-hole
The muffin-tin potential

Scattering potential partition into muffin-tins

\[ V = \sum_{i} v_i \]
The overlapped muffin-tin potential (~10%)

Improved density:
Resembles “bonding”
Charge redistribution
Charge neutrality built in

? Spherical approximation?
FEFF Density of States vs full potential codes

NaNO$_2$

DOS (Arbitrary units)

E-E$_F$ (eV)

VASP

FEFF
FEFF electron density in real space vs full potential codes
Disorder and Debye-Waller factors

**DW factors:**
- **Crucial** for EXAFS
- Very little effect in XANES region
- Can be included anyway in single-scattering approx.
- Both *ab initio* and model forms

**Static Disorder:**
- May be important in XANES
- Need external input for FEFF simulations
- Methods **MD** trajectories, MC sampling ...
Quick intro to DW factors

Multiple Scattering Path

XAFS DW Factor

Average commonly expressed in terms of the cumulant expansion

\[
\left\langle e^{i2kr}\right\rangle \equiv e^{2ikR_0} e^{-W(T)}
\]

\[
W(T) = - \sum_{n=1}^{\infty} \frac{(2ik)^n}{n!} \sigma^{(n)}(T)
\]

Leading cumulants

\[
\begin{align*}
\sigma^{(1)} &= \left\langle r - R_0 \right\rangle \\
\sigma^{(2)} &= \left\langle (r - \bar{r})^2 \right\rangle \equiv \sigma^2(T) \\
\sigma^{(3)} &= \left\langle (r - \bar{r})^3 \right\rangle
\end{align*}
\]
EXAFS near-neighbor DW Factor of Cu

CD (Correlated Debye):
Standard FEFF

LDA, hGGA:
Ab initio DW

Isotropic bonding:
Good CD results

Expt: Fornasini et al. (2004)
EXAFS near-neighbor DW Factor of Ge

CD (Correlated Debye): Default in FEFF

LDA, hGGA: Ab initio DW

Directional bonding: Needs AIDW

Expt: Dalba et al. (1999)
Ab Initio DW factors: Lanczos algorithm

XAFS DW Factor for path R:

\[ \sigma^2_R(T) = \frac{\hbar}{2\mu_R} \int_0^\infty \frac{1}{\omega} \coth \left( \frac{\beta \hbar \omega}{2} \right) \rho_R(\omega) \, d\omega \]

VDOS expressed as imaginary part of the phonon propagator

\[ \rho_R(\omega) = -\frac{2\omega}{\pi} \text{Im} \langle 0 | \frac{1}{\omega^2 - D + i\varepsilon} | 0 \rangle \]

Seed state: Displacement along path

Dynamical Matrix: Calculated using ab initio methods (Abinit, Gaussian, VASP, etc)
Ab Initio DW Factors in Metal-Ligand Complexes

Ru(bpy)²(AP)(H₂O)²⁺

Good agreement for tight ligands (bpy)

Useful agreement for weak ligands (AP and H₂O)
Still within error margin

<table>
<thead>
<tr>
<th>Path</th>
<th>$R_{M-L}$ (in Å)</th>
<th>$\sigma^2$ (in $10^{-3}$ Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Theory</td>
<td>Exp</td>
</tr>
<tr>
<td>Ru-N(bpy)</td>
<td>2.08</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.04</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.10</td>
<td>2.05±0.01</td>
</tr>
<tr>
<td></td>
<td>2.09</td>
<td></td>
</tr>
<tr>
<td>Ru-N(AP)</td>
<td>2.14</td>
<td>2.10±0.03</td>
</tr>
<tr>
<td>Ru-O</td>
<td>2.22</td>
<td>2.06±0.05</td>
</tr>
</tbody>
</table>

Beyond DFT: Quasi-particle Self-Energy Effects

Quasi-particle (QP) effects:

\[ G = \left[ E - H - \Sigma \right]^{-1} \]

BN 89 atom cluster

Ground state potential:
Usually insufficient
Need QP effects
and SCF potentials
Treatment of the core hole:
  - Screening DFT or RPA
  - Chemical shifts

**Self-energy** approximations:
  - Need more than single-pole self-energy

Many-body effects:
  - Multi-electron excitations $S_0^2$
  - Charge transfer excitations:
Quick overview of other FEFF capabilities:

- XES
- RIXS
- Compton Profiles
- Reciprocal space: EELS and impurity GF
- Hubbard U method
Non-resonant X-ray Emission (XES)

Vila et al., J. Phys. Chem. A 2011, 115, 3243
Real-space Green’s function approach to resonant inelastic x-ray scattering

\[
\frac{d^2\sigma}{d\Omega d\omega} = \frac{\omega}{\Omega} \sum_F \left| \sum_M \frac{\langle F | \Delta_2 | M \rangle \langle M | \Delta_1 | \Psi_0 \rangle}{E_M - \Omega - E_0 + i \Gamma_M} \right|^2 \\
\times \delta(\Omega - \omega + E_0 - E_F)
\]

\[
\frac{d^2\sigma}{d\Omega d\omega} \propto \frac{\omega}{\Omega} \int d\omega_1 \frac{\mu_e(\omega_1) \mu(\Omega - \omega - \omega_1 + E_b)}{|\omega - \omega_1 - i \Gamma_b|^2}
\]

TiO\textsubscript{2} (Ti K\textalpha)
Real-space Green’s function calculations of Compton profiles

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Finite-temperature calculations of the Compton profile of Be, Li, and Si

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(Received 3 August 2016; published 2 December 2016)

\[ S(q,\omega) = \sum_F \left| \langle F | \sum_j \exp(i q \cdot r_j) | I \rangle \right|^2 \delta(E_F - E_I - \hbar \omega) \]

\[ S(q,\omega) = (m/\hbar q) J(p_q) \]

\[ J(p_q) \equiv \int d^3 r \rho(p) \delta(p_q - (\omega m/q - \hbar q / 2)) \]
Strongly correlated systems: Hubbard GW+U

U calculated using constrained RPA within RSMS

(Nearly) parameter free

Further information

The FEFF Project website:  
URL: feffproject.org

The FEFF Users Guide:  
URL: feffproject.org/feffproject-feff-documentation.html

Developers contact:  
URL: feffproject.org/feffproject-contact.html.html
Take away messages

Know the basics of RSMS/RSGF theory
Understand the key approximations in FEFF
Know some of FEFF’s advanced capabilities
Acknowledgments: the FEFF group

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