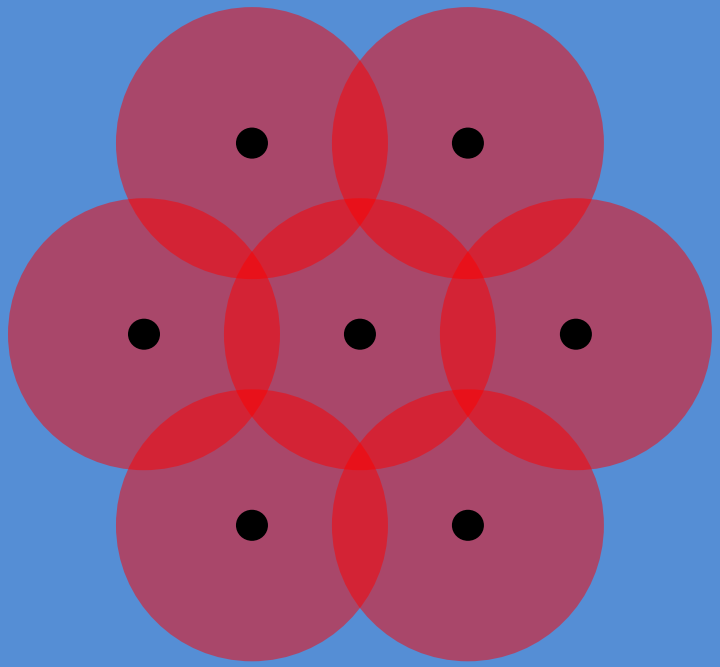
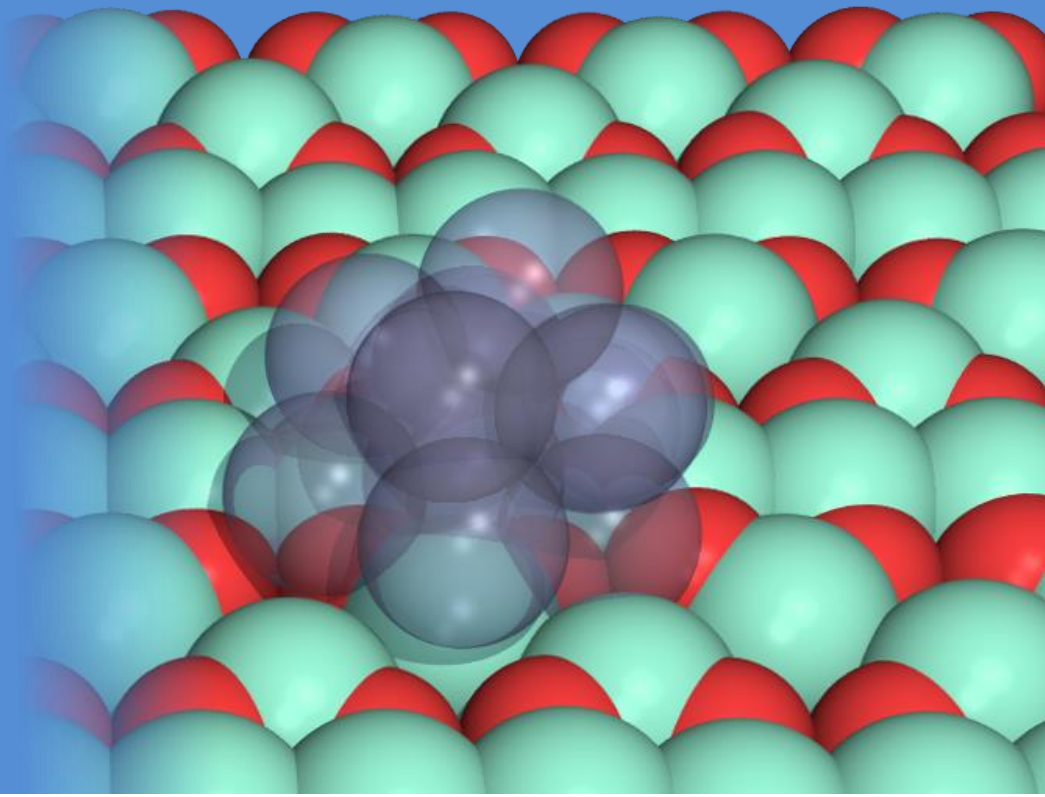
Advances in electronic structure, vibrations and disorder in FEFF





UNIVERSITY OF WASHINGTON

F. D. Vila

Outline

Goals, philosophy and useful literature
Multiple scattering theory in FEFF
Key approximations in FEFF
FEFF structure and parallel implementation
Recent advances:
    RPA Core-hole
    Many-pole Self-Energy
Augmenting FEFF with DFT
    Ab Initio Debye-Waller factors
    Importance of structure and disorder

The FEFF project

Goals of the FEFF project

Ab initio theory of XAS and related spectra

No adjustable parameters

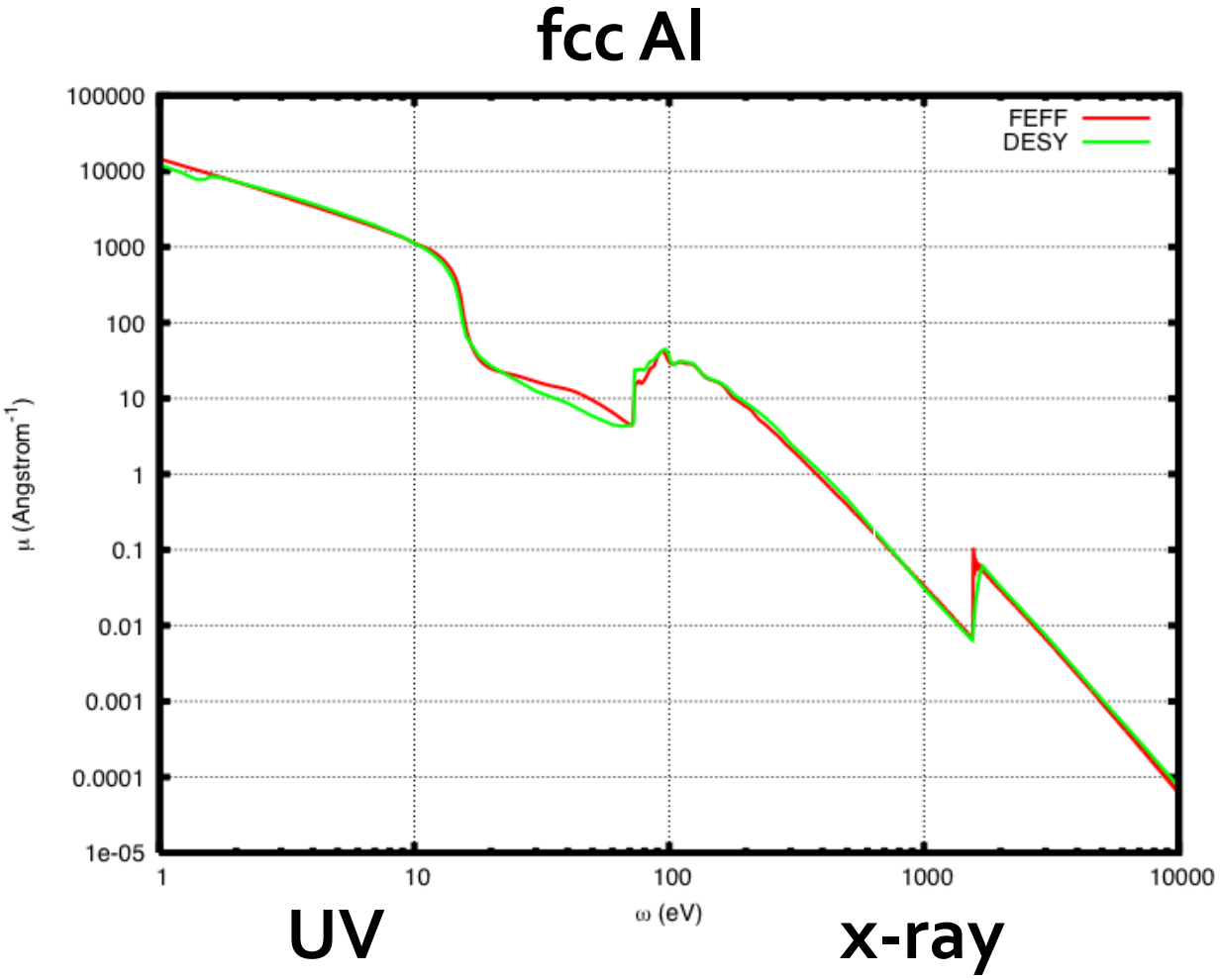
Accuracy ~ experiment

Quantitative interpretation

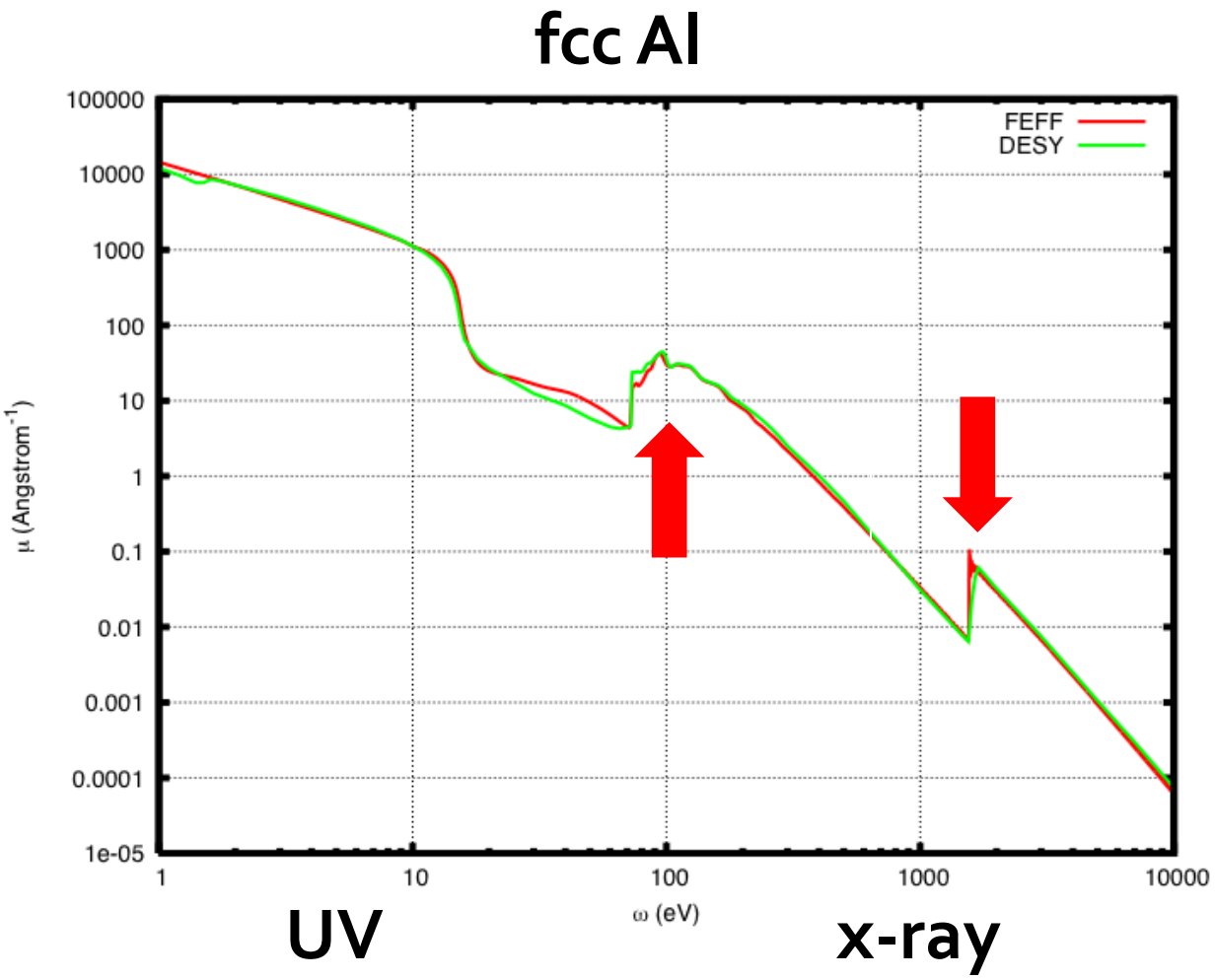
Inverse problem: What's in a spectrum?

Atomic structure, chemistry, …

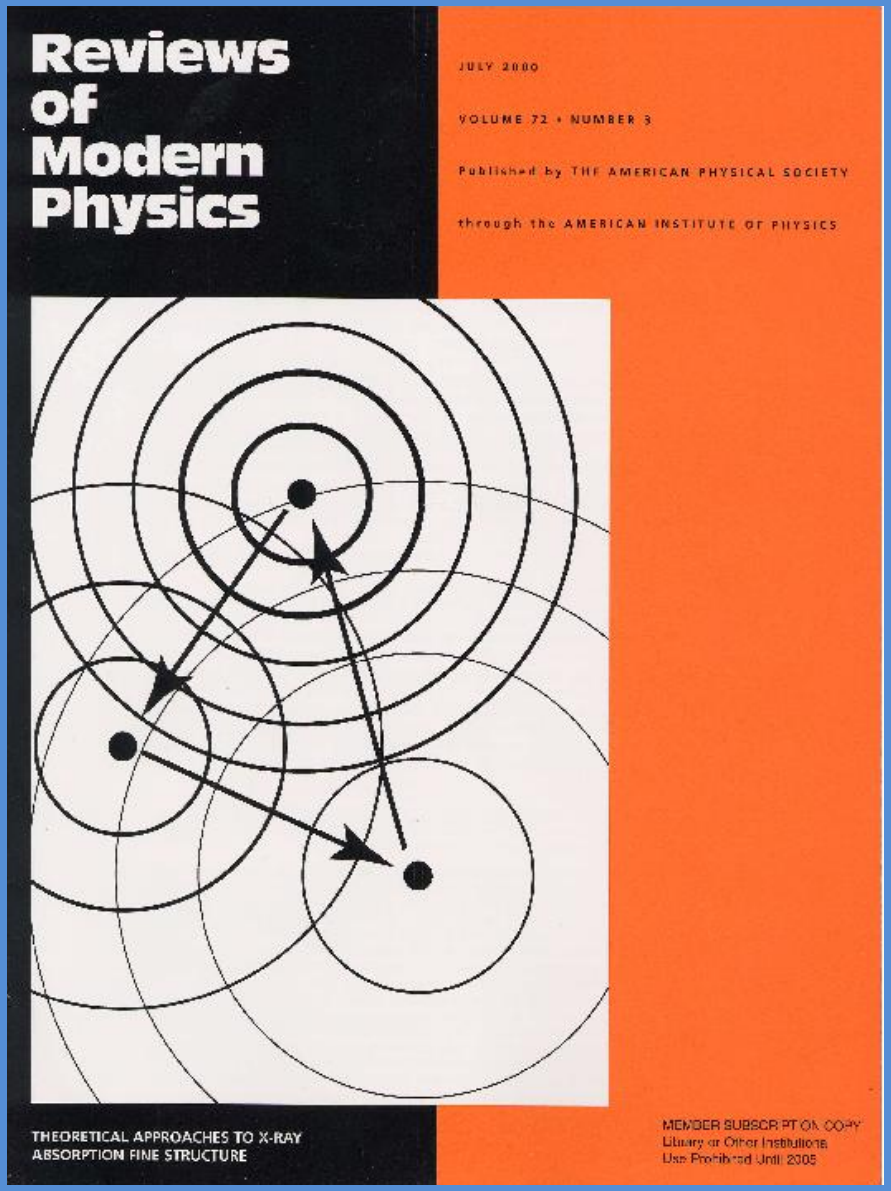
Full spectrum: Expt. Vs Theory



The devil is in the details



Basic recommended literature: Theoretical MS



Quantitative theory:

Theory behind FEFF8
Good general summary

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

Basic recommended literature: Advanced methods

Available online at www.sciencedirect.com
ScienceDirect
C. R. Physique 10 (2009) 548–559
COMPTES RENDUS PHYSIQUE
http://france.elsevier.com/direct/COMREN/

Theoretical spectroscopy / Spectroscopie théorique

Ab initio theory and calculations of X-ray spectra

John J. Rehr *, Joshua J. Kas, Micah P. Prange, Adam P. Sorini, Yoshinari Takimoto, Fernando Vila

Department of Physics, University of Washington, Seattle, WA 98195-1560, USA

Available online 5 December 2008

PERSPECTIVE www.rsc.org/pccp | Physical Chemistry Chemical Physics

Parameter-free calculations of X-ray spectra with FEFF9

John J. Rehr,*[a] Joshua J. Kas,[a] Fernando D. Vila,[a] Micah P. Prange[bc] and Kevin Jorissen[a]

Received 15th December 2009, Accepted 27th April 2010
First published as an Advance Article on the web 6th May 2010
DOI: 10.1039/b926434e

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

FEFF development philosophy

"Workhorse":

- Does a good job most of the time

Main advantages:

- Real-space
- Fully relativistic
- Easy to use
- Built for spectroscopy
- Fairly robust

Not always the right tool:

- Spherical potentials
- Quasi-particle theory
- There are more advanced theories

FEFF development philosophy (cont'd)

Under active development:

Currently FEFF9.x

Successful:

20+ years of use

1,000s of users/references

Synergy with experimental science:

Meant to be used by experimentalists

When new methods appear, we try to model them

Theory and Practice Behind FEFF

FEFF in the hierarchy of spectroscopy methods

sophistication

Atomic models:

e.g. de Groot. Atomic cross-sections, multiplet theory with fitted parameters, model Hamiltonians

DFT (Density Functional Theory):

WIEN2k, ABINIT, VASP, CASTEP …,
Accurate for ground-state properties, less reliable for excited states,
"Final State Rule" with core-hole

Quasi-particle Green's Function Theory:

FEFF. Appropriate for excited states; efficient; missing some many-body physics

BSE (Bethe-Salpeter Equation):

Exc!ting, OCEAN, AI2NBSE. Most accurate but demanding.
Less established, less user friendly. Still missing some physics

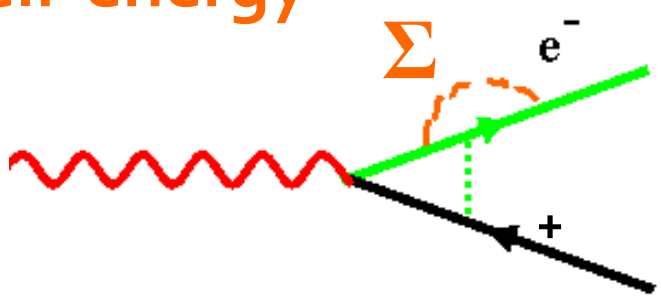
QC methods:

MRCI, MRCC, CASPT2, QMC, etc, highly accurate but completely intractable

FEFF quantitative XANES theory in one picture

Inelastic Losses
Self-energy

Real-Space
Green's Function



x-ray

Screened
core-hole

FEFF: Many-body to effective single particle

XAS absorption coefficient

Many-body Fermi's Golden Rule

$$\mu(\omega) \propto \sum_F |\langle I|\Delta|F\rangle|^2 \, \delta\left(E_F - E_I - \omega\right)$$

Effective Single particle Fermi's Golden Rule

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

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

$$H' = H + V_{ch} + \Sigma(E)$$

FEFF: From sum-over-states to Green's function

Effective Single particle Fermi's Golden Rule

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

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

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

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

Substitute sum over final states with Green's function

$$\mu(\omega) \propto \mathrm{Im} \sum_i \langle i | d^{\dagger} G(\omega + E_i) d | i \rangle \, \theta_{\Gamma}(\omega + E_i - E_{Fermi})$$

FEFF: Local basis and matrix elements

$$\mu(\omega) \propto \mathrm{Im} \sum_i \langle i | d^\dagger G(\omega + E_i) d | i \rangle \, \theta_\Gamma(\omega + E_i - E_{Fermi})$$

Insert complete set of states $1 = \sum_L |i, L\rangle\langle i, L|$

Matrix elements

$$\mu(\omega) \propto \mathrm{Im} \sum_{iLL'} \langle i | d^\dagger | i, L \rangle \, G_{LL'}(\omega + E_i) \, \langle i, L' | d | i \rangle \, \theta_\Gamma(\omega + E_i + E_{Fermi})$$

Green's Function matrix

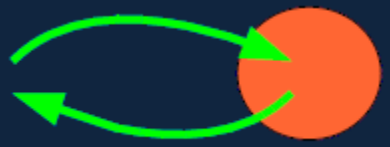
Getting *G*: Multiple Scattering

Dyson's equation: $G = G^0 + G^0 V G$

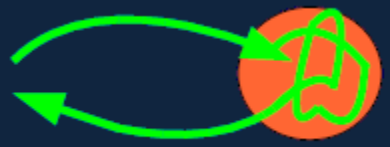
Iterating: $G = G^0 + G^0 V G^0 + G^0 V G^0 V G^0 + \cdots$

Atomic pot. partition $V = \sum_i v_i$ $\quad G = G^0 + \sum_i G^0 v_i G^0 + \sum_{ij} G^0 v_i G^0 v_j G^0 + \ldots$

Site scatt. matrix $t_i = v_i + v_i G_0 t_i$ $\quad G = G^0 + \sum_i G^0 t_i G^0 + \sum_{i \neq j} G^0 t_i G^0 t_j G^0 + \ldots$



$G_0 V G_0$



$G_0 T G_0$

Getting *G*: Multiple Scattering

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

Central atom contrib.

$$G_c = G_0 + G_0 t_c G_0$$

EXAFS

$$G = G_c + G_c \sum_{i \neq c} t_i G_c + G_c \sum_{i \neq c} \sum_{j \neq c} t_i G_0 t_j G_c + \cdots$$

Graphically: Path expansion

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

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

$$G = G^0 + G^0 T G^0 + G^0 T G^0 T G^0 + \ldots$$

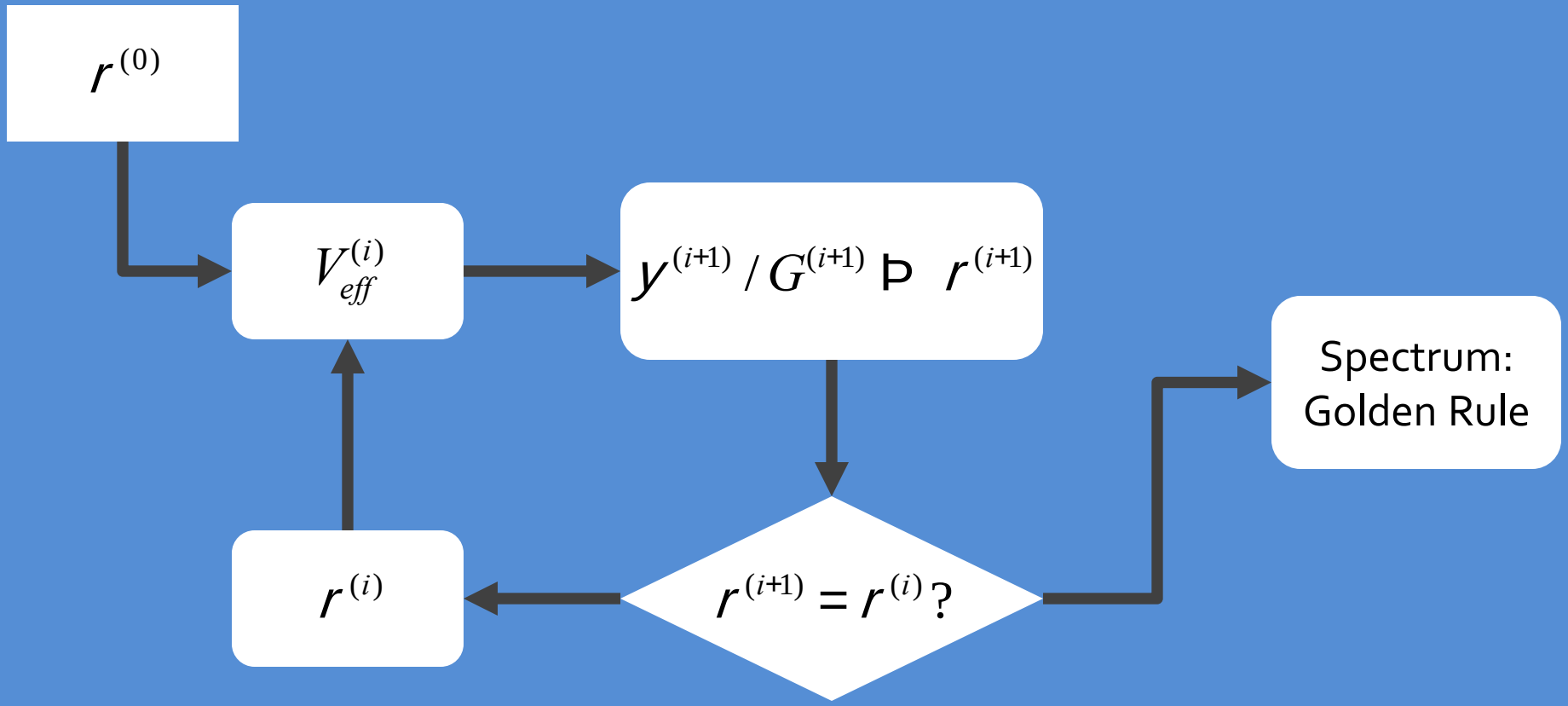
Sum and invert

XANES

$$G = \left[1 - G^0 T\right]^{-1} G^0$$

Self-consistent Densities and Potentials

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



Key approximations in FEFF

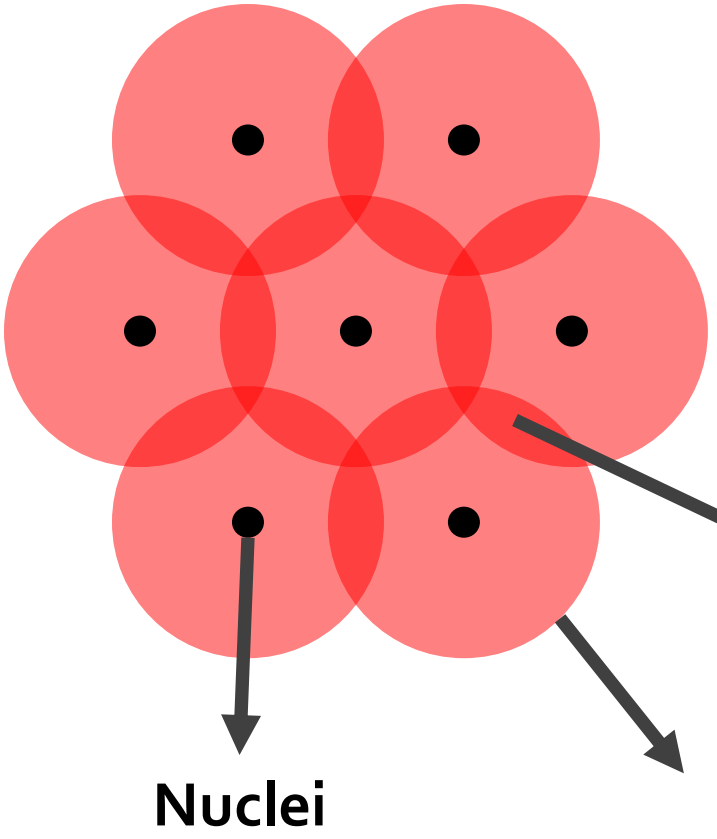
Spherical overlapped muffin-tin potentials:
Easier solution of the problem

Local Density Approximation:
LDA approximation to self-energy

Quasi-particle approximation:
Electron propagates in medium
Approximate electron-hole interaction

Core-hole treatment:
Screened core-hole

The overlapped muffin-tin potential



Better density:

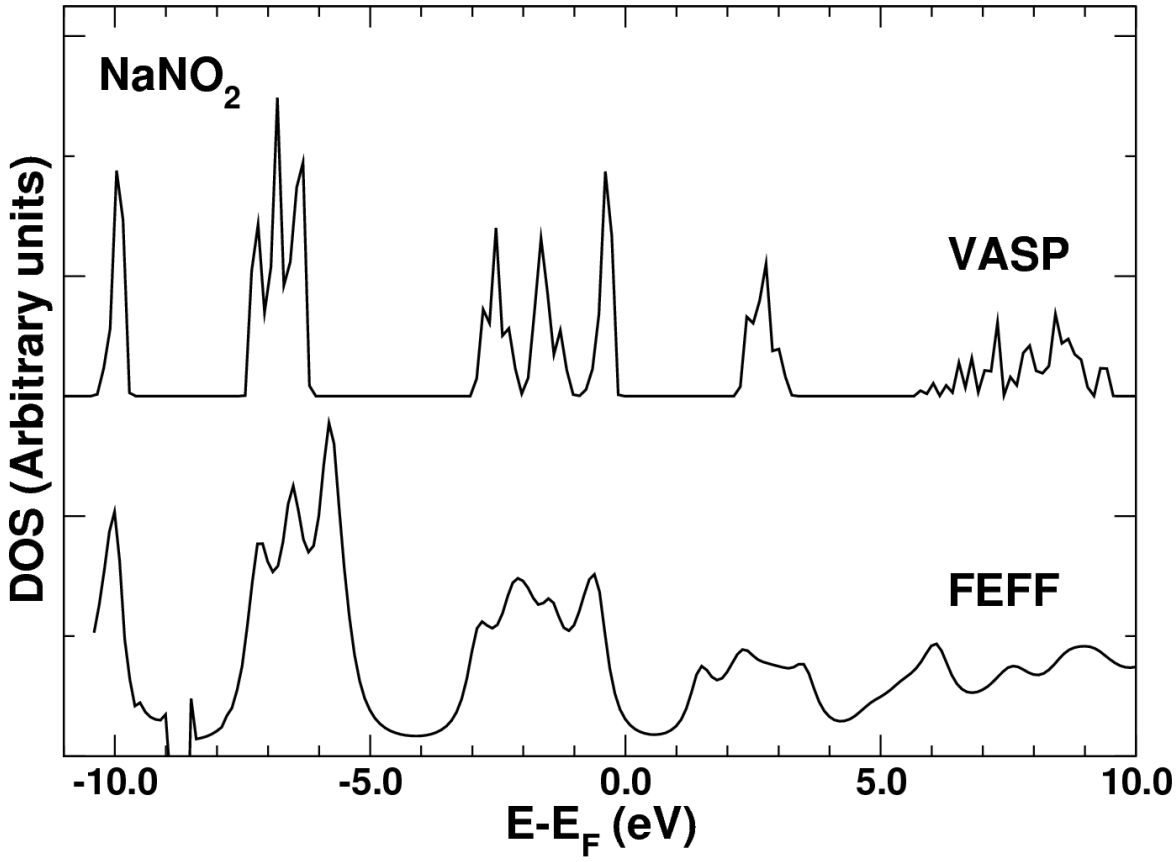
Resembles "**bonding**"

Charge **redistribution**

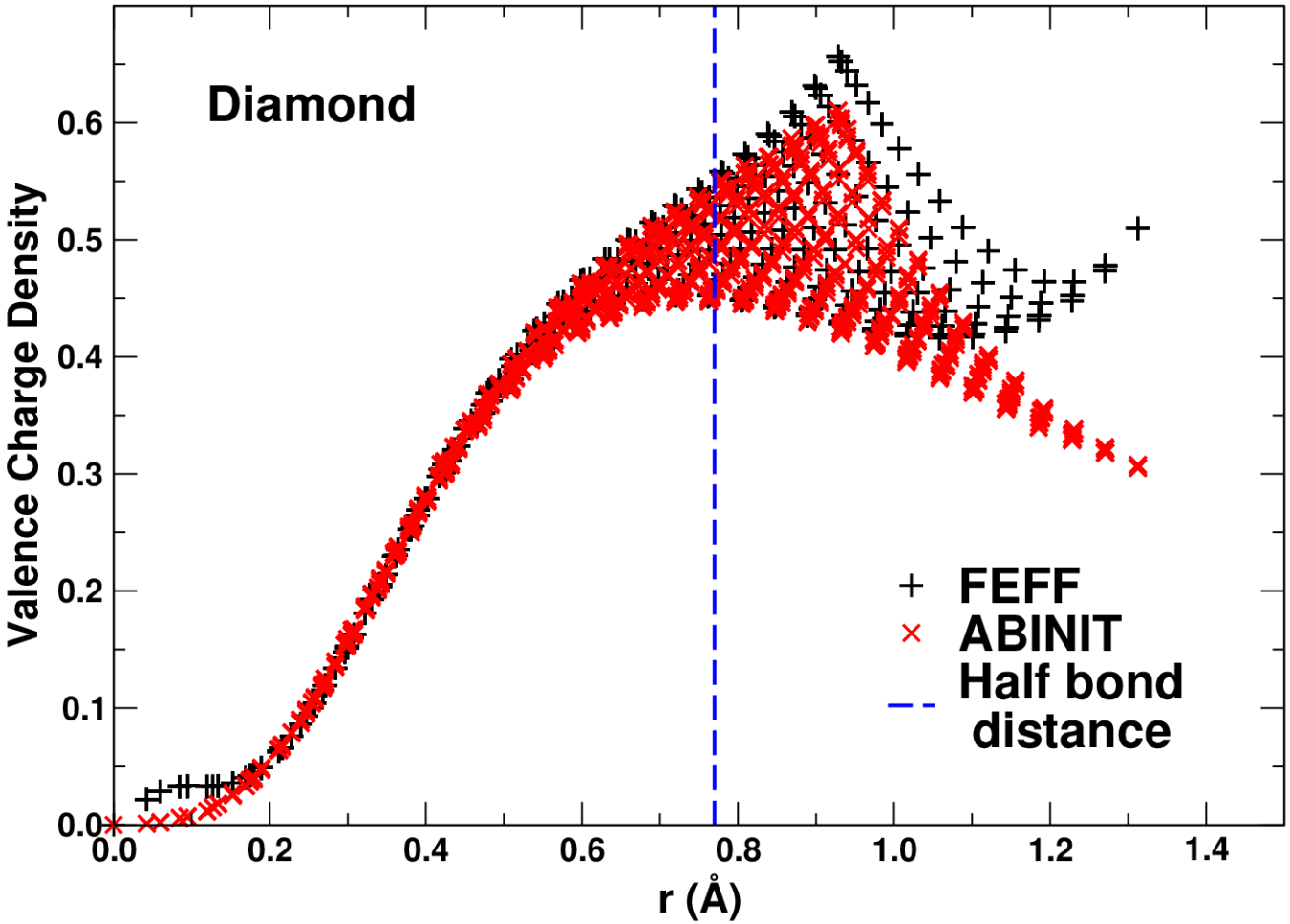
Overlap Region

Muffin-tin potential

FEFF Density of States

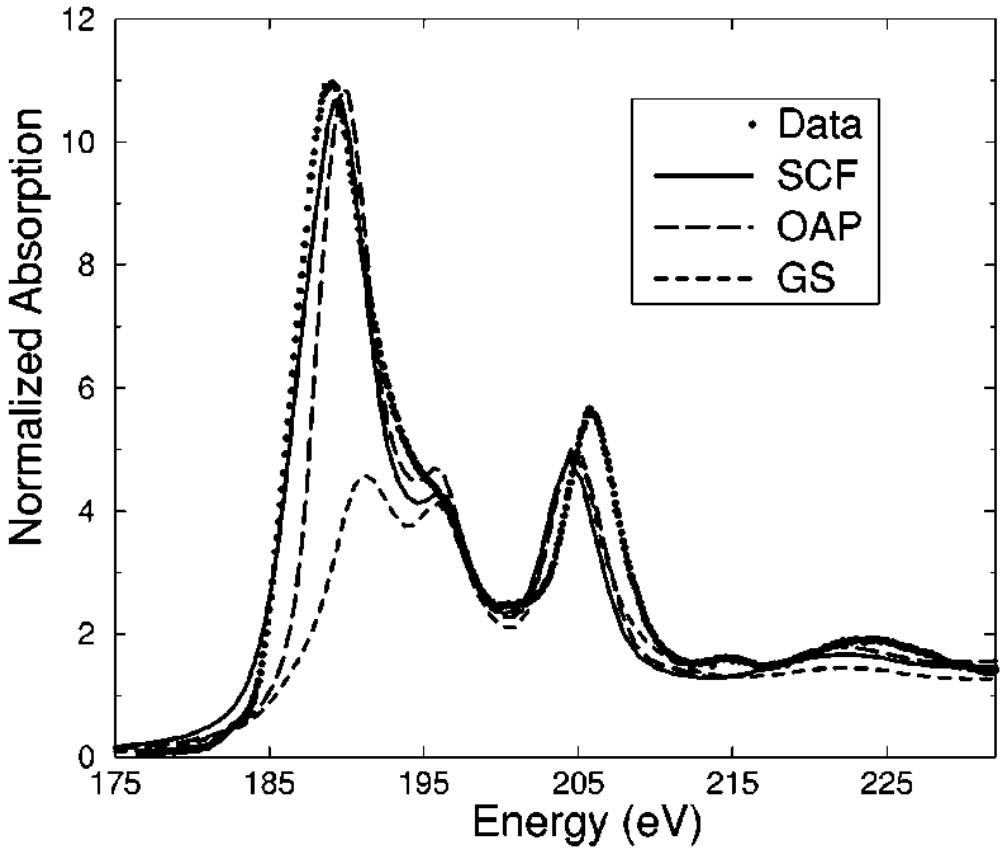


FEFF electron density



Beyond DFT: Quasi-particle Self-Energy Effects

Quasi-particle (QP) effects: $G = [E - H - \Sigma]^{-1}$



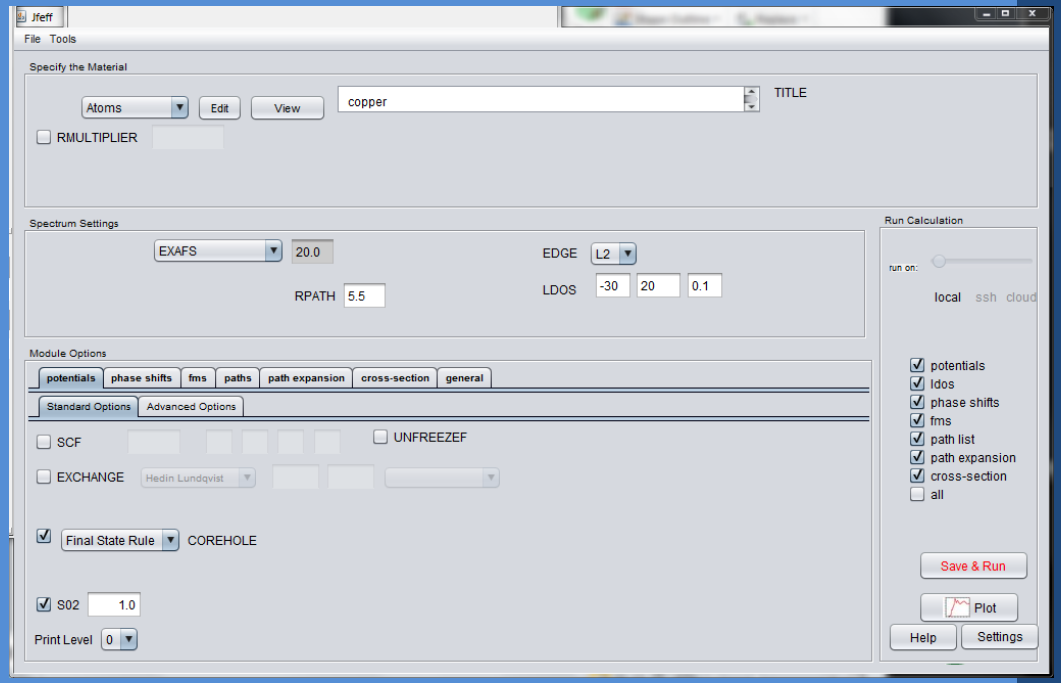
BN 89 atom cluster

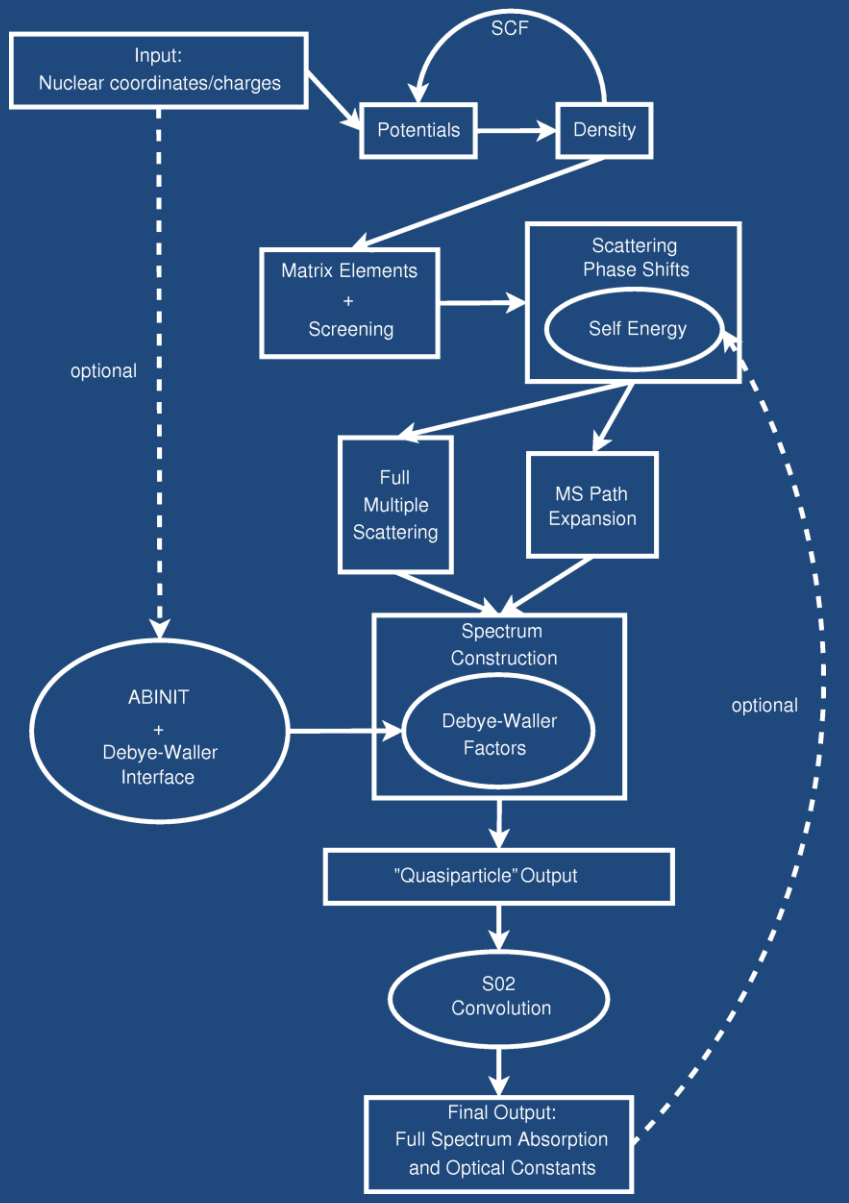
Ground state potential:

Usually insufficient

Need QP effects

FEFF: Flow Diagram





GUI "hides" most of this
Good to know anyway

Feff structure: Modules

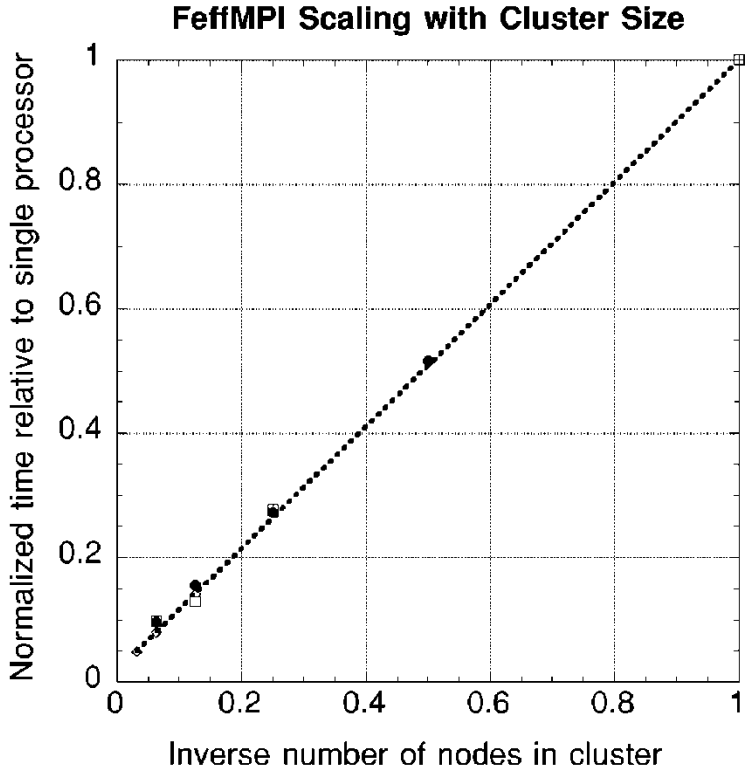
rdinp	Read Input
dmdw	Standalone vib. properties
atomic	Solve atomic overlap problem
pot	Self-consistent scattering pot. solver
ldos	Calculate local projected DOS
screen	Screen potential (if requested)
crpa	RPA core-hole (if requested)
opconsat	Full spectrum setup (if requested)
xsph	Calculate phase shifts, mat. elements and cross sections
fms	Do full multiple scattering
mkgtr	Trace Green's function
path	Do path expansion (EXAFS)
genfmt	Calculate scattering amplitudes
ff2x	Build the XANES/EXAFS spectrum
sfconv	Spectral function convol. (if requested)
compton	Compute Compton spectra (if requested)
eels	Compute EELS spectra (if requested)

Parallel (MPI) FEFF

PHYSICAL REVIEW B, VOLUME 65, 104107

Parallel calculation of electron multiple scattering using Lanczos algorithms

A. L. Ankudinov,[1] C. E. Bouldin,[2] J. J. Rehr,[1] J. Sims,[2] and H. Hung[2]
[1]*Department of Physics, University of Washington, Seattle, Washington 98195*
[2]*National Institute of Standards and Technology, Gaithersburg, Maryland 20899*



MPI: "Natural parallelization"
Each proc. does a few energies

Needed for state-of-the-art XANES simulations

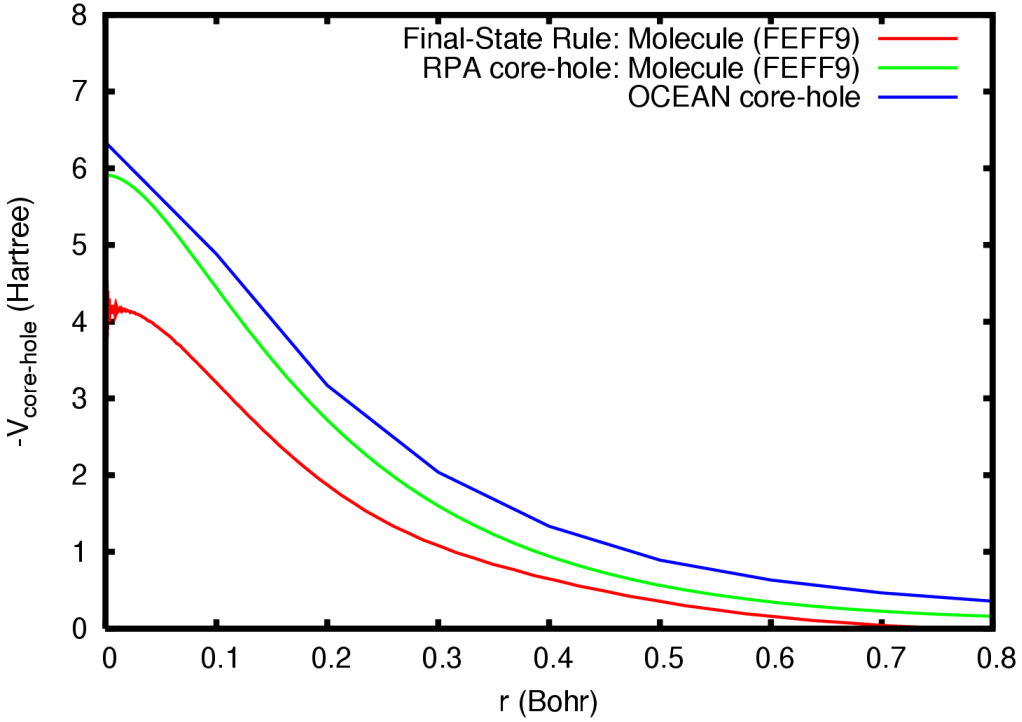
Recent Advances: RPA Core-hole

Core-hole issues: RPA Screened Core-hole

Linear response: $W = \epsilon^{-1} V_{core-hole}$

$$\epsilon^{-1} = (1 - K\chi_0)^{-1}$$

$$K = \frac{1}{v} + f_{xc}$$



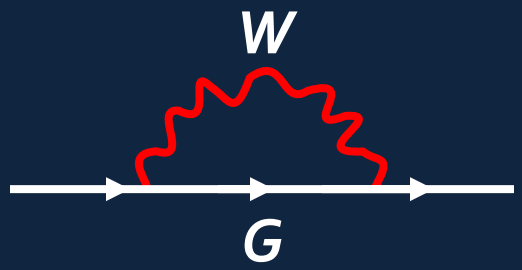
Comparison of the core-hole in H_2O

Recent Advances: Many-Pole Self-Energy

Self-energy issues: Many-pole model

Based* on GW approx.:

$$\Sigma = iGW$$



W: Screened Coulomb interaction

$$W = \varepsilon^{-1} V$$

Dielectric function:

Key ingredient

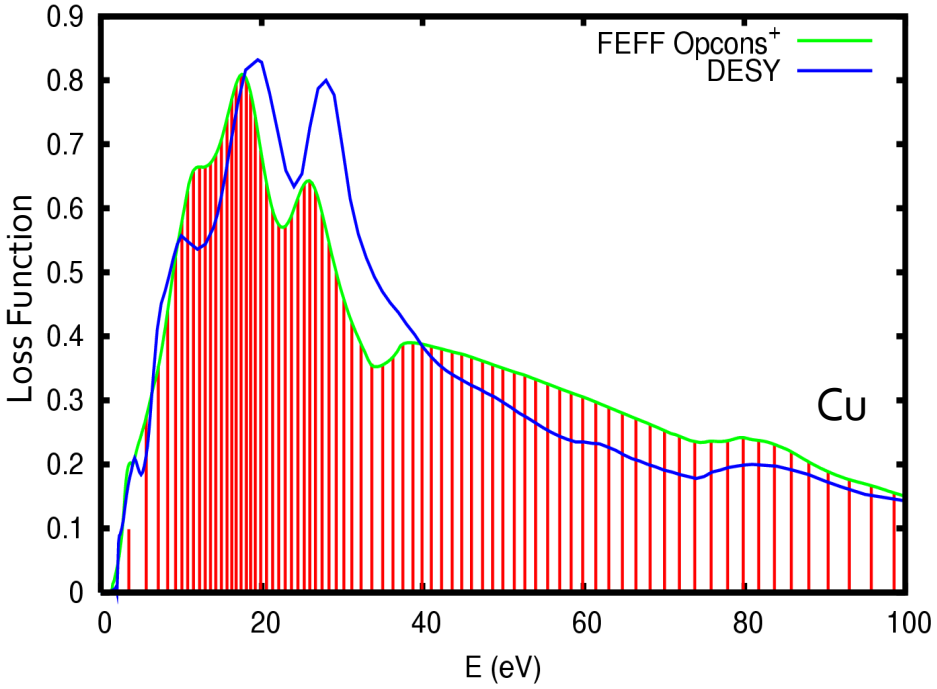
Usually external source

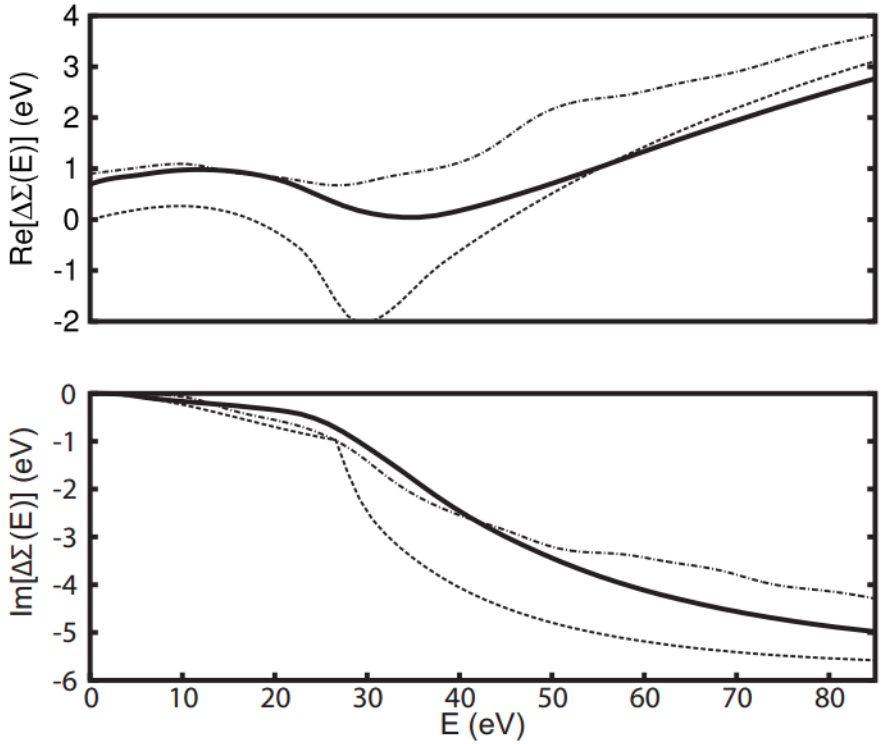
FEFF OPCONS:

Qualitative approximation

*B.I. Lundqvist Phys. Kondens Materie, 6, pp. 206, (1967)

Self-energy issues: Many-pole model

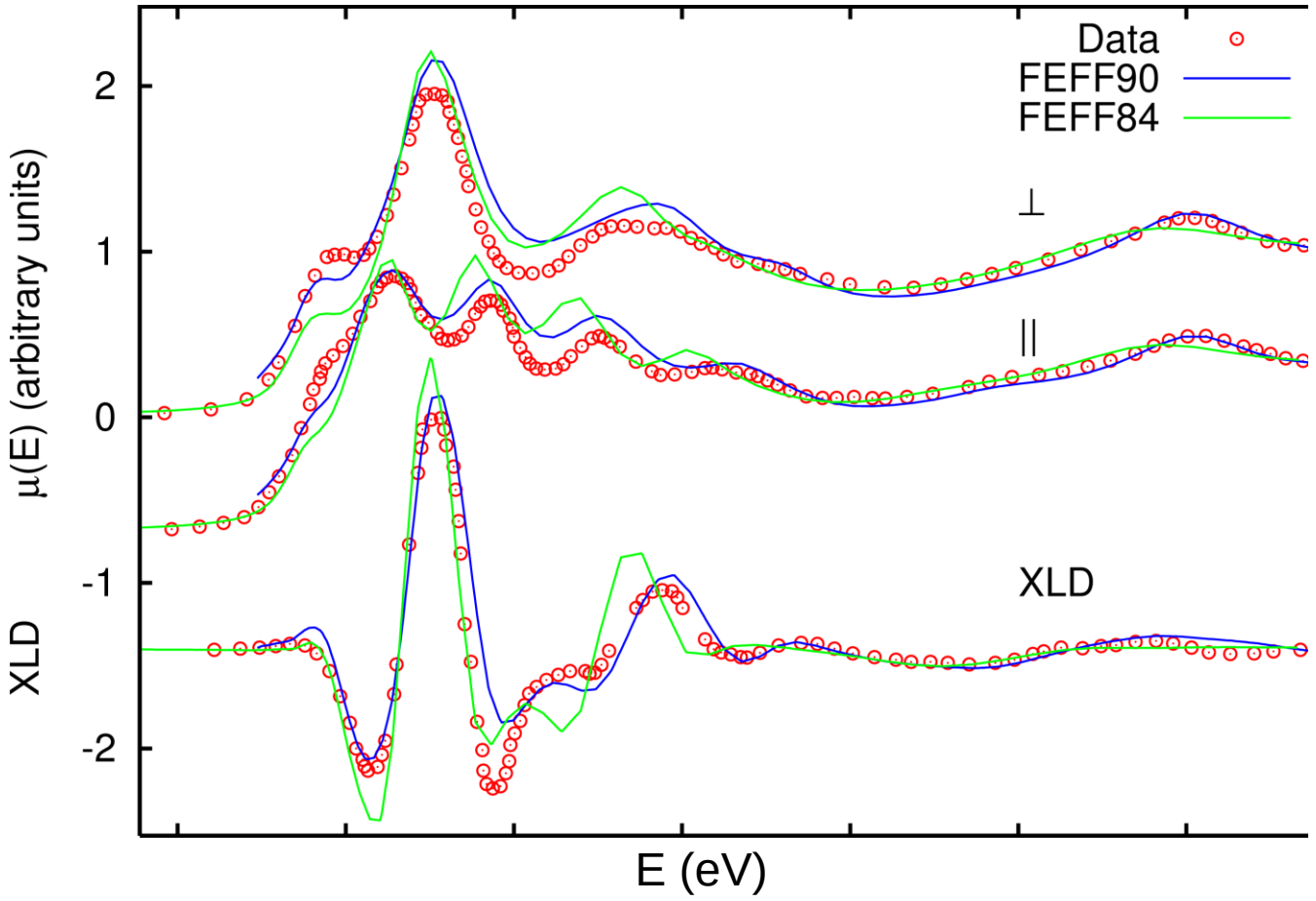




Many-pole (full) much better than Hedin-Lundqvist (dashed) vs better theory (dot-dashed)

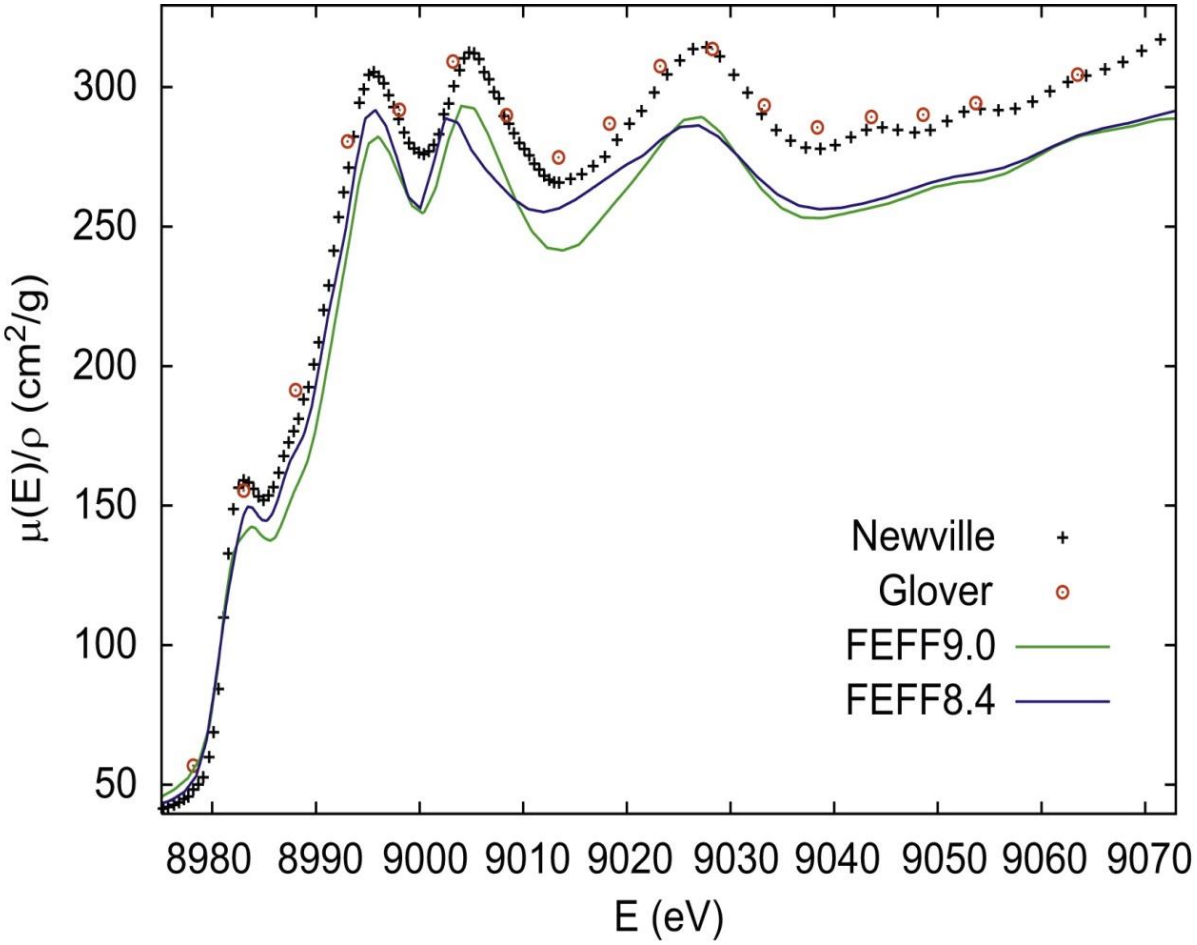
Kas et al., PRB 76, 195116 (2007)

ZnO: Zn K edge XANES



Expt: Ney et al., PRL 100, 157201 (2008)

Cu XANES: Comparison in absolute units



Kas et al., NIMA, doi:10.1016/j.nima.2010.01.024

Recent Advances: FEFF + DFT

Augmenting FEFF with DFT

Structures:

- Find possible structures
- Data for *ab initio* DW factors
- Find dynamical properties

Potentials:

- Check full potential effects
- Feed full potentials to FEFF (very, very beta)

Energies:

- Check accuracy of Fermi level
- Check accuracy of LDOS
- Find/check chemical shifts

Ab Initio 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

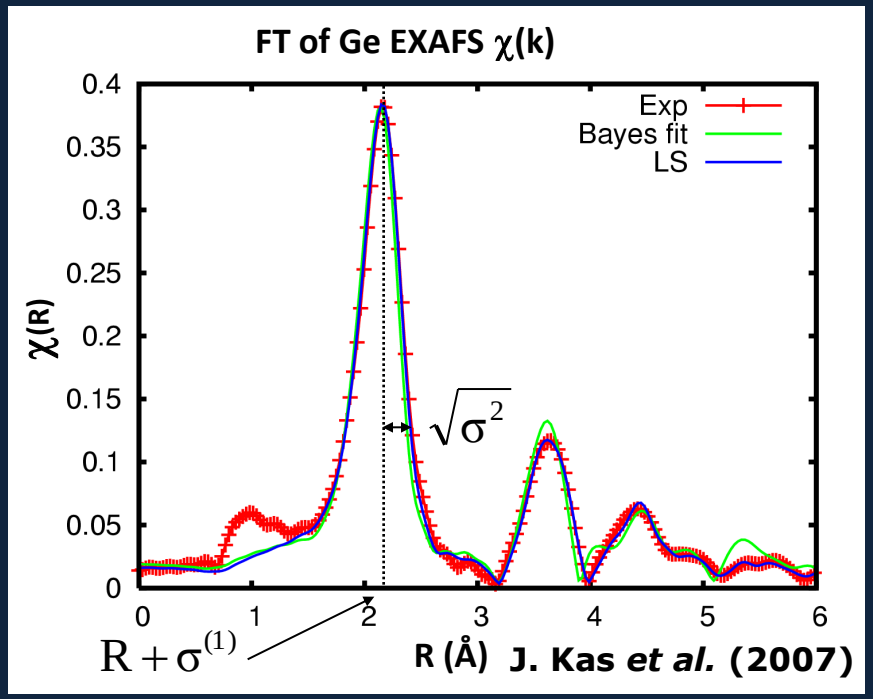
Quick intro to *Ab Initio* DW factors

Multiple Scattering Path XAFS DW Factor

Average commonly expressed in terms of the cumulant expansion

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

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



First cumulants

$$\begin{cases} \sigma^{(1)} = \langle r - R_0 \rangle \\ \sigma^{(2)} = \left\langle (r - \bar{r})^2 \right\rangle \equiv \sigma^2(T) \\ \sigma^{(3)} = \left\langle (r - \bar{r})^3 \right\rangle \end{cases}$$

Ab Initio DW factors: Lanczos algorithm

XAFS DW Factor for path R:

$$\sigma_R^2(T) = \frac{\hbar}{2\mu_R}\int_0^\infty \frac{1}{\omega}\coth\left(\frac{\beta\hbar\omega}{2}\right)\rho_R(\omega)\,d\omega$$

VDOS expressed as imaginary part of the phonon propagator

$$\rho_R(\omega) = -\frac{2\omega}{\pi}\mathrm{Im}\left\langle 0\right|\frac{1}{\omega^2 - \mathbf{D} + i\varepsilon}\left|0\right\rangle$$

Seed state: Displacement along path

Dynamical Matrix: Calculated using ab initio methods (abinit, Gaussian, VASP, etc)

Using Ab Initio DW factors in FEFF

```
DEBYE Temp Debye_Temp [DW_Opt [dymFile DMDW_Order DMDW_Type DMDW_Route]]

            DEBYE    500.0  1073.0  5 feff.dym  6  0  1
```

DMDW_Type - Type of DW calculation, the possible values are:
0 - Parallel σ^2 (default)

DMDW_Route - Which paths to use in the dmdw module. These paths do not affect the path selection in the XAS calculations, they are used for the generation of an input for the independent dmdw module. The possible values are:

- 0 - Skip dmdw module (default)
- 1 - All SS paths from absorber
- 2 - Same as 1 + all DS paths from absorber
- 3 - Same as 2 + all TS paths from absorber
- 11 - All SS paths
- 12 - Same as 1 + all DS paths
- 13 - Same as 2 + all TS paths

Computing a dym file

Ab initio codes:

- Gaussian
- VASP
- Siesta
- NWChem
- Abinit
- Quantum Espresso
- Orca (almost)

Talk to me if you are interested

Typical DMDW output

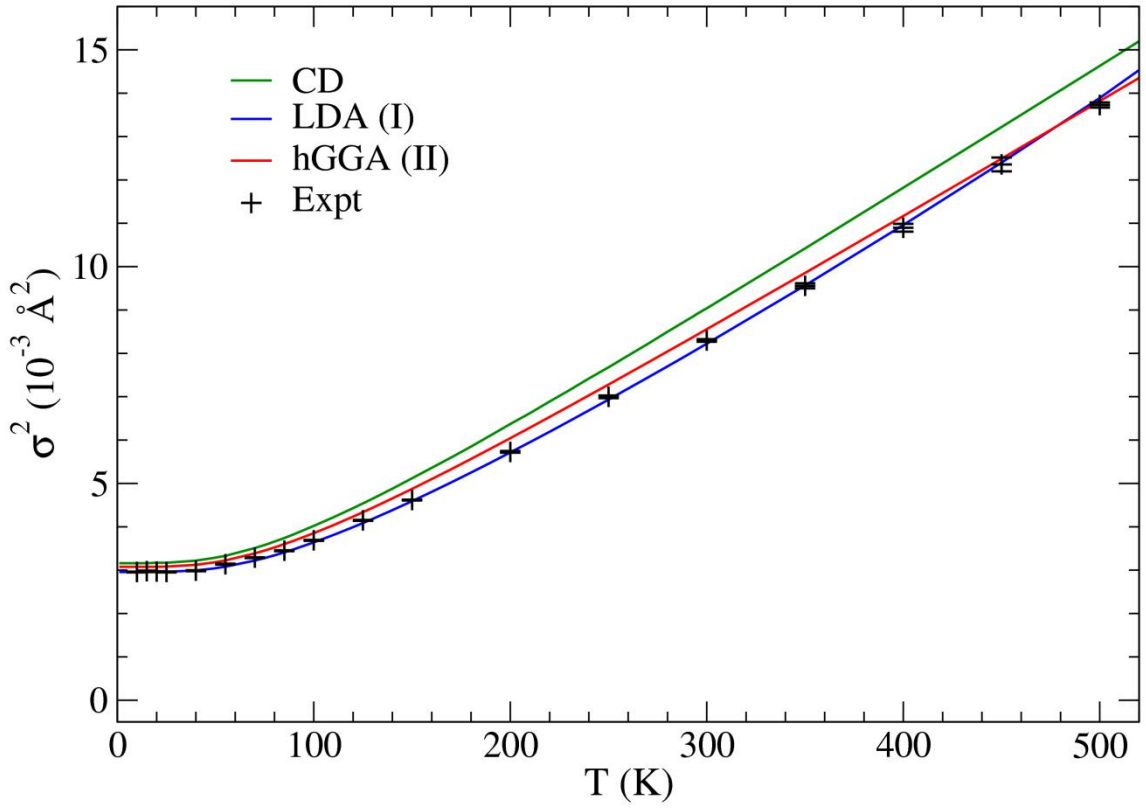
```
Path Indices:     1    2
 pDOS Poles:
     Freq. (THz)     Weight
        7.609        0.00055
       14.776        0.00077
       24.890        0.00587
       31.463        0.00623
       33.972        0.70221
       34.762        0.28436

 pDOS Einstein freq (single pole) and associated temp:
 Freq (THz)    Temp (K)
  34.118       1637.35

 pDOS n Moments and associated Einstein freqs and temps:
  n      Mom (THz^n)    Freq (THz)      Temp (K)
 -2        0.00087       33.85132       1624.55
 -1        0.02941       34.00240       1631.80
  0        1.00000      ---------      --------
  1       34.09808       34.09808       1636.40
  2     1164.03434       34.11795       1637.35

 Path Length (Ang), s^2 (1e-3 Ang^2):  1.583    1.234
```

EXAFS near-neighbor DW Factor of Cu



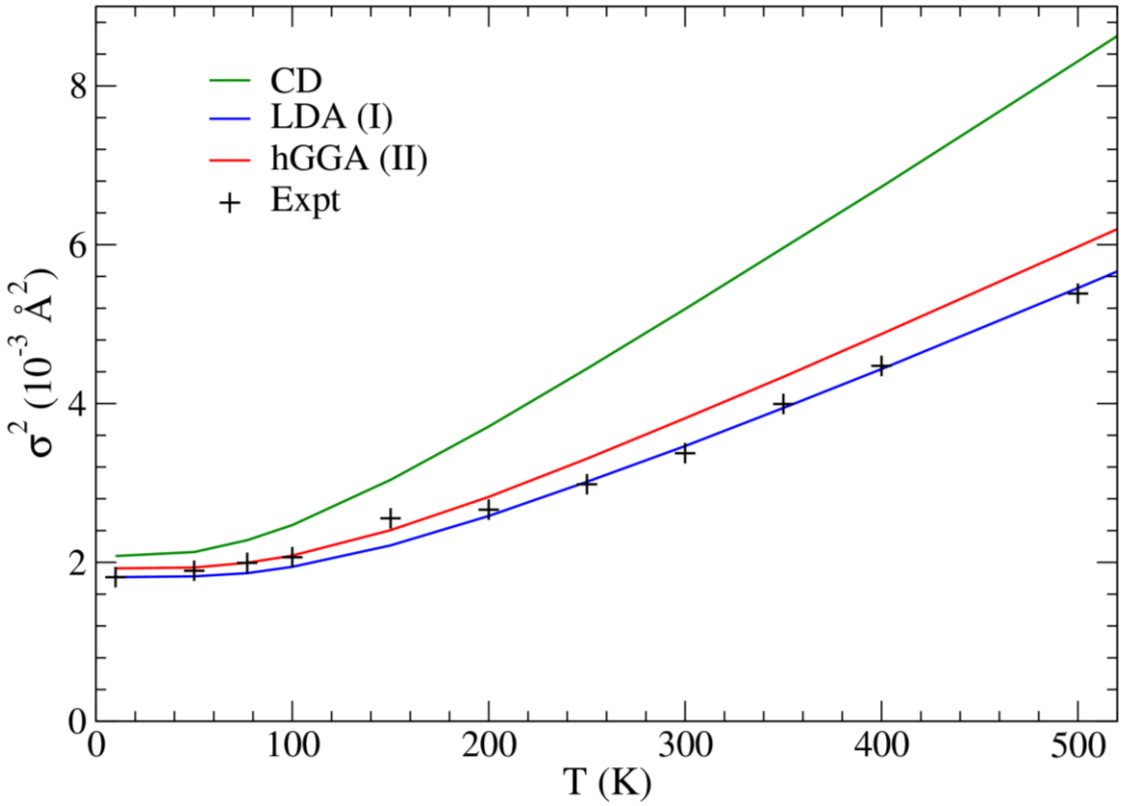
CD (Correlated Debye):
Standard FEFF

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):
Standard FEFF

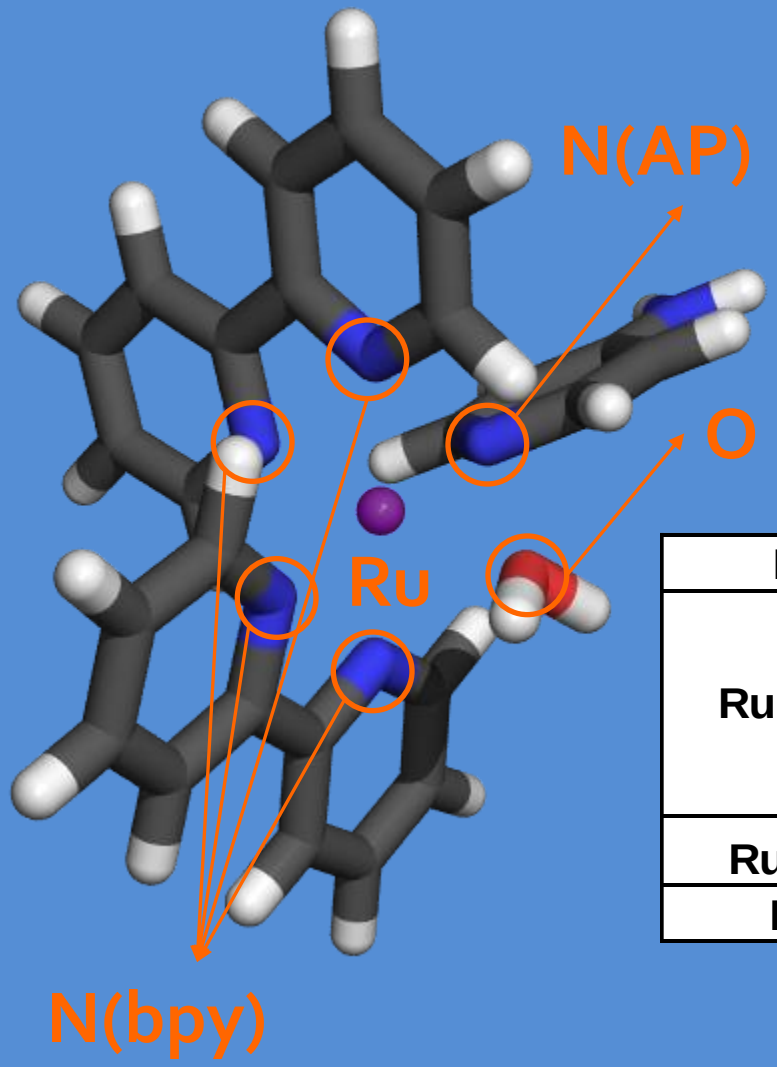
LDA, hGGA:
Ab initio DW

Directional bonding:
Needs AIDW

Expt: Dalba et al. (1999)

Ab Initio DW Factors in Metal-Ligand Complexes

$Ru(bpy)^2(AP)(H2O)^{++}$



Good agreement for tight ligands (bpy)

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

	R_{M-L} (in Å)		σ^2 (in 10^{-3} Å^2)	
Path	Theory	Exp	Theory	Exp.
Ru-N(bpy)	2.08 2.04 2.10 2.09	2.05±0.01	2.49 2.32 2.60 2.50	2.6±0.9
Ru-N(AP)	2.14	2.10±0.03	2.61	4±3
Ru-O	2.22	2.06±0.05	4.93	9±7

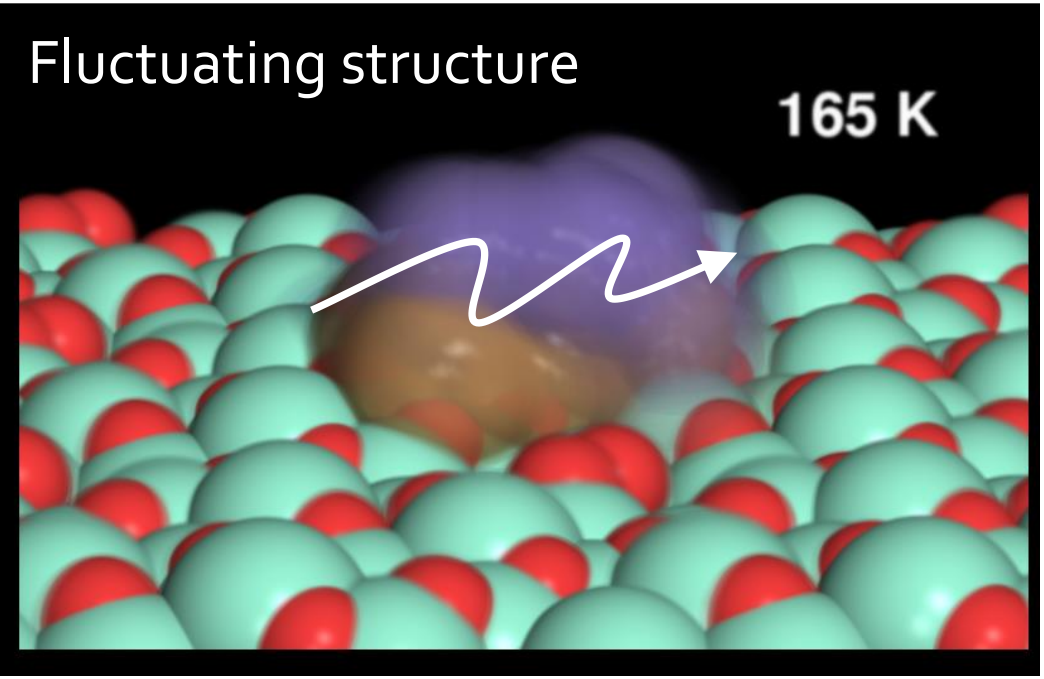
Expt: Salassa et al., J. of Physics: Conference Series 190, 012141 (2009)

Disorder in XANES

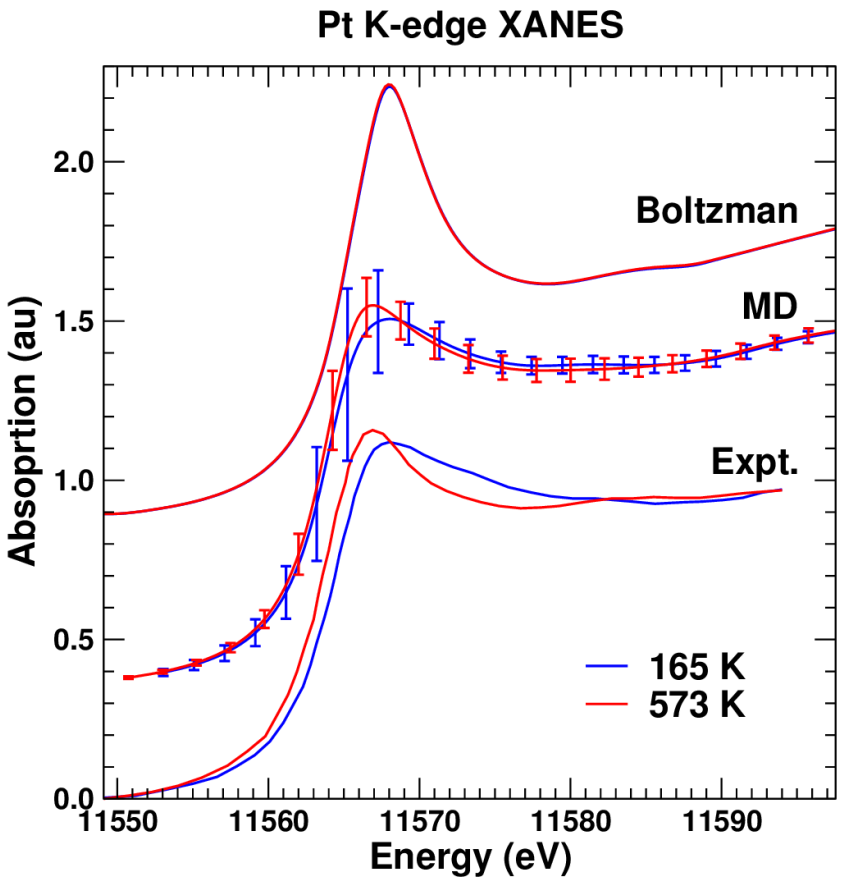
Disorder:

- Can be crucial in XANES
- Need external input for FEFF simulations
  - MD trajectories
  - MC sampling

Disorder effects



Pt_{10} on γ-Al_2O_3



Need dynamics to reproduce experiment

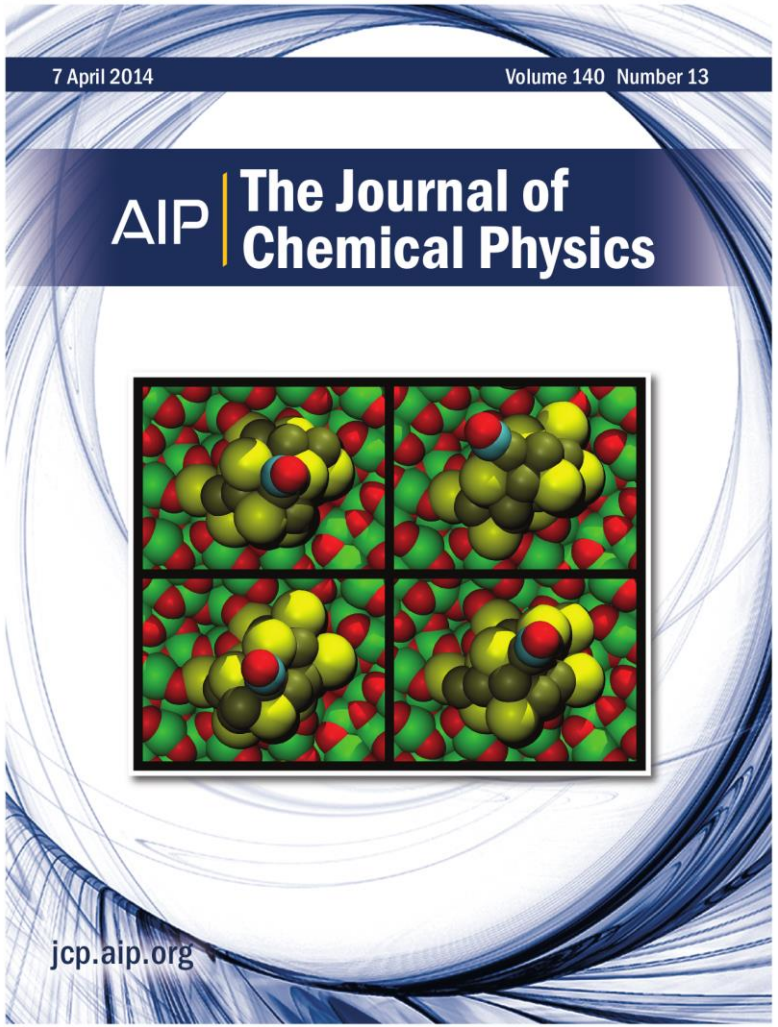
Vila et al. Physical Review B 78, 121404(R), 2008

Dynamic Structural Disorder (DSD) in Nanoparticles

DSD drives:

- Fluctuating bonding
- Cluster mobility
- Charge separation
- Layering and segregation
- Adsorbate dynamics (right)
- Adsorbate reactivity

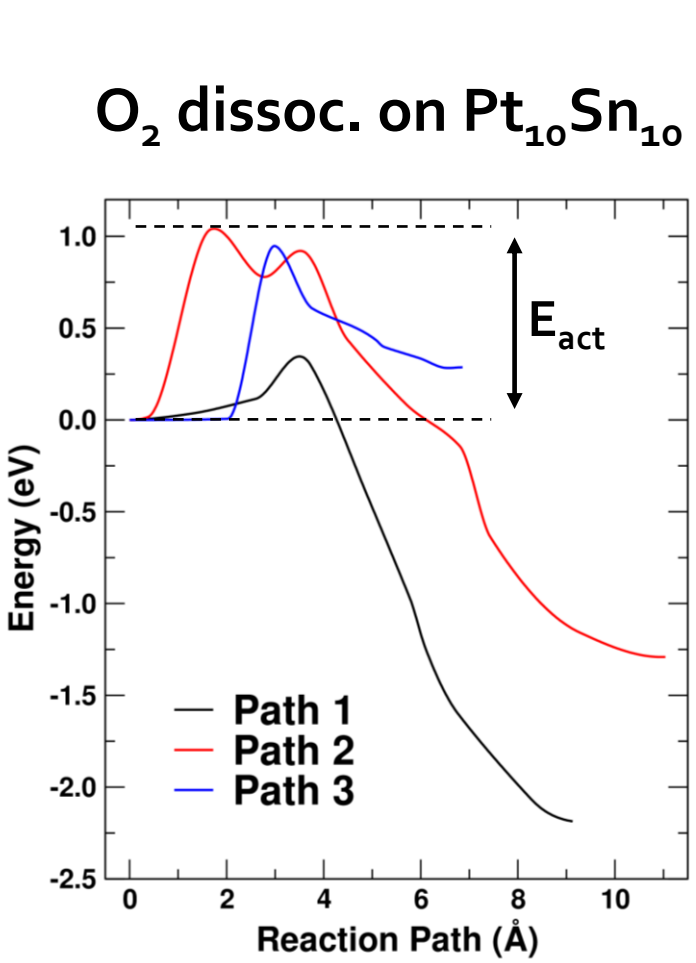
Inhomogeneity

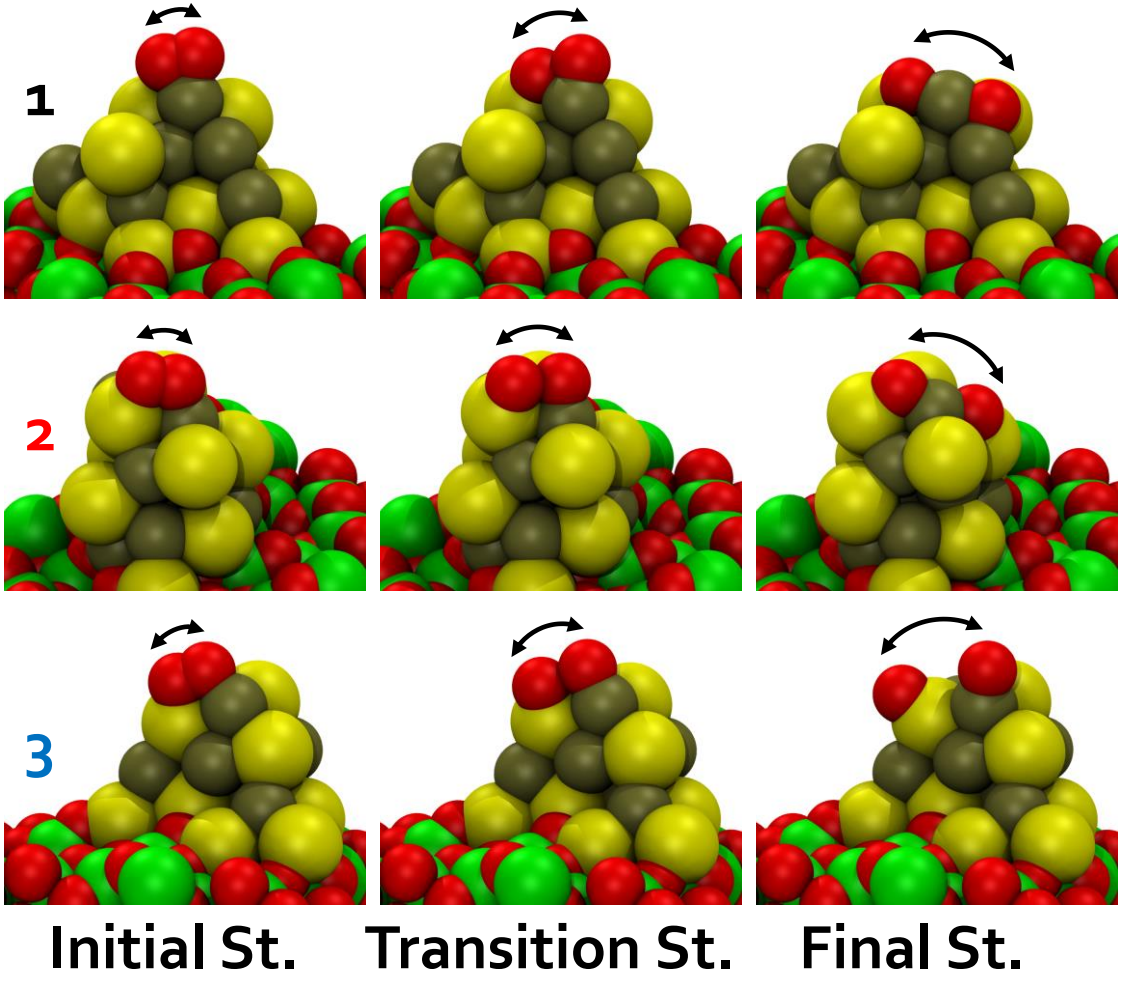


CO dynamics on $Pt_{10}Sn_{10}$

Rehr and Vila J. Chem. Phys. 140, 134701 (2014)

Disorder affects reactivity

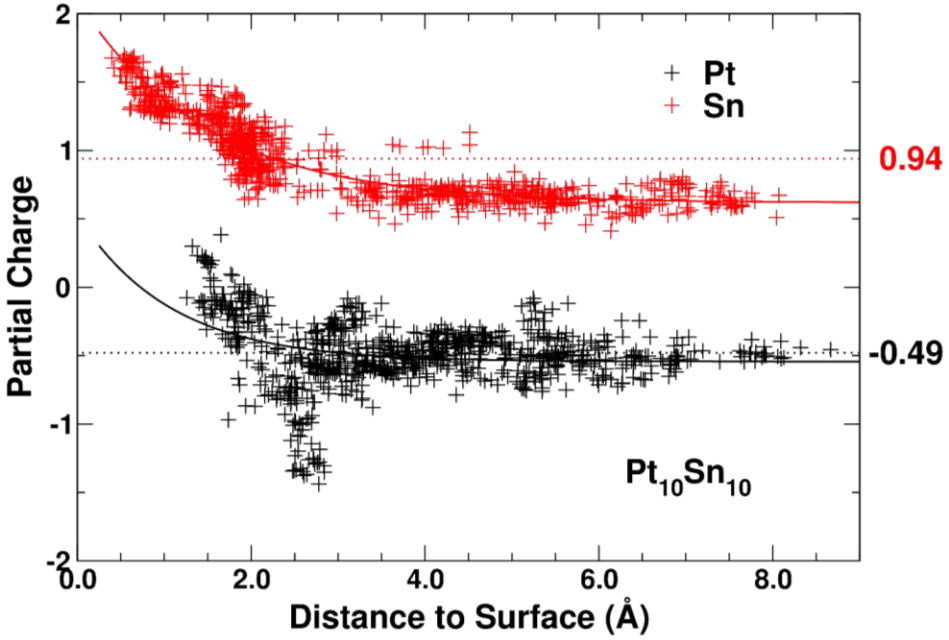


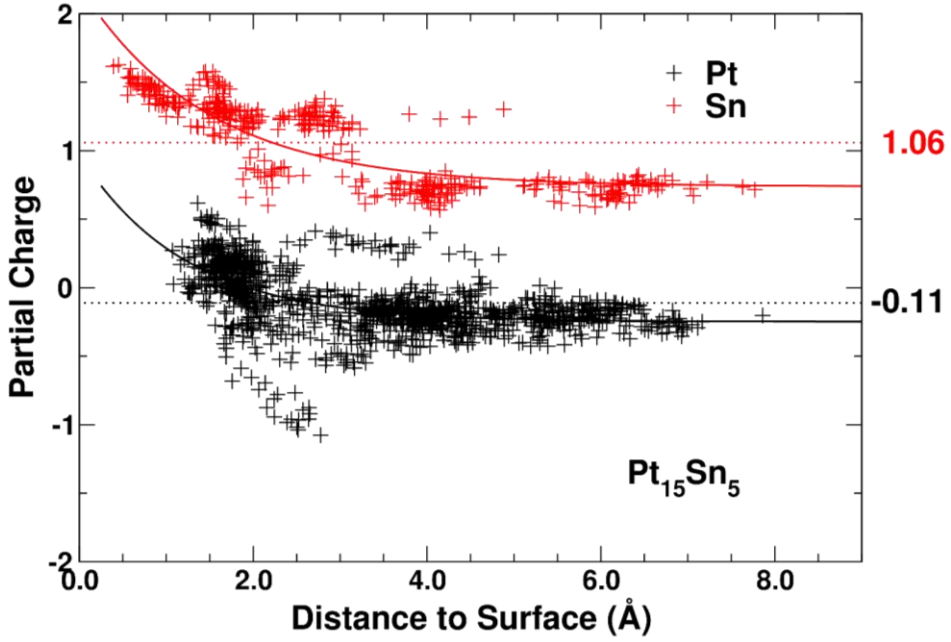


Large differences in activation energy (E_{act})

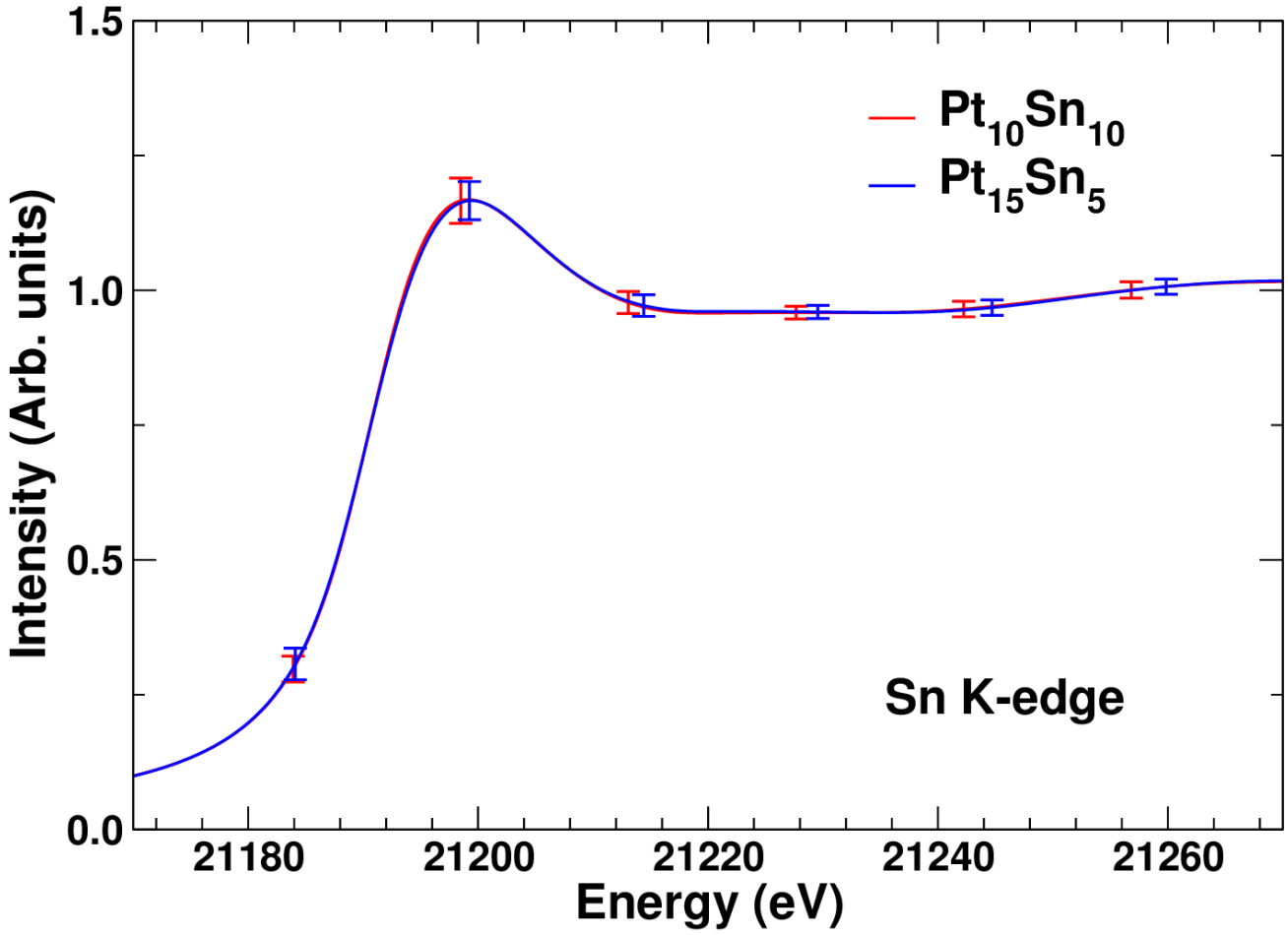
Reaction path depends on DSD

Pt charge modulation in PtSn nanoparticles

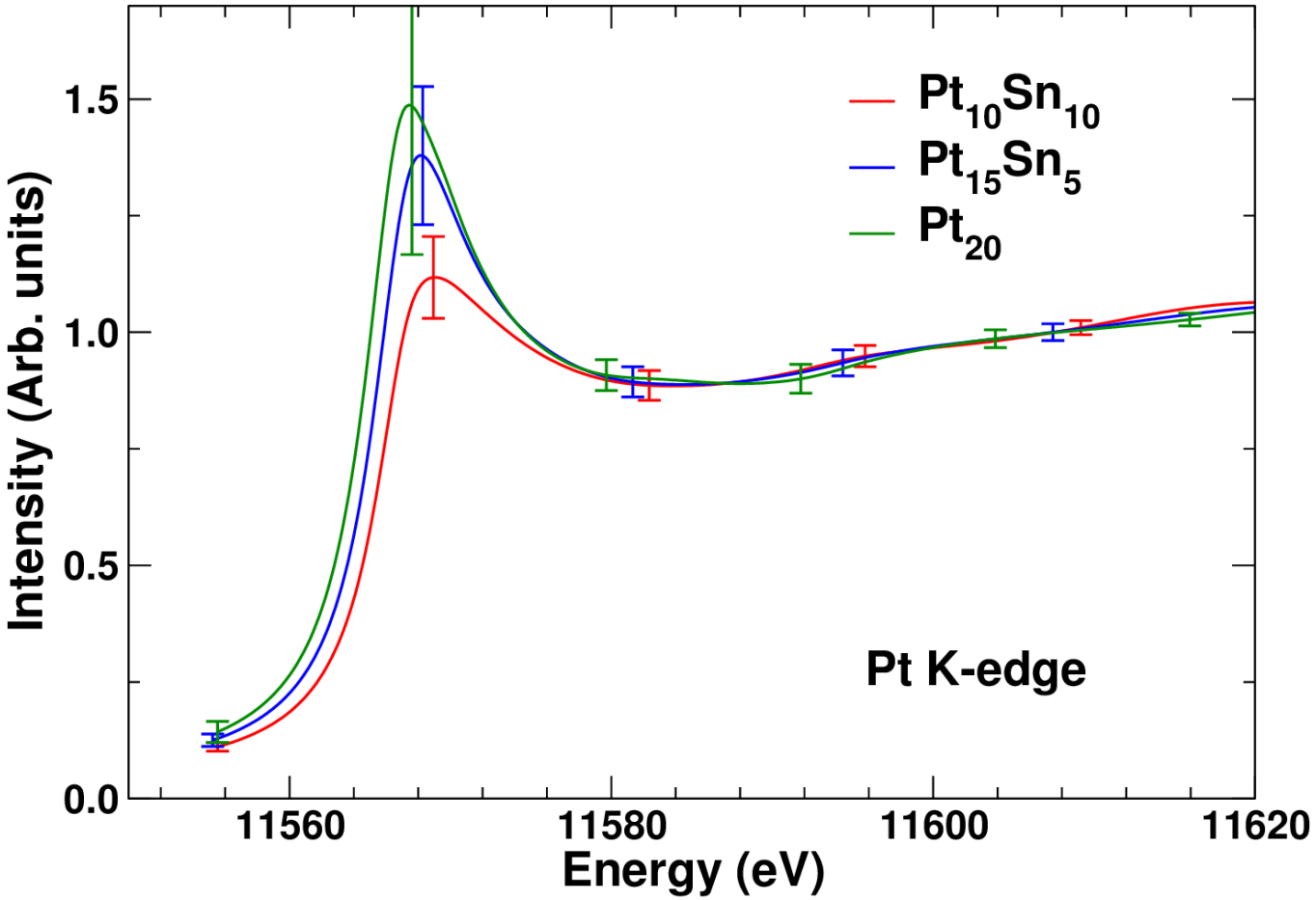




Edge position and charge transfer



Edge position: Fermi level shift on charge transfer

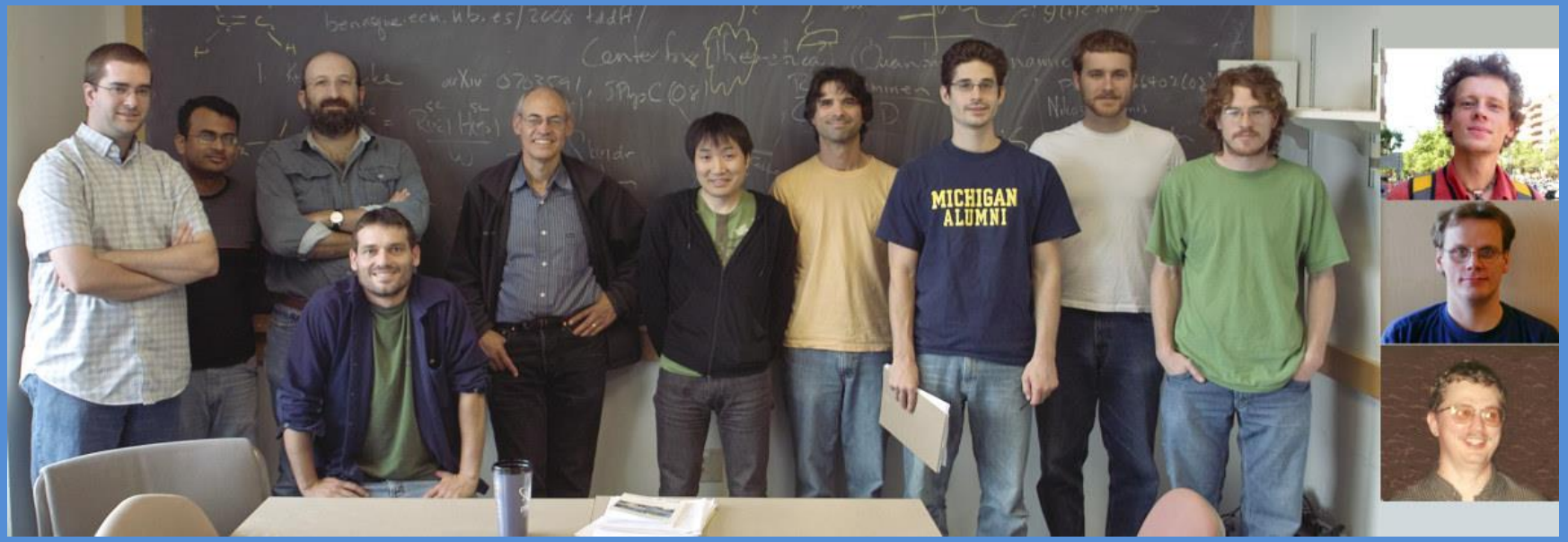


Summary

A broad introduction to FEFF
- Basic understanding of the MS method
- The code structure of FEFF

Introduction to the more advanced methods in FEFF
- Electronic structure:
  - Many-pole self-energy
  - RPA core-hole
- Augmenting FEFF with DFT
  - Structure and disorder are key to good results

The FEFF group: Seattle and beyond



From left to right:

Ken Nagle
Towfiq Ahmed
Fernando Vila
Micah Prange
John Rehr

Yoshi Takimoto
Hadley Lawler
Adam Sorini
John Vinson
Josh Kas

Kevin Jorissen
Aleksi Soininen
Alex Ankudinov
(Shauna Story)
(Egor Clevac)

Expectations for Demo tomorrow

Brief introduction to (might skip depending on audience):

- Installing and running the code
- FEFF input and output
- Simple examples of FEFF calculations

User problems and discussion:

- PLEASE, bring your own problem
- Will briefly show very advanced calculations

Possible roundtable with feature requests