Calculation of X-Ray Spectra with FEFF9

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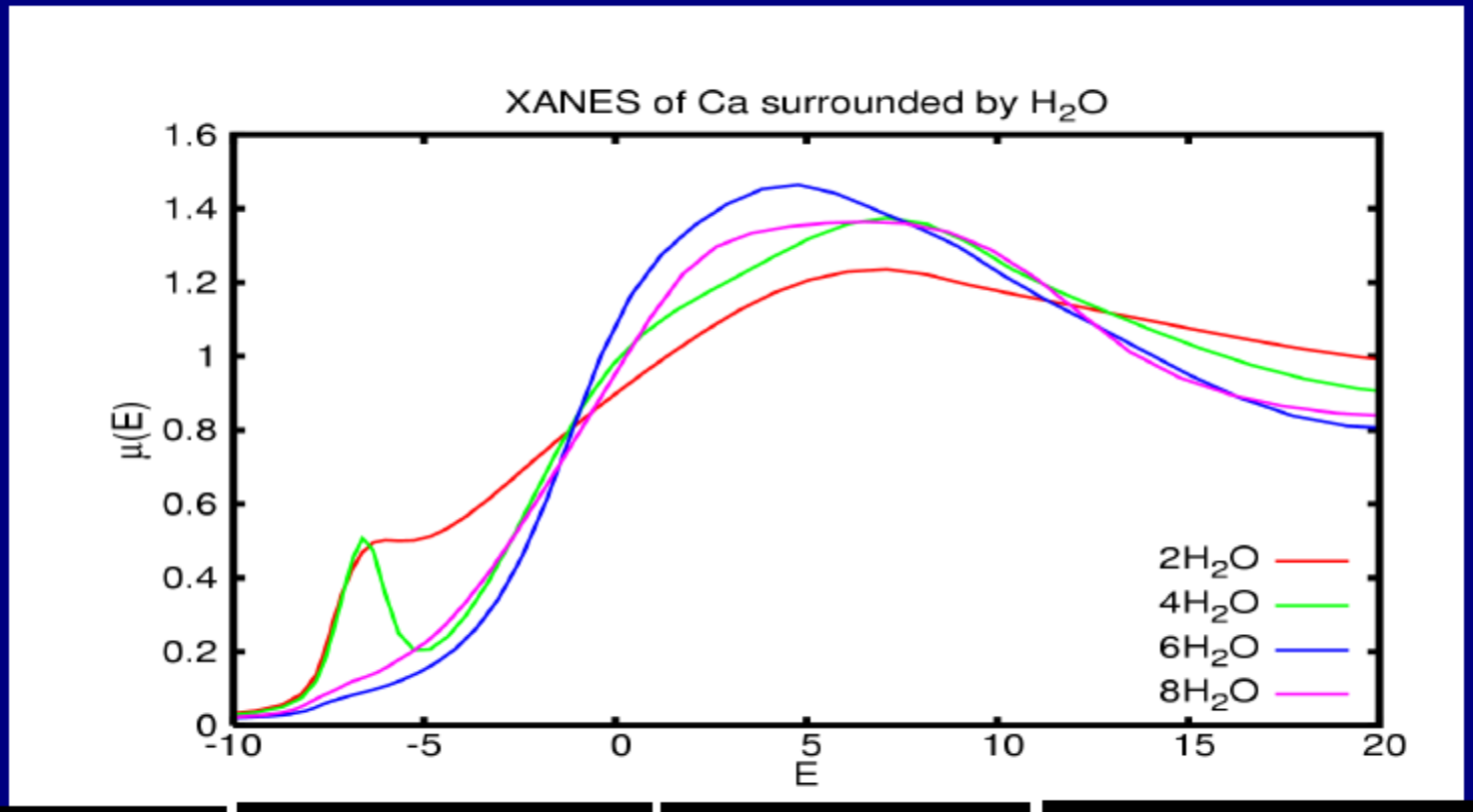
Outline

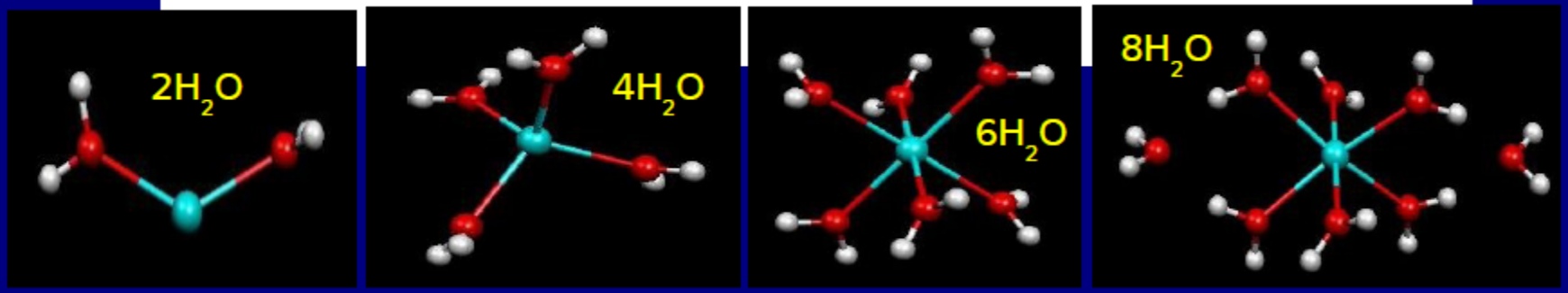
- XANES – What is it good for?
- How to simulate XANES with FEFF
- What does FEFF actually do?
- Calculating XANES with FEFF and JFEFF
- Modeling with auxiliary theory
  - Structure (DFT)
  - Dynamics (MD)

XANES is sensitive to …

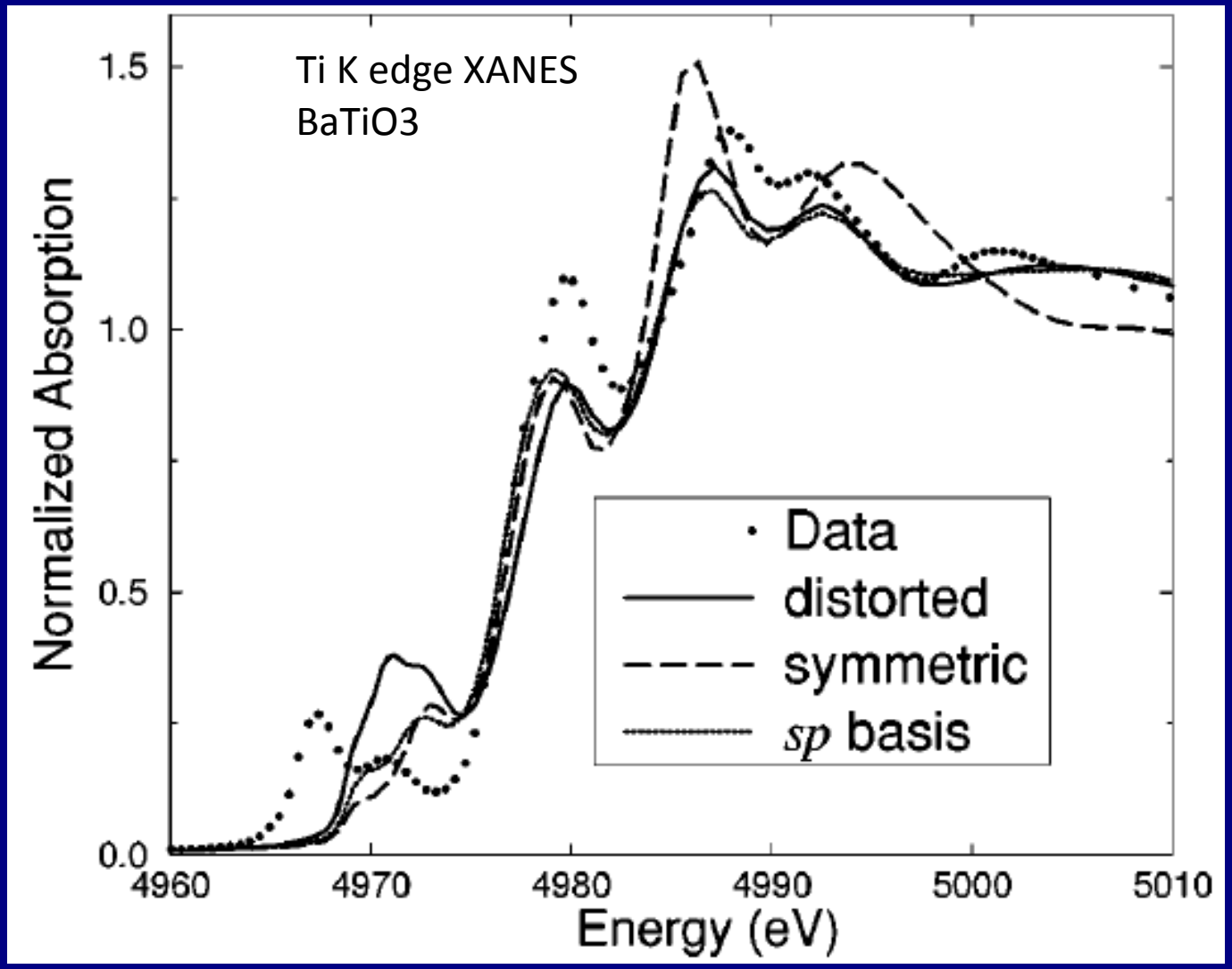
- Unoccupied local DOS
- Symmetry
- Charge transfer (oxidation state)
- Occupation (L-edges)

Symmetry and Pre/Near-Edge Features

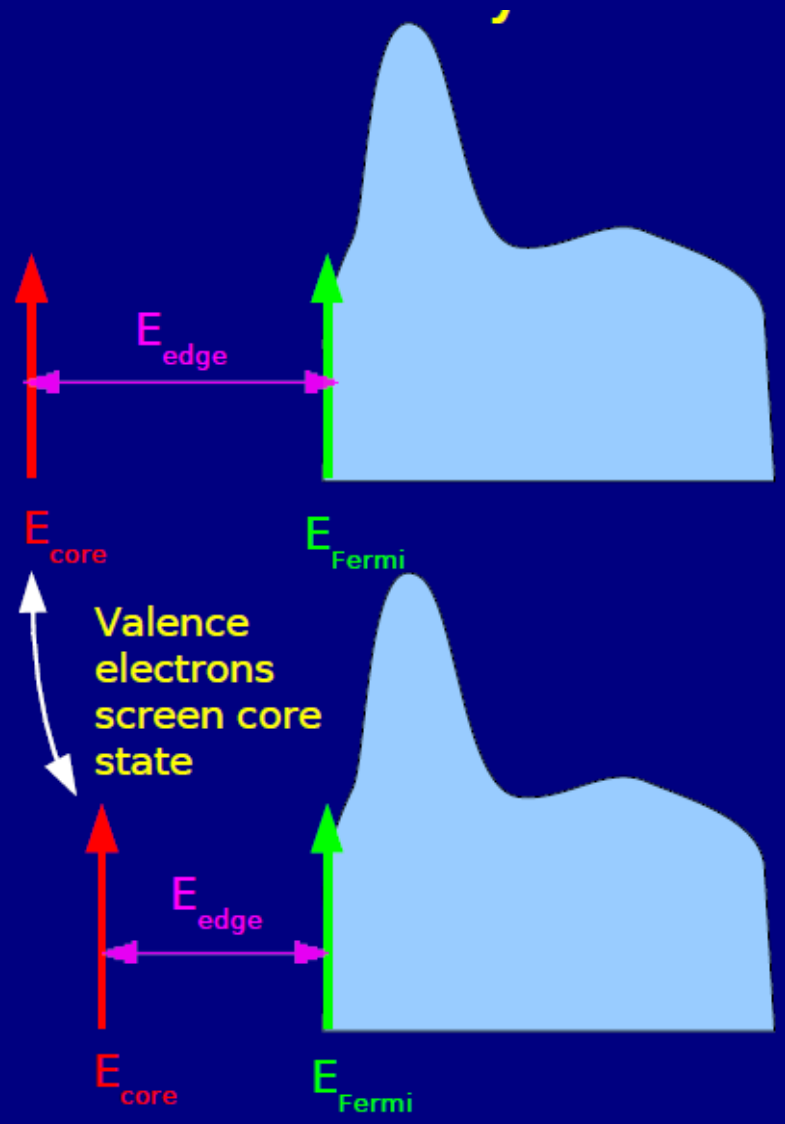


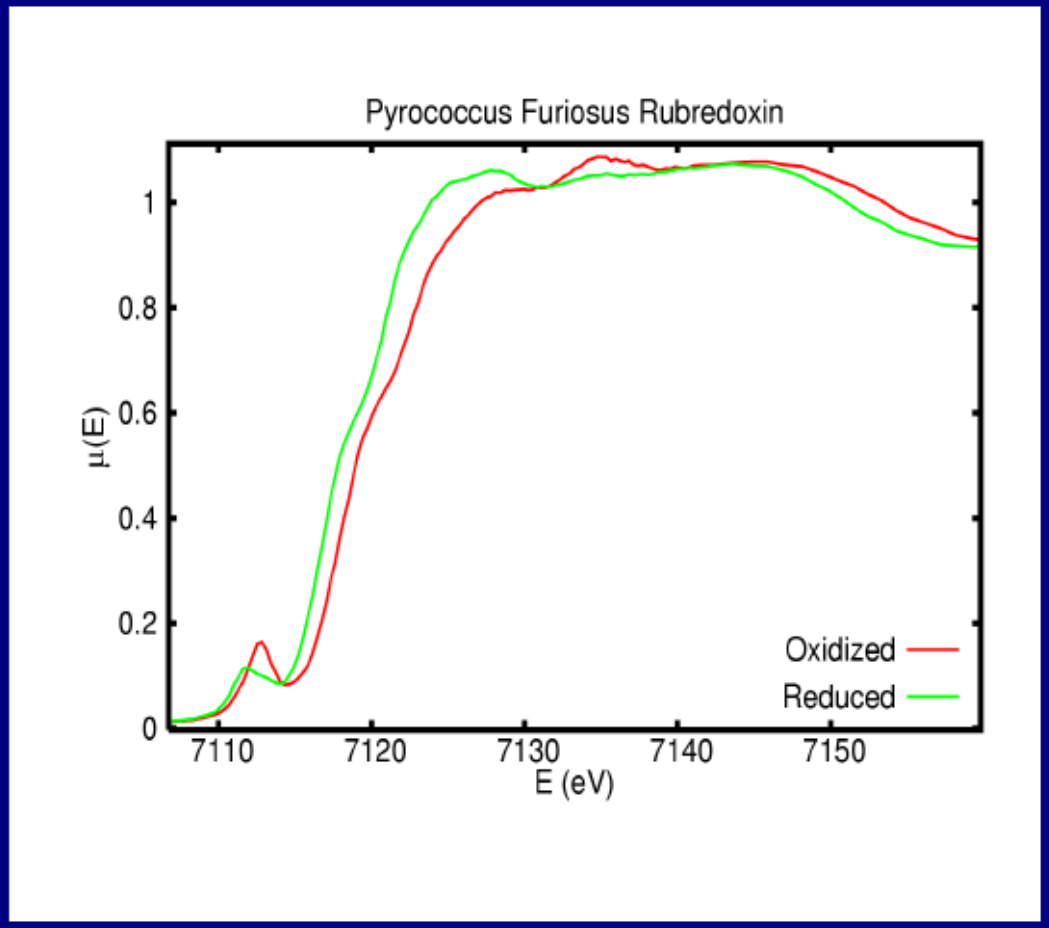


Symmetry and Pre/Near-Edge Features



Edge Position and Charge Transfer





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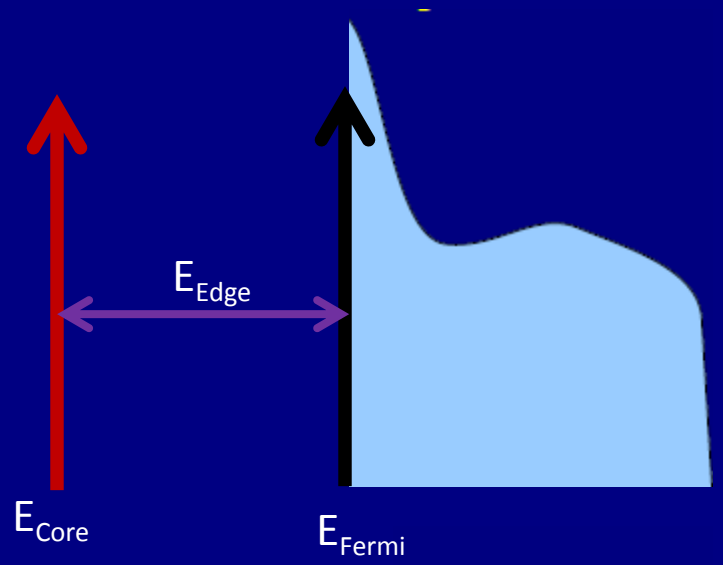
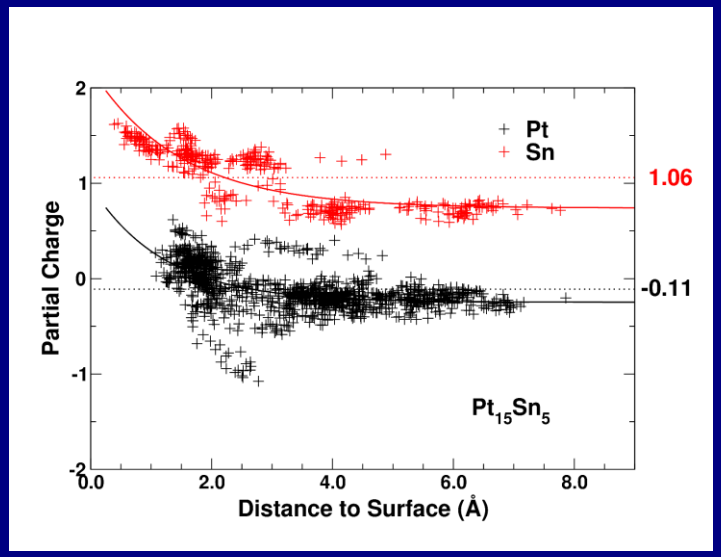
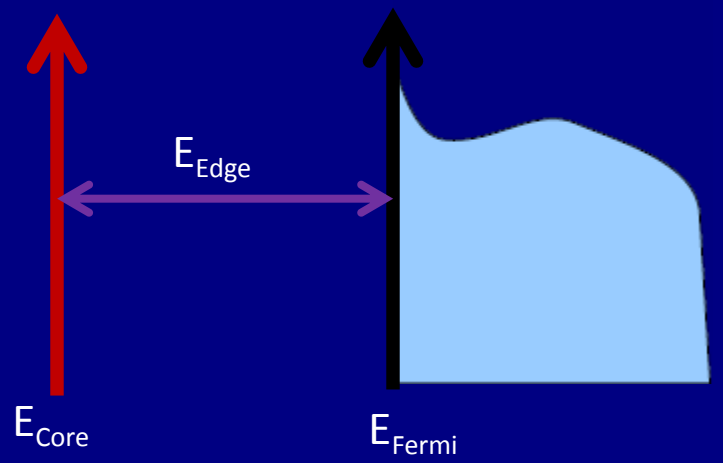
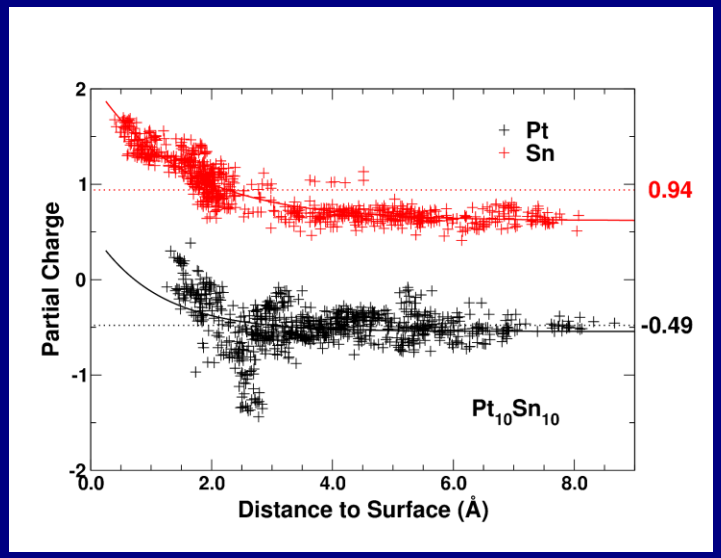
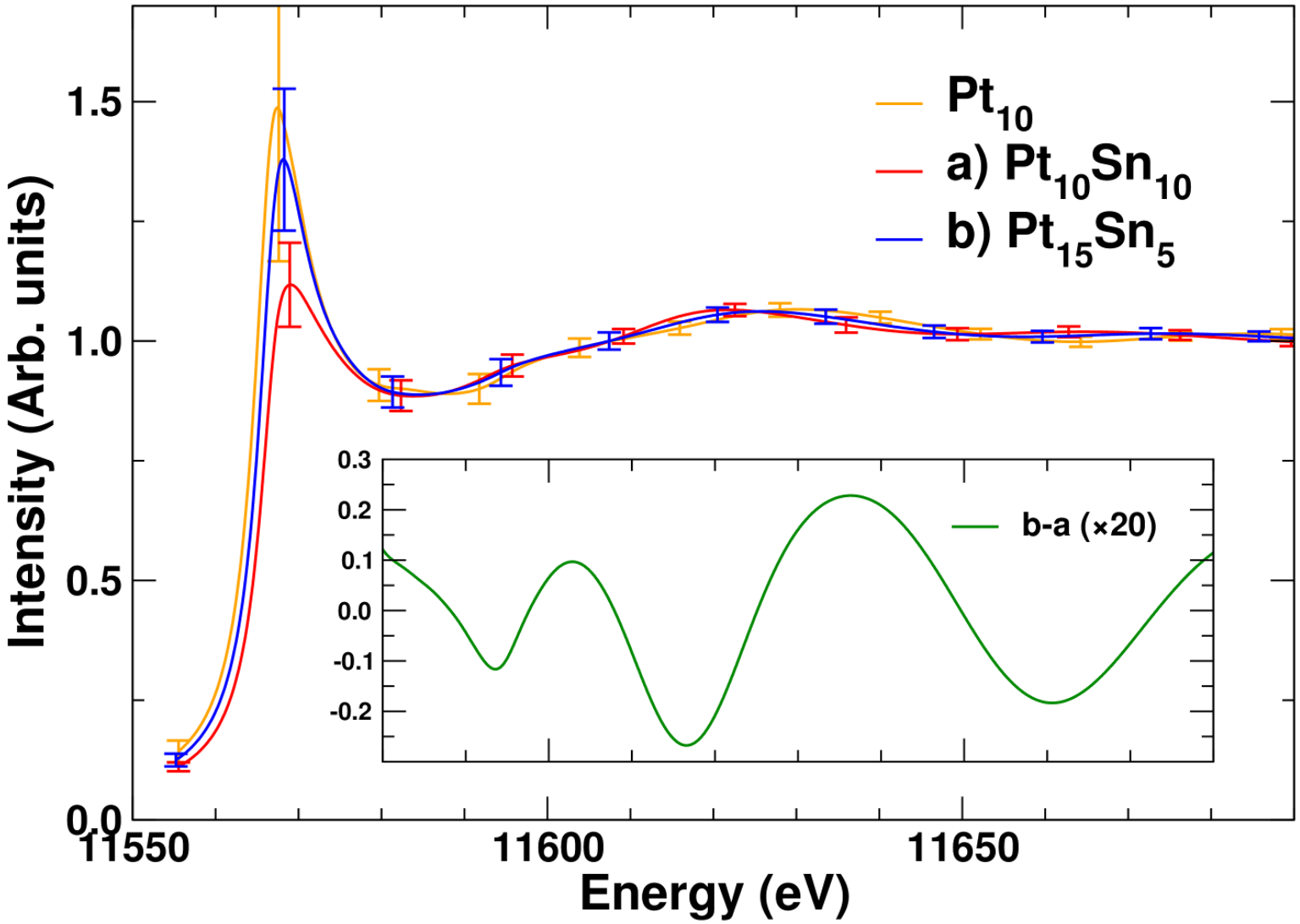








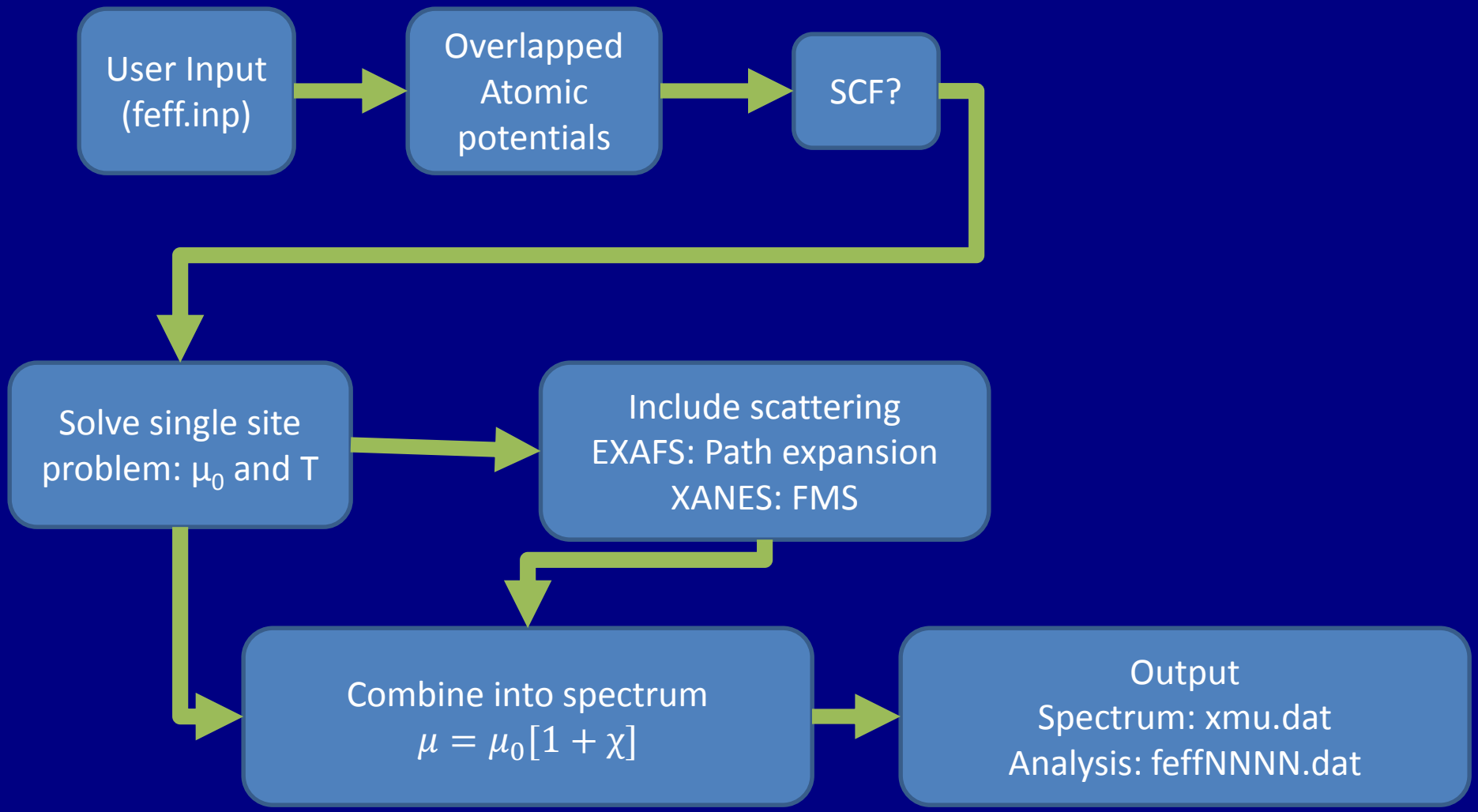
F. D. Vila


Pt10
a) Pt10Sn10
b) Pt15Sn5
b-a (×20)
Intensity (Arb. units)
Energy (eV)
0.0
0.5
1.0
1.5
11550
11600
11650
0.3
0.2
0.1
0.0
-0.1
-0.2

Simulation of XANES with FEFF

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

What does FEFF actually do?



What does FEFF actually do?

User Input (feff.inp)

Solve single site problem: μ_0 and T

```
HOLE 1   1.0   *  Cu K edge  (8979.0 eV), second number is S0^2

*        mphase,mpath,mfeff,mchi
CONTROL   1     1     1     1
PRINT     1     0     0     0

RMAX       6.0

*CRITERIA    curved   plane
*DEBYE       temp     debye-temp
NLEG        4

POTENTIALS
*    ipot   Z  element
      0   29   Cu
      1   29   Cu

ATOMS                          * this list contains 79 atoms
*   x         y         z      ipot  tag            distance
   0.00000   0.00000   0.00000  0 Cu1            0.00000
   1.80500   1.80500   0.00000  1 Cu1_1          2.55266
  -1.80500   1.80500   0.00000  1 Cu1_1          2.55266
   1.80500  -1.80500   0.00000  1 Cu1_1          2.55266
  -1.80500  -1.80500   0.00000  1 Cu1_1          2.55266
   1.80500   0.00000   1.80500  1 Cu1_1          2.55266
  -1.80500   0.00000   1.80500  1 Cu1_1          2.55266
   0.00000   1.80500   1.80500  1 Cu1_1          2.55266
   0.00000  -1.80500   1.80500  1 Cu1_1          2.55266
   1.80500   0.00000  -1.80500  1 Cu1_1          2.55266
  -1.80500   0.00000  -1.80500  1 Cu1_1          2.55266
```

t

dat

What does FEFF actually do?

User Input (feff.inp)

Solve single site problem: μ_0 and T

Com

Analysis: feffNNNN.dat

Run ATOMS | Clear | Reset

Titles

Operational Parameters

Space Group: | Rmax: 10 | Edge:

Output Type: feff6.inp | Shift:

Lattice Constants and Angles

A: | B: | C:

Alpha: | Beta: | Gamma:

Run ATOMS | Clear | Reset

Table of Crystallographic Sites

Cent.	Element	X	Y	Z	Tag
1					
2					
3					
4					
5					
6					

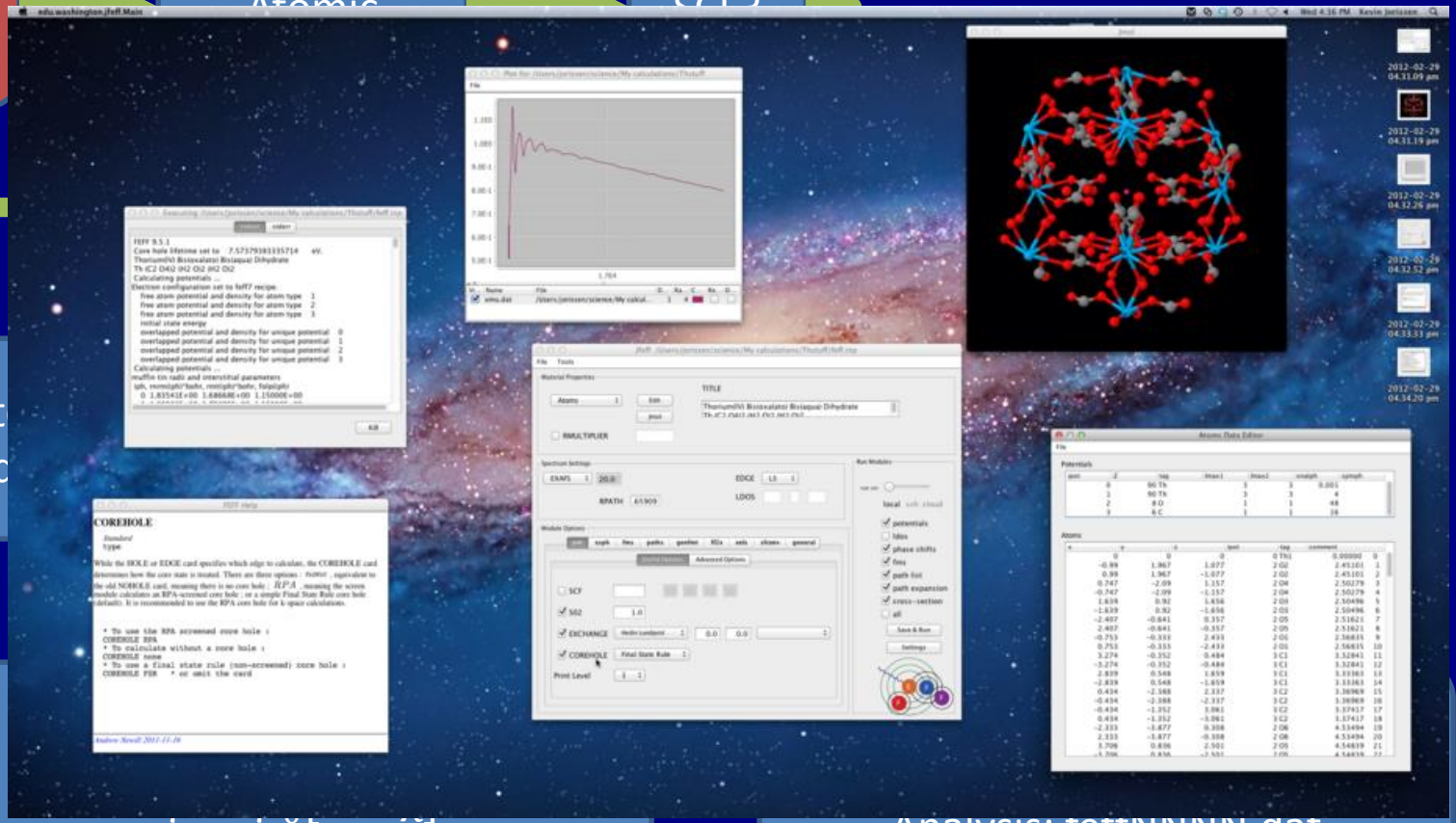
What does FEFF actually do?

User Input (feff.inp)

Overlapped Atomic

SCF?

Solve single sit problem: μ_0 and



Analysis: feffNNNN.dat

Simple Example: Cu EXAFS

```
HOLE 1   1.0   *  Cu K edge  (8979.0 eV), second number is S0^2

*        mphase,mpath,mfeff,mchi
CONTROL  1     1    1    1
PRINT    1     0    0    0

RMAX       6.0

*CRITERIA    curved   plane
*DEBYE       temp    debye-temp
NLEG        4

POTENTIALS
*    ipot   Z  element
      0   29   Cu
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  -1.80500    1.80500    0.00000  1 Cu1_1          2.55266
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   1.80500    0.00000    1.80500  1 Cu1_1          2.55266
  -1.80500    0.00000    1.80500  1 Cu1_1          2.55266
   0.00000    1.80500    1.80500  1 Cu1_1          2.55266
   0.00000   -1.80500    1.80500  1 Cu1_1          2.55266
   1.80500    0.00000   -1.80500  1 Cu1_1          2.55266
  -1.80500    0.00000   -1.80500  1 Cu1_1          2.55266
```
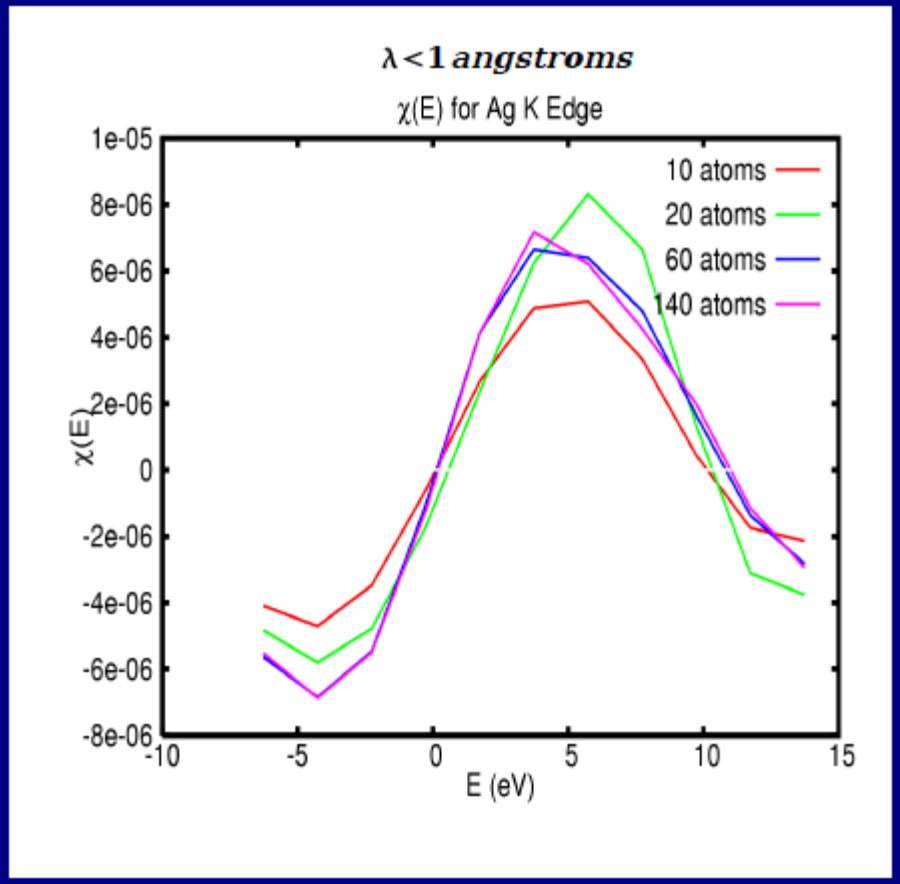
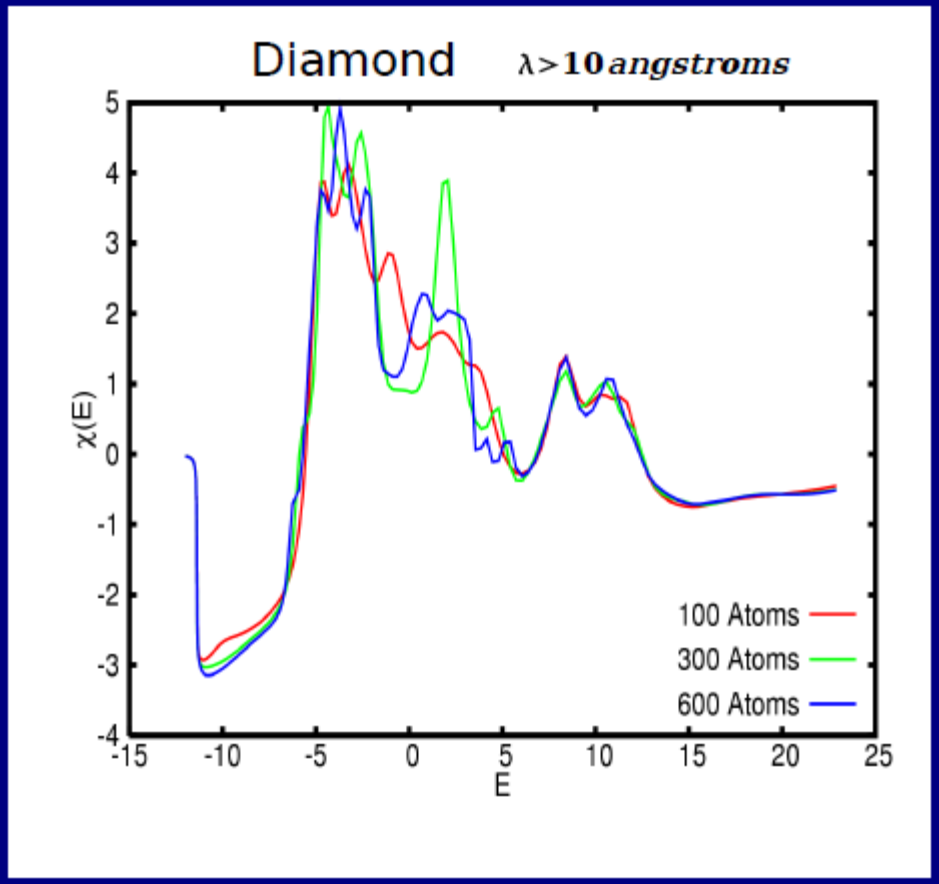

FMS Convergence

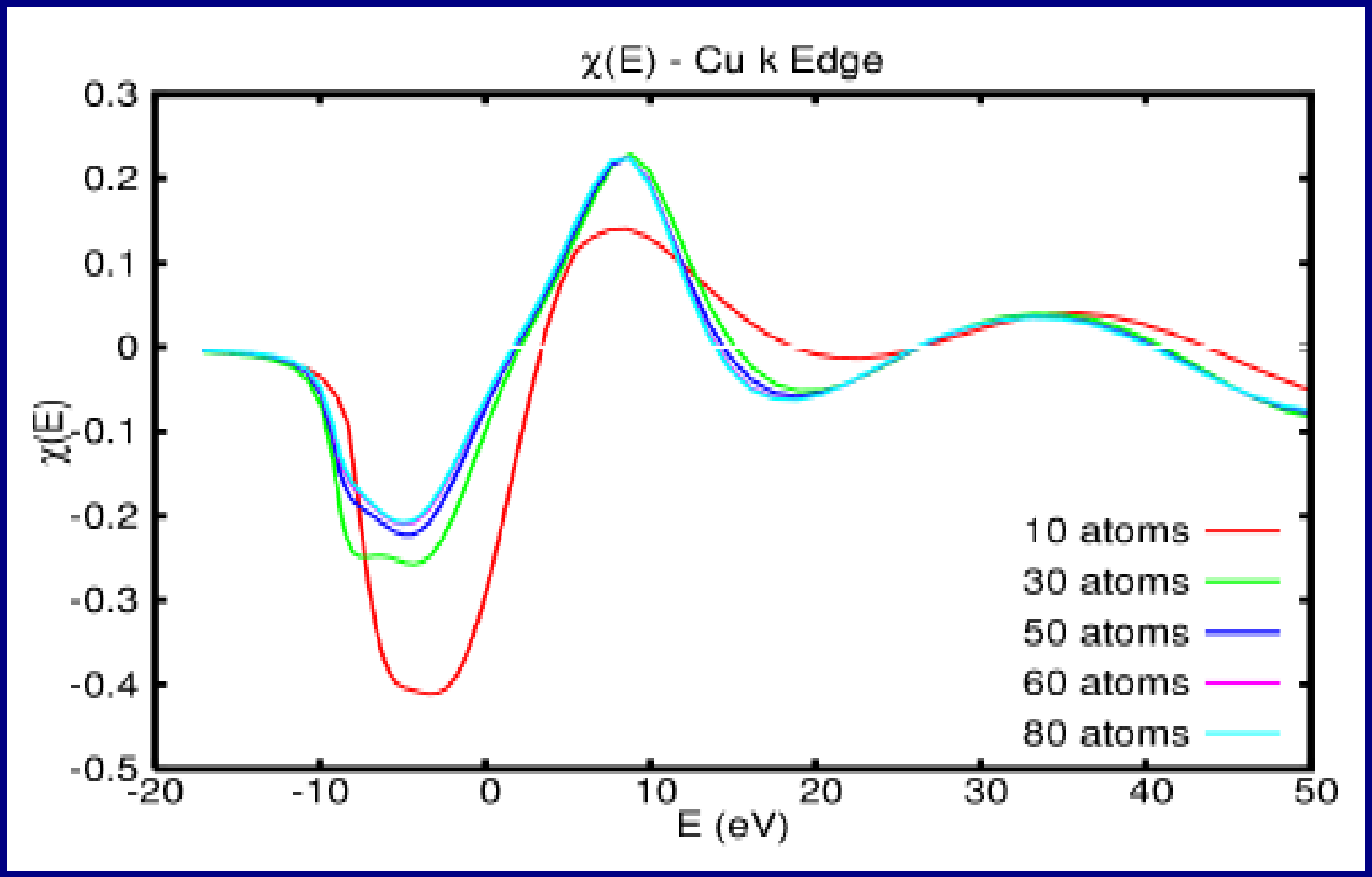
- Guess: Inelastic mean free path



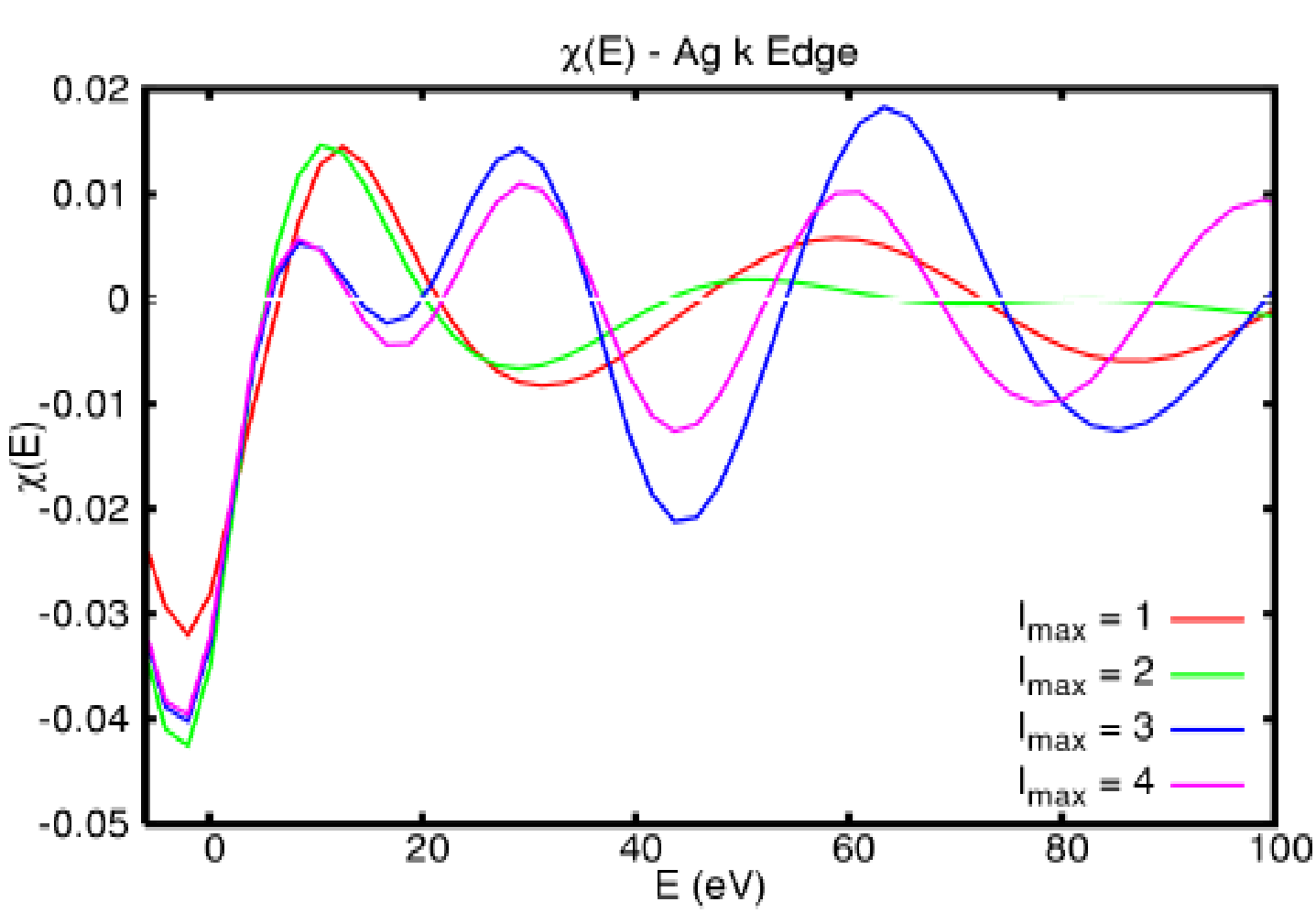


Example: CaO

SCF Convergence



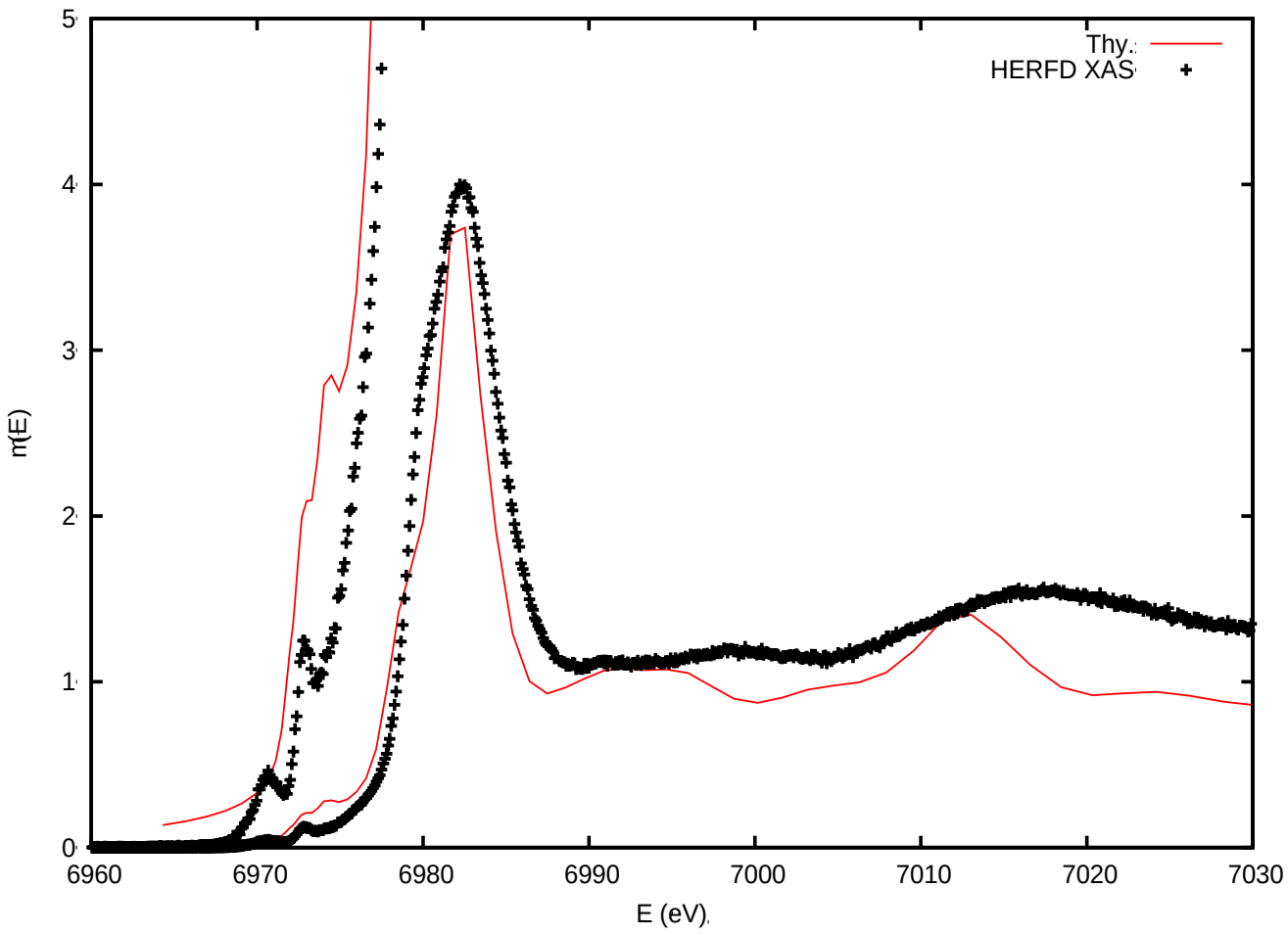
L_{max} Convergence



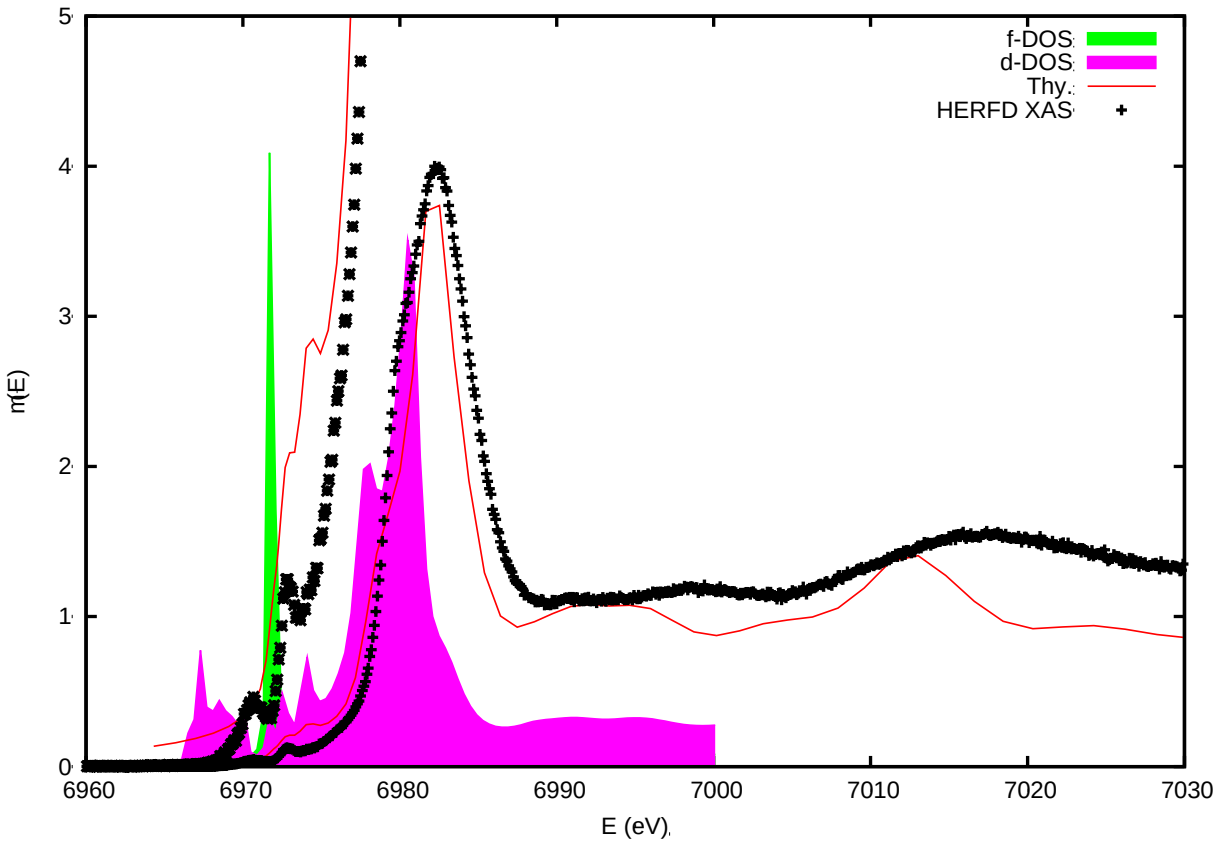
Potentials in FEFF

- 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

Eu_2O_3 L3 XANES



Eu_2O_3 L3 XANES



Augmenting FEFF with DFT

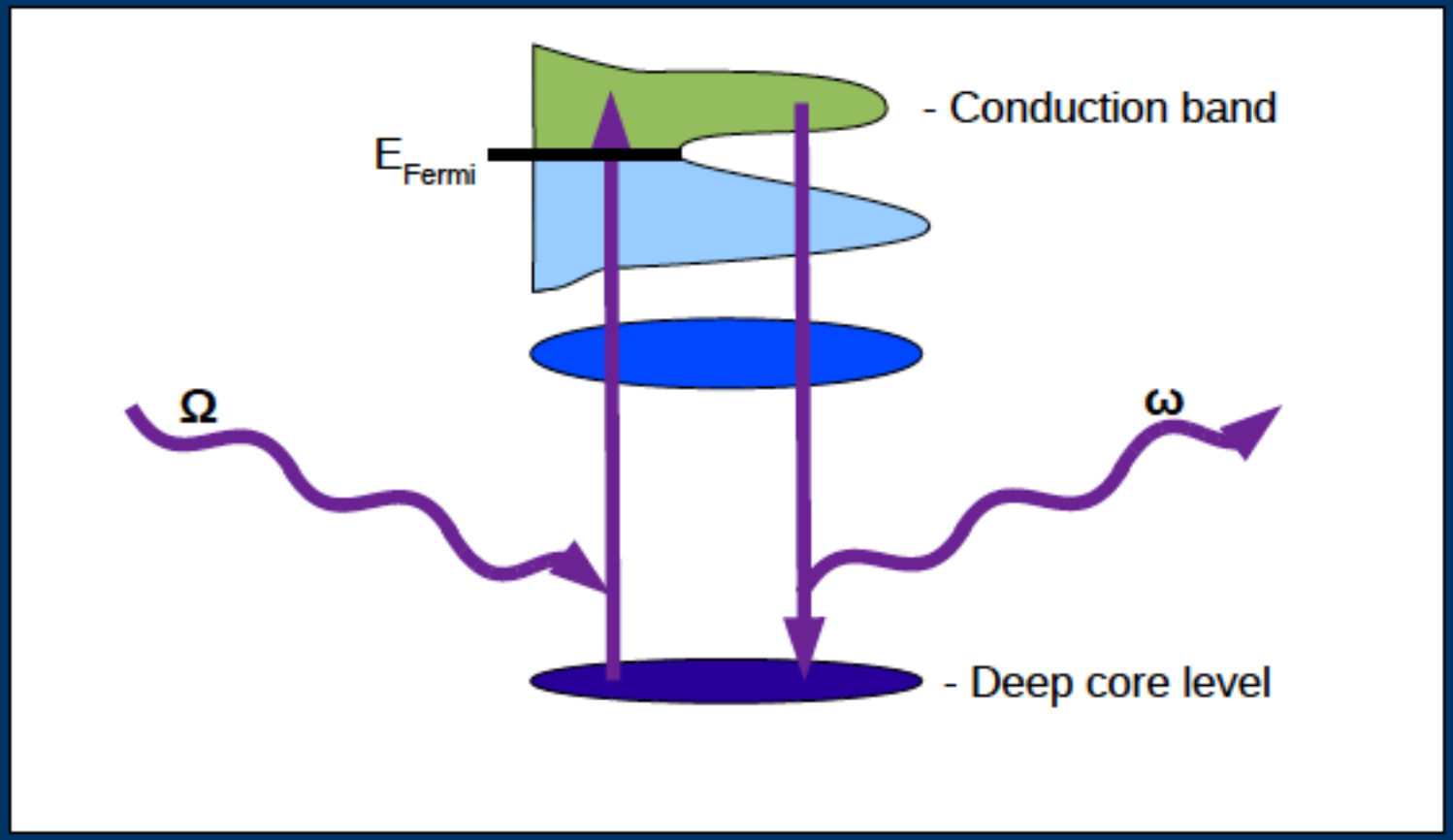
- Find possible structures
- Check full potential effects (compare DOS)
- Check accuracy of Fermi level
- Find chemical shifts
- Find dynamical properties

Thank You!

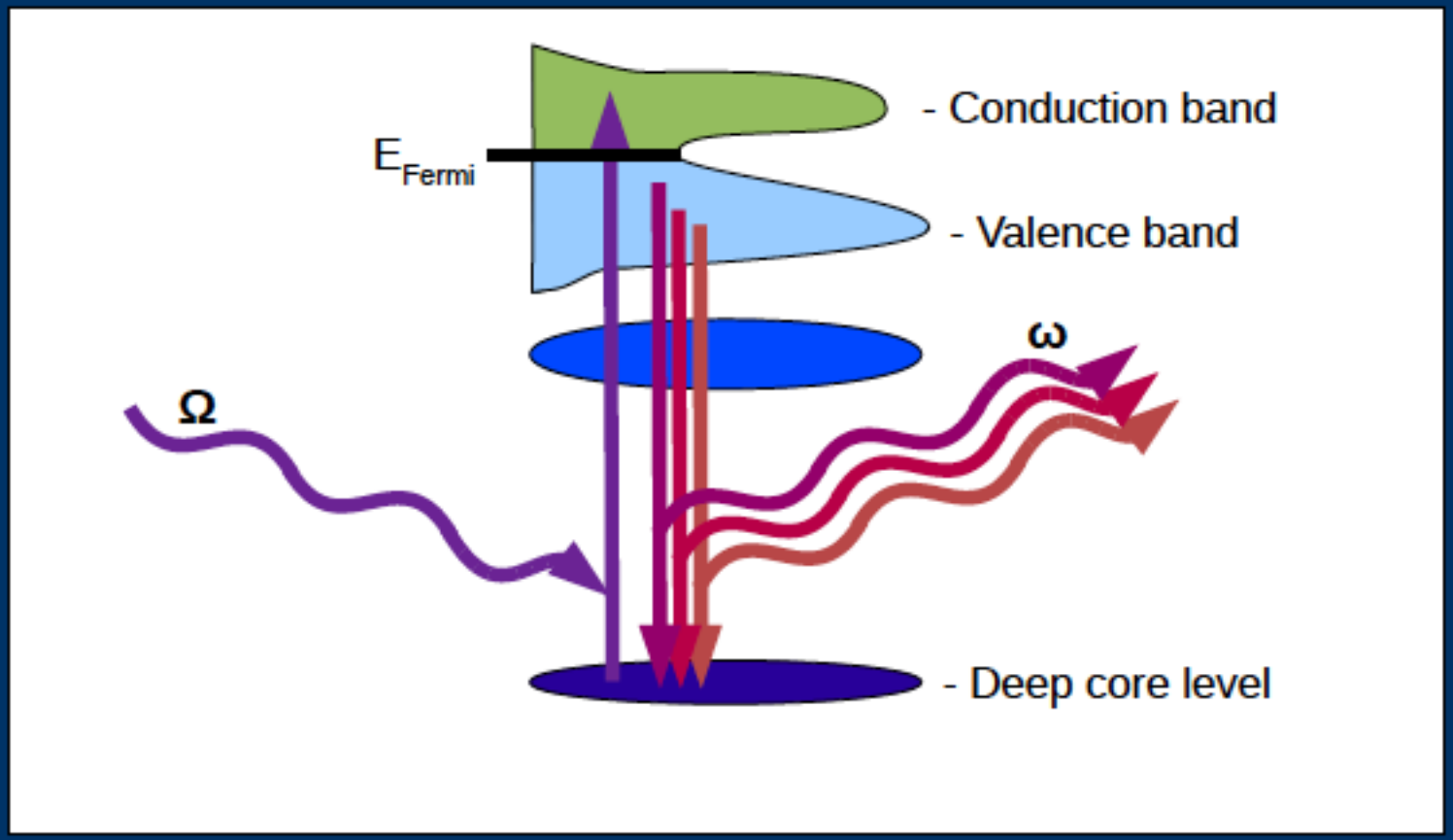
Theory of RIXS

- Core excitation: similar to XANES
- Probes unoccupied and occupied states
- Many-Body effects more evident

I. "Indirect" RIXS



I. "Direct" RIXS or RXES



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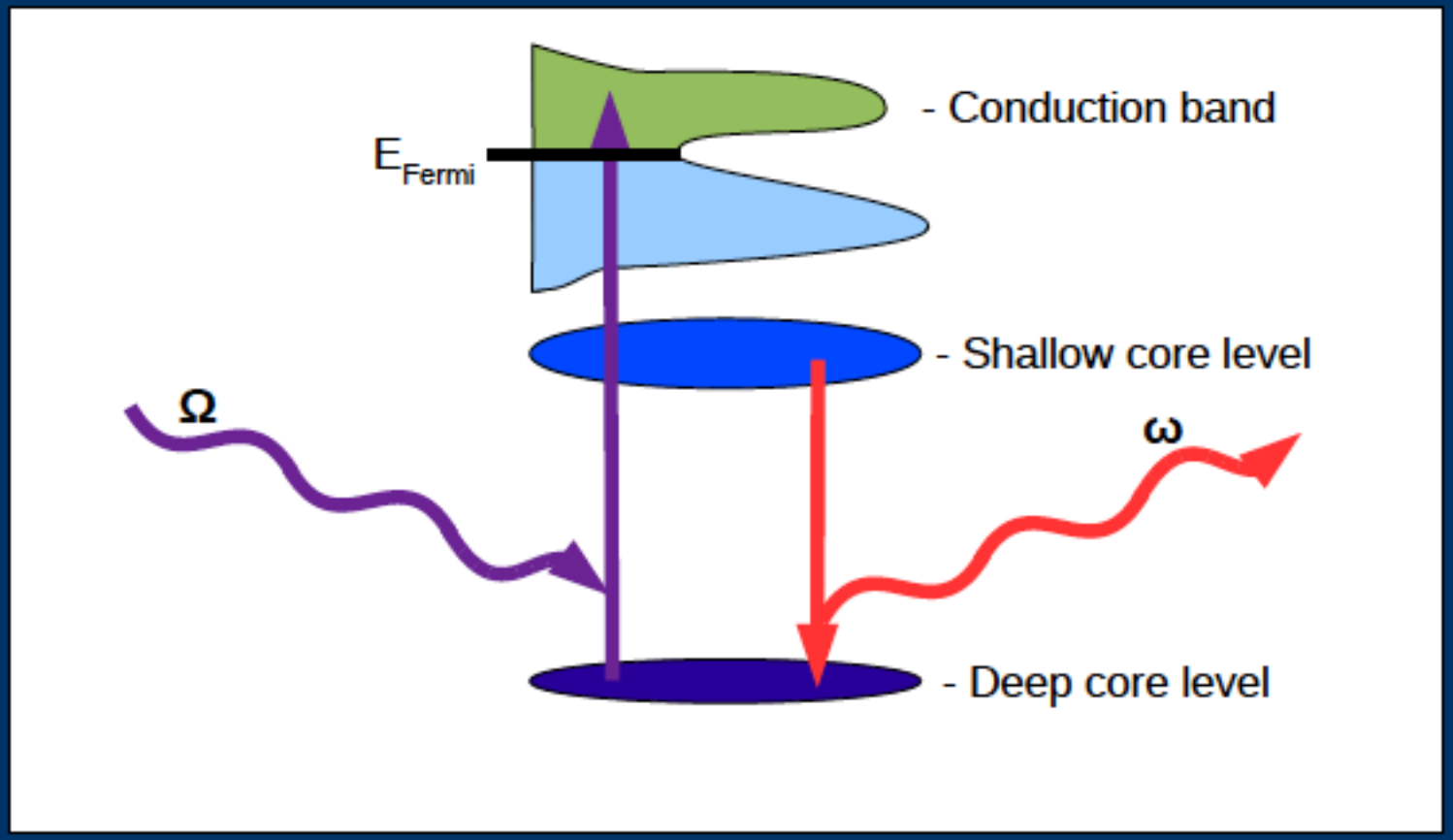


II. RIXS, XAS, and XES[1]

Kramers-Heisenberg and Green's functions

$$\frac{d^2\sigma}{d\omega\, d\Omega} = \frac{\omega}{\Omega}\sum_F \left| \sum_M \frac{\langle F|\Delta_2^*|M\rangle\langle M|\Delta_1|I\rangle}{E_M - \Omega - E_I + i\Gamma_M} \right|^2 \delta(\Omega - \omega + E_I - E_F)$$

$$G(\omega) = \sum_M \frac{|M\rangle\langle M|}{\Omega - E_M + i\Gamma_M}; \qquad \rho(\omega) = \sum_F |F\rangle\langle F|\,\delta(\omega - E_F)$$

$$\frac{d^2\sigma}{d\omega\, d\Omega} = \frac{\omega}{\Omega}\left\langle I \middle| \Delta_1^* G(\Omega + E_I)\,\Delta_2\,\rho(\Omega - \omega + E_I)\,\Delta_2^* G(\Omega + E_I)^*\,\Delta_1 \middle| I \right\rangle$$

II. RIXS, XAS, and XES[1]

Effective single particle theory[1,2]: XAS/XES

$$\frac{d^2\sigma}{d\omega\, d\Omega} = \frac{\omega}{\Omega}\int d\omega_1 \frac{a(\omega_1)\tilde{\mu}(\Omega, \Omega-\omega-\omega_1)}{|\omega-\omega_1+i\Gamma_b|}$$

XAS-XES convolution

$$\tilde{\mu}(\omega_1,\omega_2) = -\frac{1}{\pi}\mathrm{Im}[\langle b|T^*(\omega_1)g^c(\omega_2)T(\omega_1)|b\rangle]$$

Effective XAS signal

$$T(\omega) = [1+\Delta V g^b(\omega)^*]d_1; \qquad \Delta V = V_c - V_b$$

Difference in core-hole potentials

$$\mathbf{FEFF90} \Rightarrow g(\omega)$$

[1]J.J. Kas et. al, PRB 83, 23114 (2011)

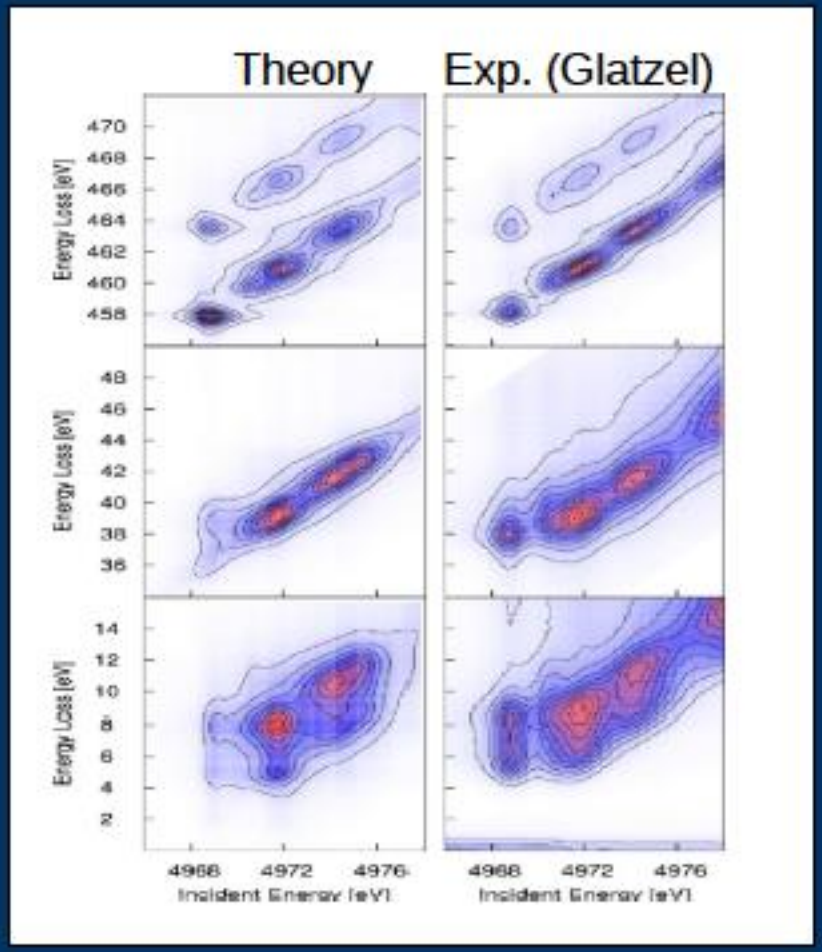
[2]Fujikawa et al., J. Electron Spectrosc. Relat. Phenom. 134, p 195 (2004)

III. Ti K RIXS: TiO_2 - Anatase

Progression with strength of ΔV

Quadrupole peak: Localized state

Qualitative behavior reproduced



Theory of XANES

- Back to Fermi's Golden Rule

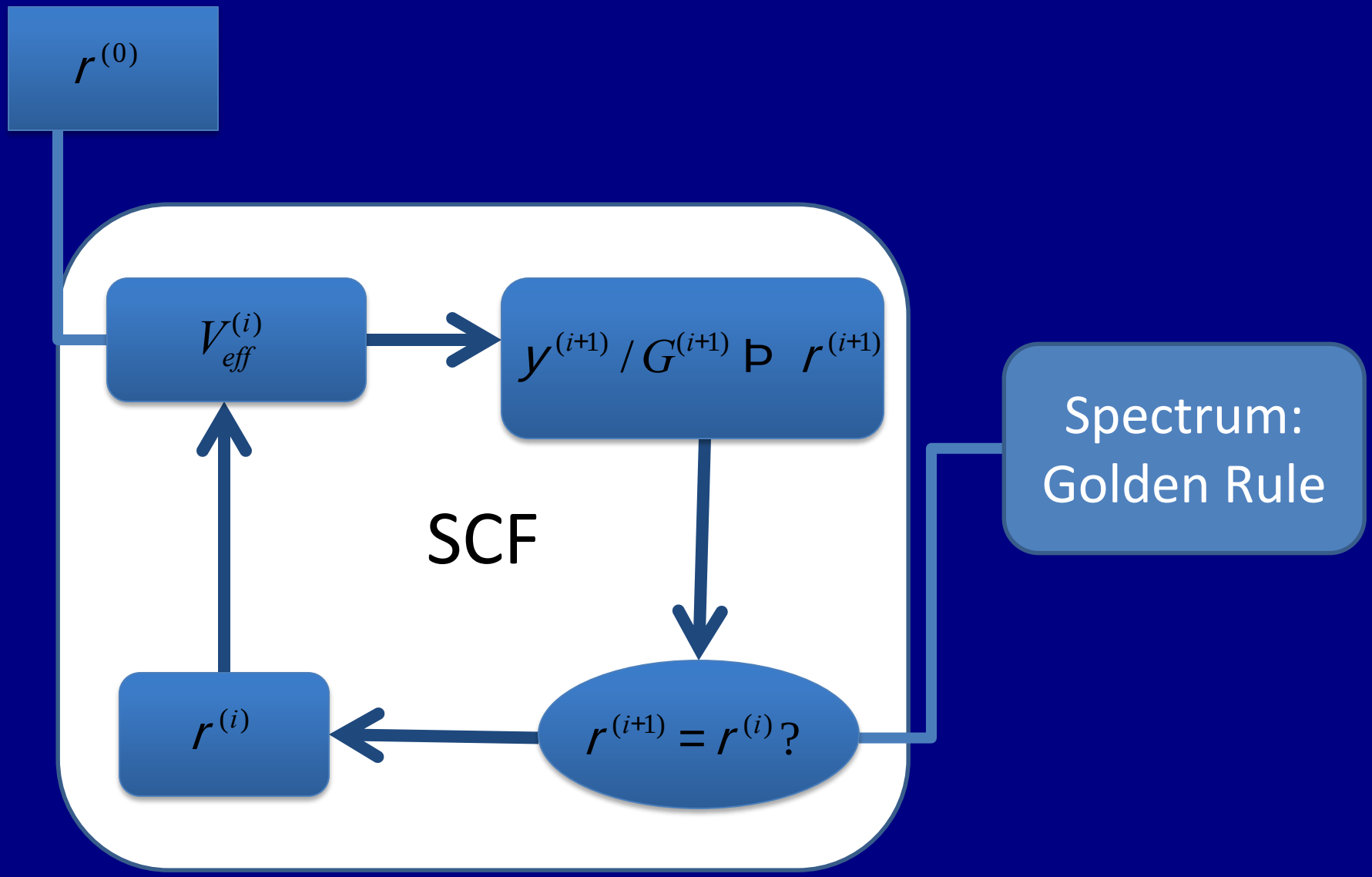
$$\mu \propto \sum_f \left|\langle i|d|f\rangle\right|^2 \delta(E_f - E_i - \hbar\omega)$$

- |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



Green's Functions and Absorption

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

2) $$\sum_f |\langle i|d|f\rangle|^2 \delta(E_f - E_i - \hbar\omega) = \langle i|d \underbrace{\sum_f |f\rangle\langle f|\delta(E_f - E_i - \hbar\omega)}_{-\frac{1}{\pi}\mathrm{Im}[G(E_i+\hbar\omega)]} d^\dagger|i\rangle$$

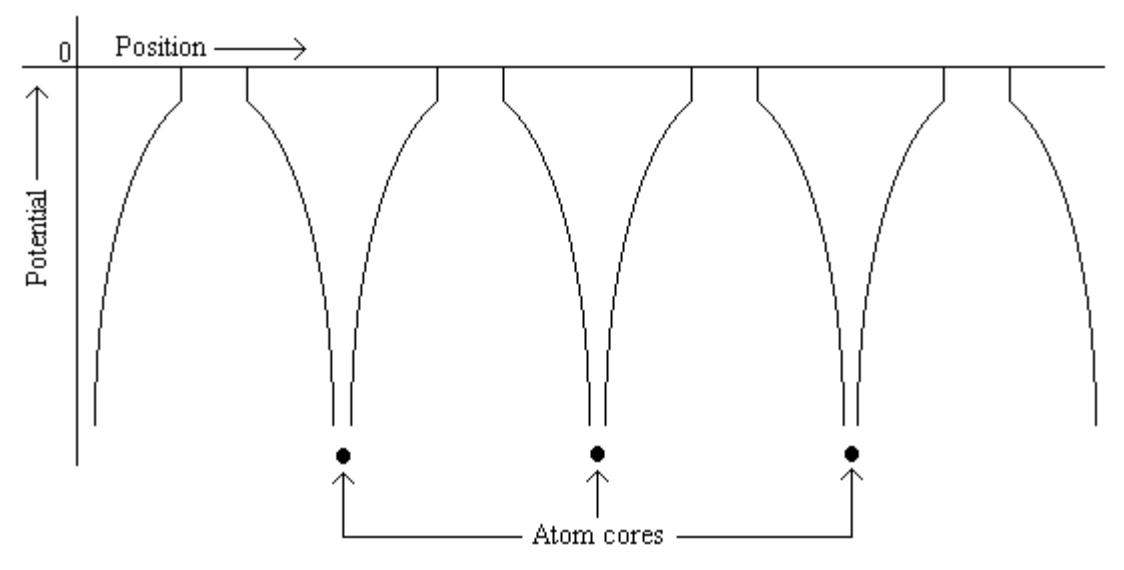
3) $$\mu \propto -\frac{1}{\pi}\mathrm{Im}\langle i|d\, G(\omega)\, d^\dagger|i\rangle$$

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

Real-Space Multiple Scattering

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

$$V = \sum_i v_i$$



Real-Space Multiple Scattering

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

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Real-Space Multiple Scattering

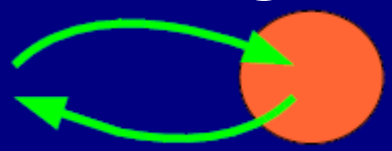
- $G = [E - H]^{-1} = G^0 + G^0 V G^0 + G^0 V G^0 V G^0 + \cdots$
-

$$V = \sum_i v_i$$

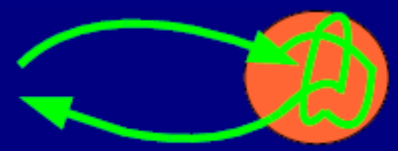
Real-Space Multiple Scattering

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

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



$G_0 V G_0$



$G_0 T G_0$

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

Structural dependence: $G^o_{iL,jL'}$

Chemical dependence: t^i_L

Path Expansion and Full Multiple Scattering

- Path Expansion – EXAFS Equation

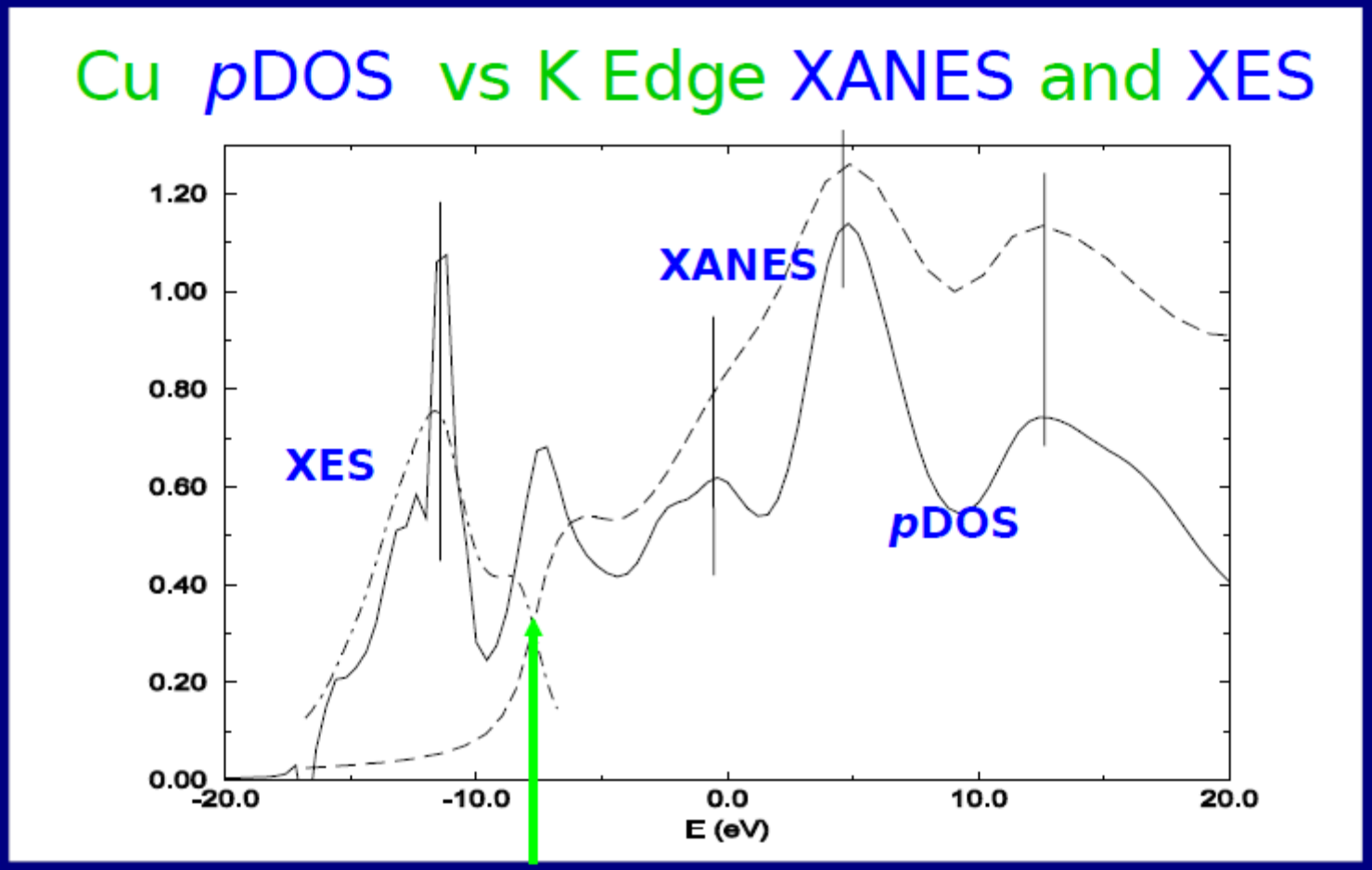
$$G = G_0 + G_0 T G_0 + G_0 T G_0 T G_0 + \ldots$$

- 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



Fermi energy E_{Fermi}

Beyond DFT – Quasiparticle Self-Energy Effects

- $G = [E - H - \Sigma]^{-1}$
- Σ: Self-Energy operator ➡ Quasi-particles

Quasi-Toddler

Core-Hole Interaction

- Photo-electron and hole interact
- Self-Consistent calculation without core electron: Final State Rule
- Linear response: $W_{ch} = \varepsilon^{-1} v_{ch}$

PHYSICAL REVIEW B VOLUME 58, NUMBER 12 15 SEPTEMBER 1998-II

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

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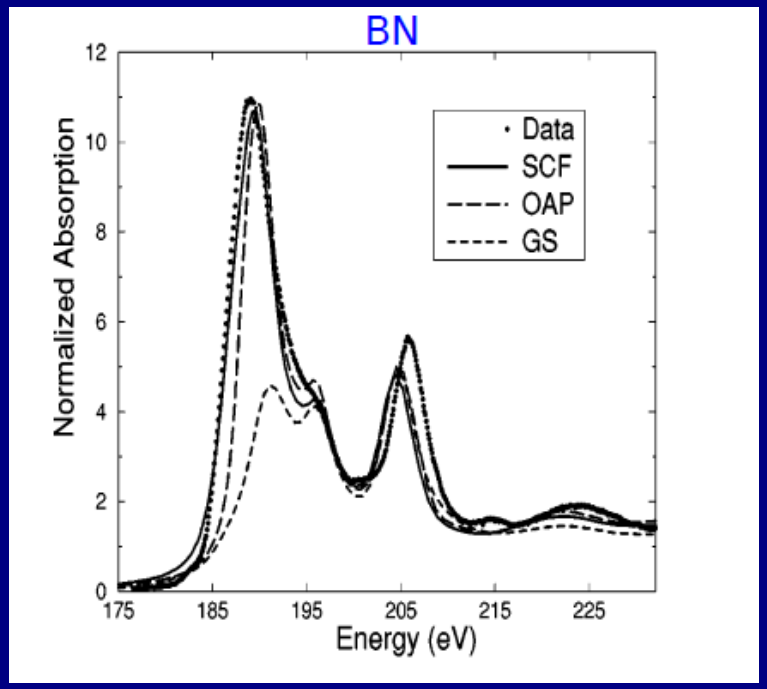
Ceramics Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

J. J. Rehr
Department of Physics, University of Washington, Seattle, Washington 98195-1560

S. D. Conradson
MST-11, Los Alamos National Laboratory, Los Alamos, New Mexico 87545



FEFF: Key Approximations

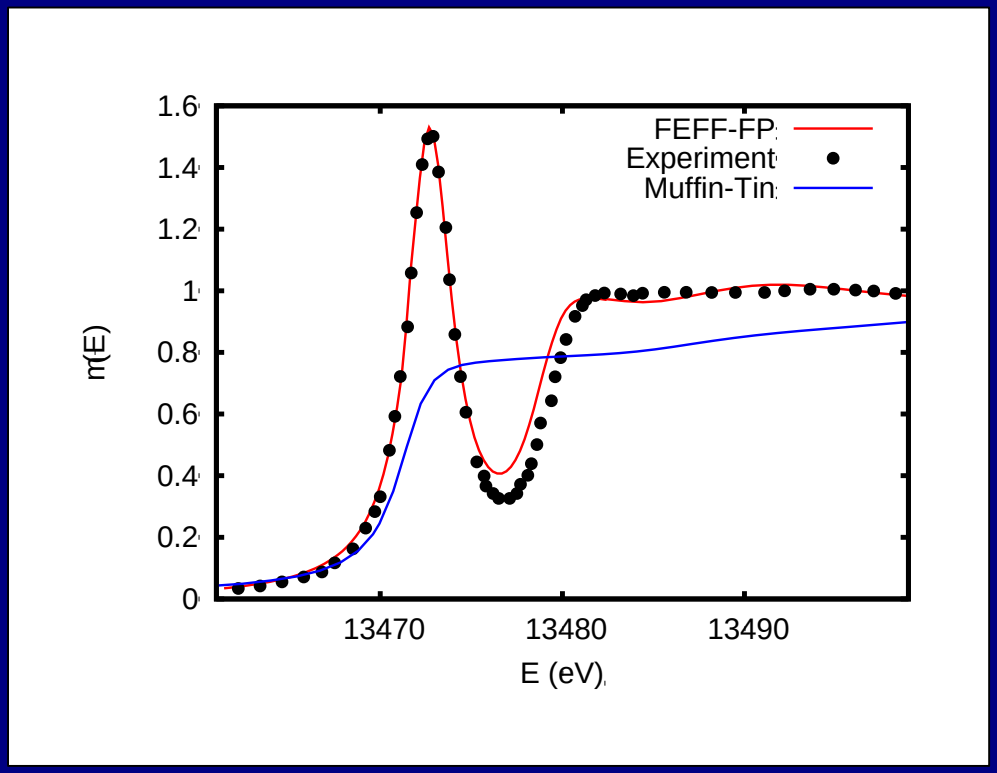
- Spherical muffin-tin potentials
- Local Density approximation
- Quasi-particle approximation
- Core-hole treatment

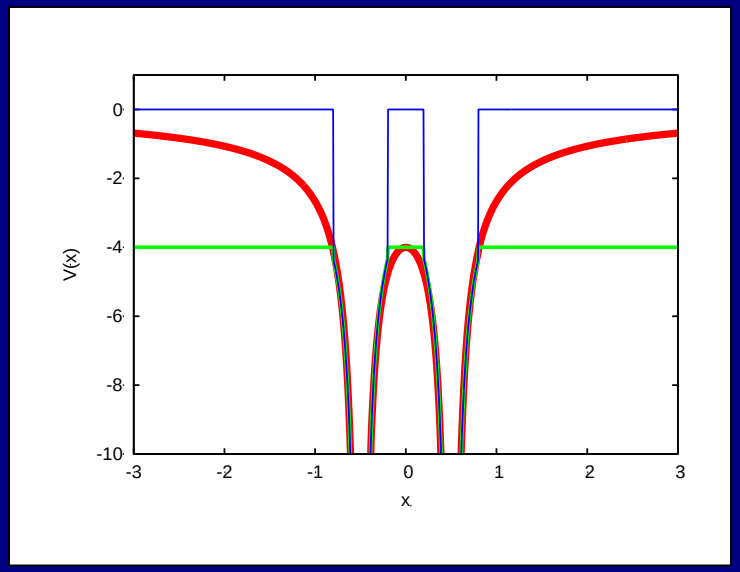
When might approximations break down?

- 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

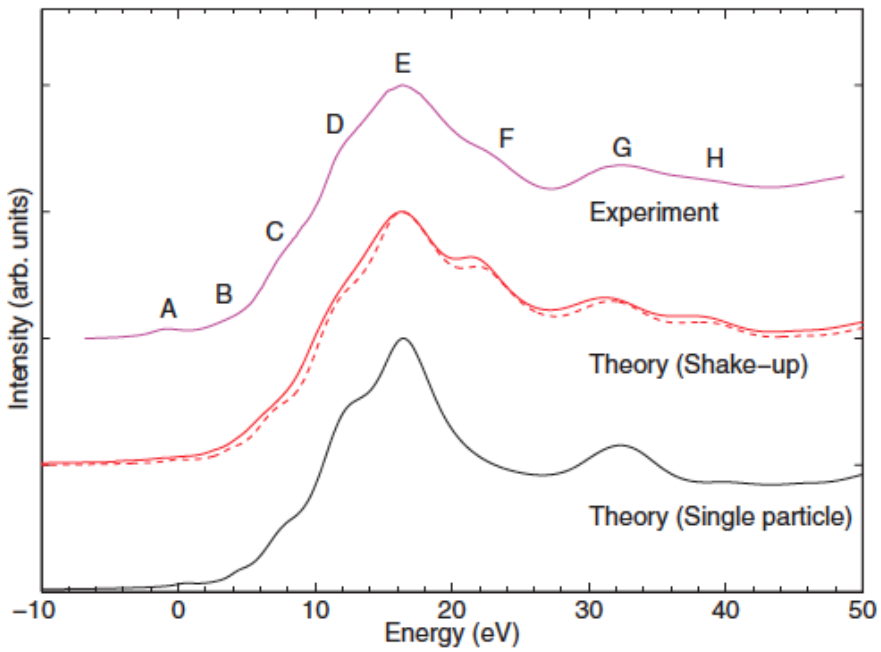
Br_2



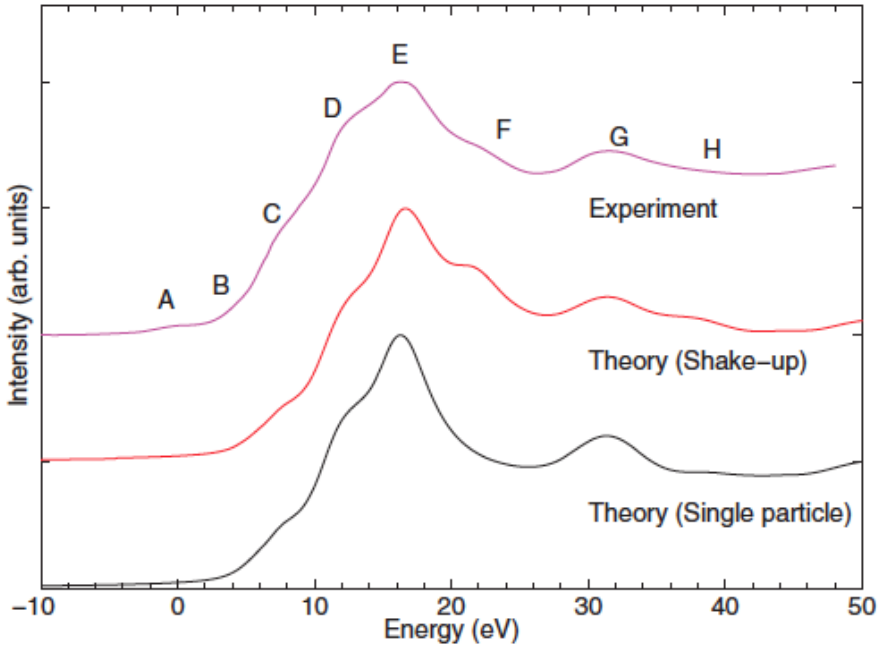


Many-Body Effects: Charge Transfer

NiO



CoO



Calandra et al, PHYSICAL REVIEW B 86, 165102 (2012)