Theory of X-Ray Absorption Spectroscopy

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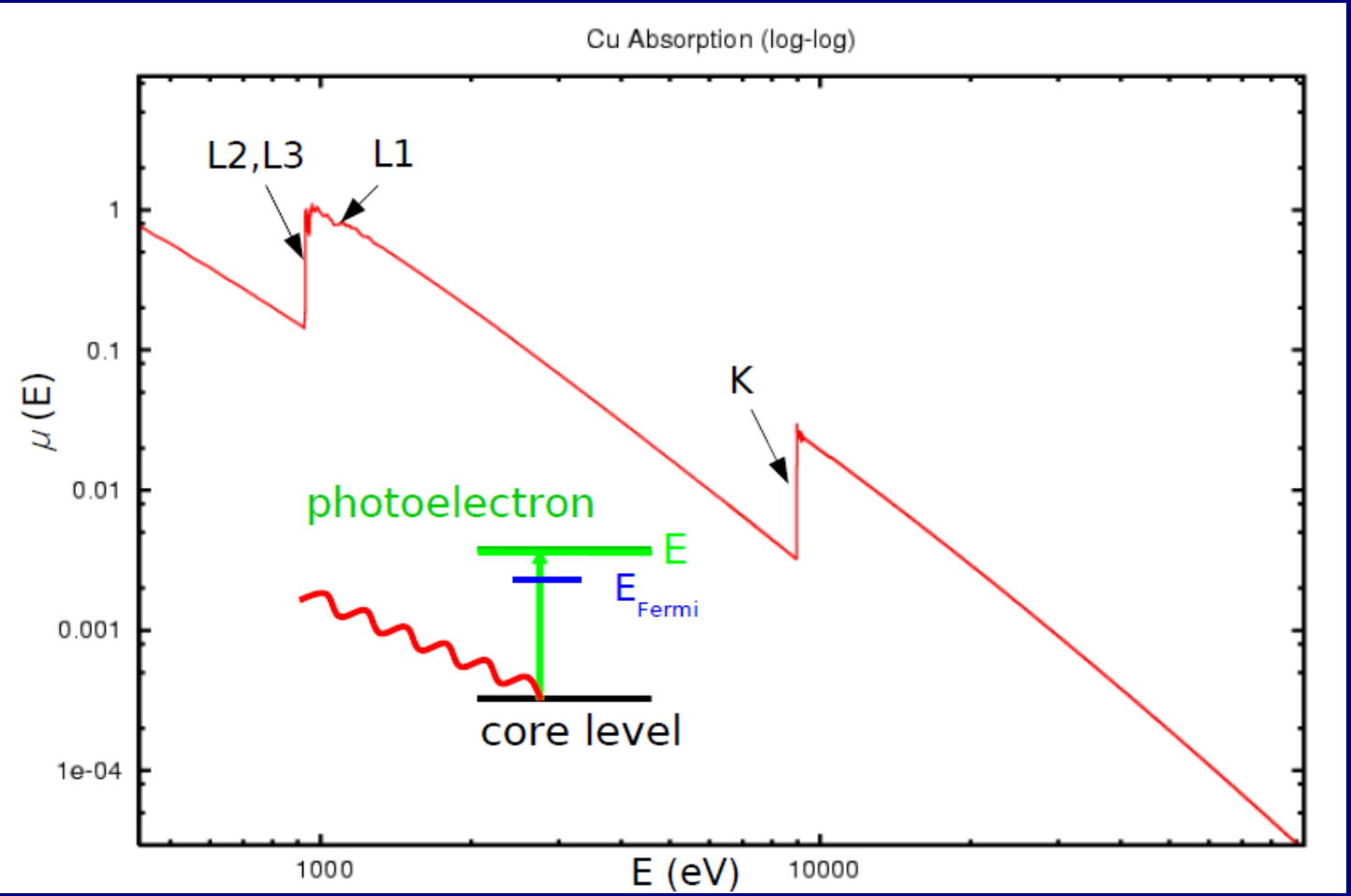
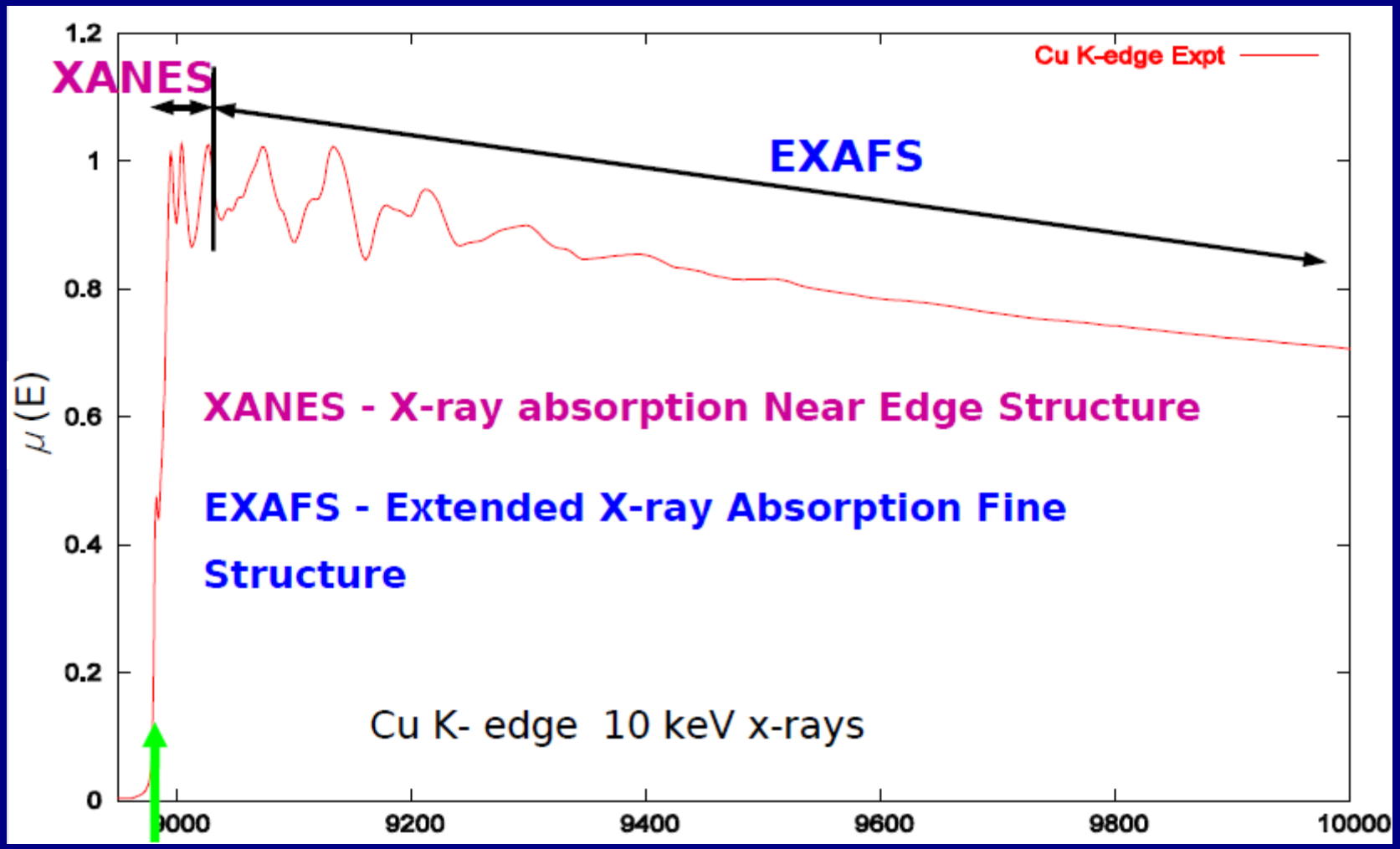
Outline

- Introduction to XAS
- Theory of EXAFS
- Theory of XANES
- Key Approximations
- Summary and Conclusion

Introduction: What is XAS?



Fine Structure – EXAFS and XANES

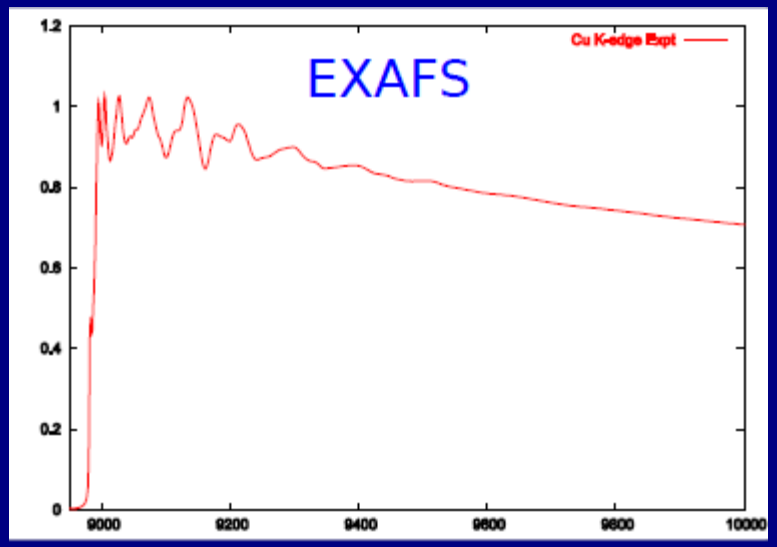


E_{Fermi}

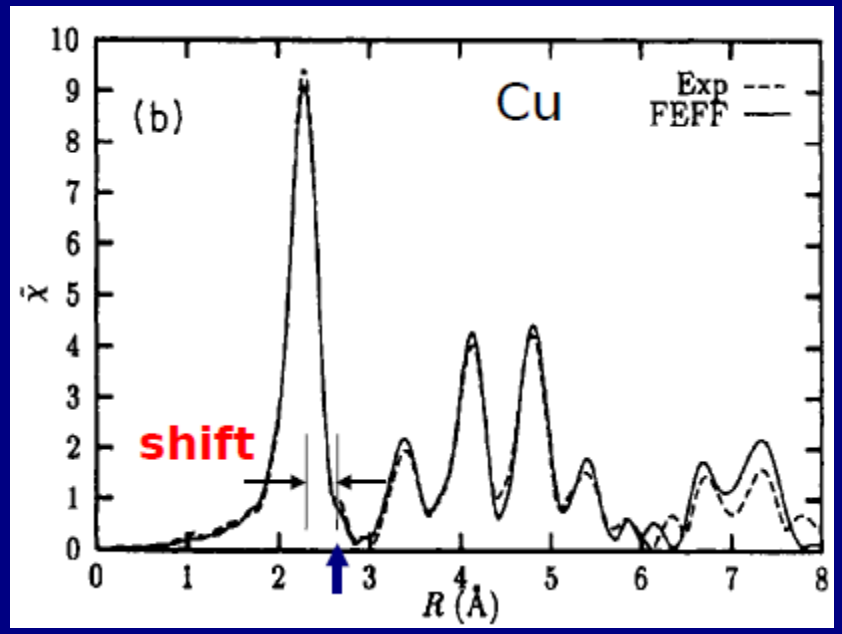
E (eV)

Qualitative Interpretation of EXAFS

Sayers, Stern, and Lytle 1970



EXAFS Fourier transform
-> Shifted Radial distribution



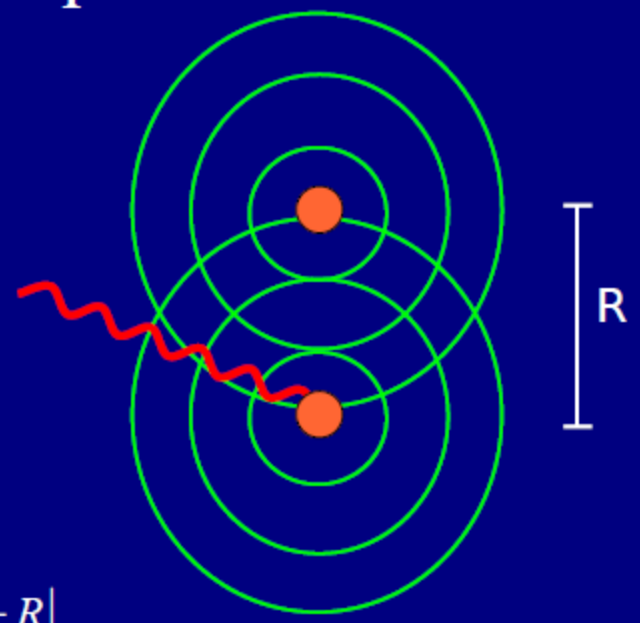
R_{NN}

Theory of EXAFS

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

$|i\rangle$ = initial "core" state $|f\rangle$ = final "photoelectron" state

2) $\langle i|d|f\rangle \approx \psi_f(0) \int_c d^3 r \psi_i(r) \vec{\epsilon} \cdot \vec{r}$



3) $\psi_f(r) \approx \frac{e^{ikr}}{kr}\left[1 + i f(\pi, k) \frac{e^{ikR}}{kR} \frac{e^{ik|r-R|}}{k|r-R|}\right]$

Theory of EXAFS

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

χ is defined as the oscillatory part of the signal

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

Many Single Scattering events

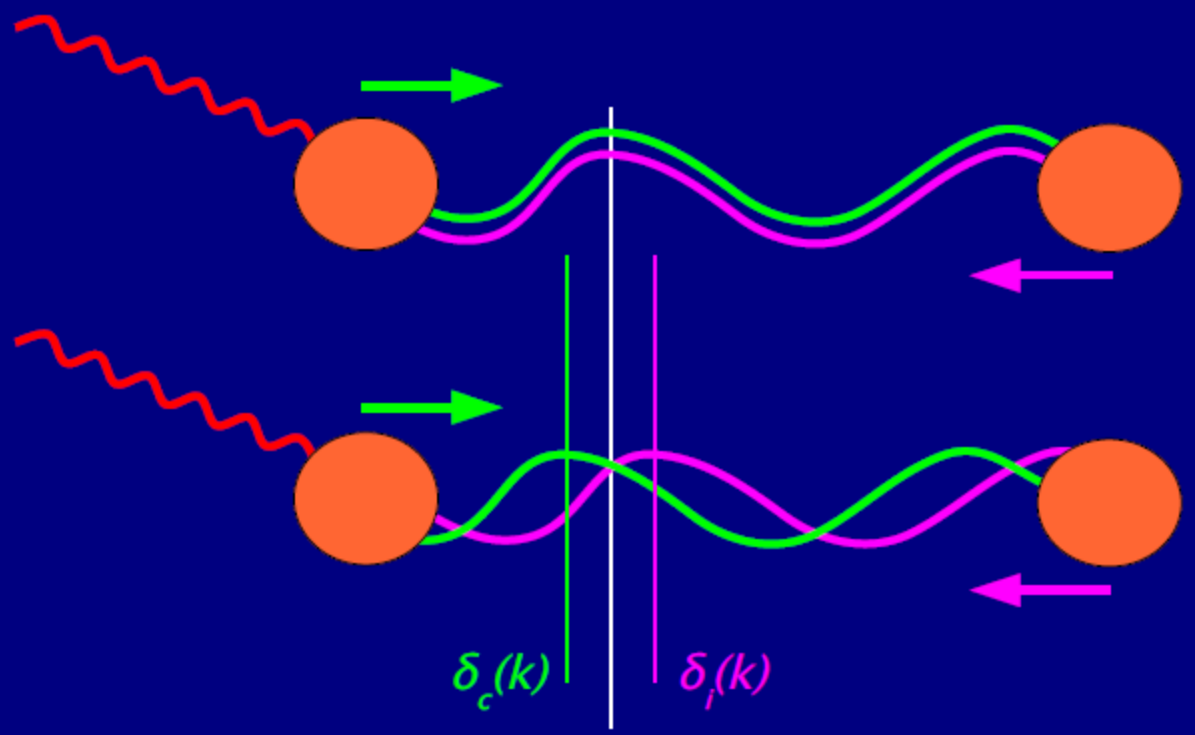
$$\Rightarrow\quad \chi = \sum_i A_i f_i(\pi,k)\frac{\sin(2\mathrm{kR}_i)}{(kR_i)^2}$$

The real EXAFS Equation

- Phase Shifts
- Debye Waller Factors
- Inelastic losses
- Many-Body S_0^2
- Curved Wave Scattering
- Multiple Scattering

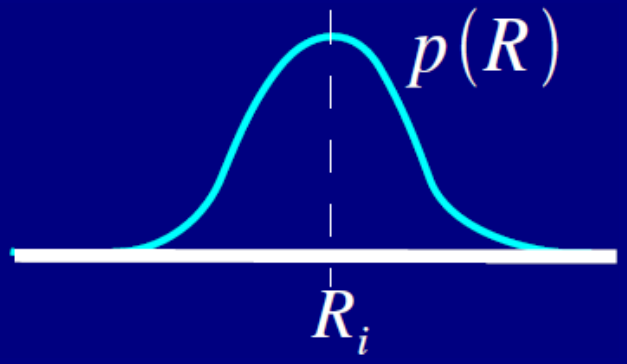
Phase Shifts

$$\Rightarrow \quad \chi = \sum_i A_i \left| f_i(\pi, k) \right| \frac{\sin\left(2kR_i + \boldsymbol{\delta_c(k)} + \boldsymbol{\delta_i(k)}\right)}{(kR_i)^2}$$

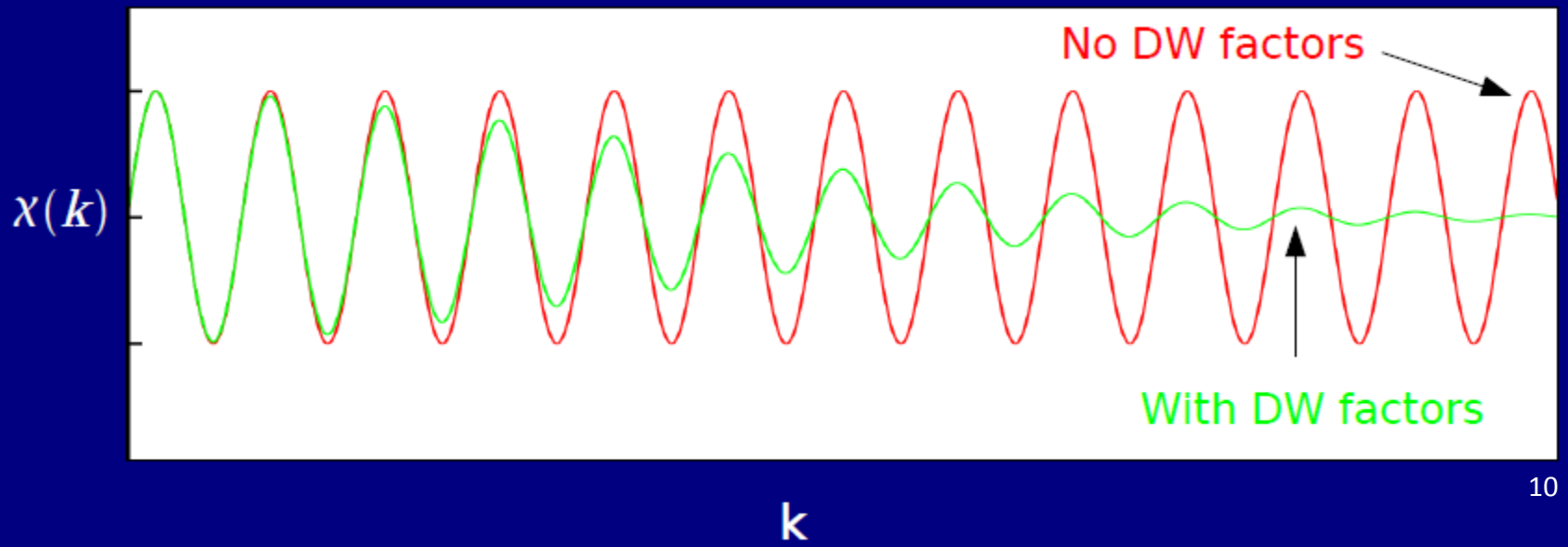


Disorder: Debye-Waller Factors

$$p(R)=(2\pi\sigma_i^2)^{\frac{1}{2}}\, e^{-\frac{(R-R_i)^2}{2\sigma_i^2}}$$



$$\Rightarrow\ \chi=\sum_i A_i\left|f_i(\pi,k)\right|\frac{\sin(2kR_i+\delta_c(k)+\delta_i(k))}{(kR_i)^2}\exp(-2\sigma_i^2k^2)$$

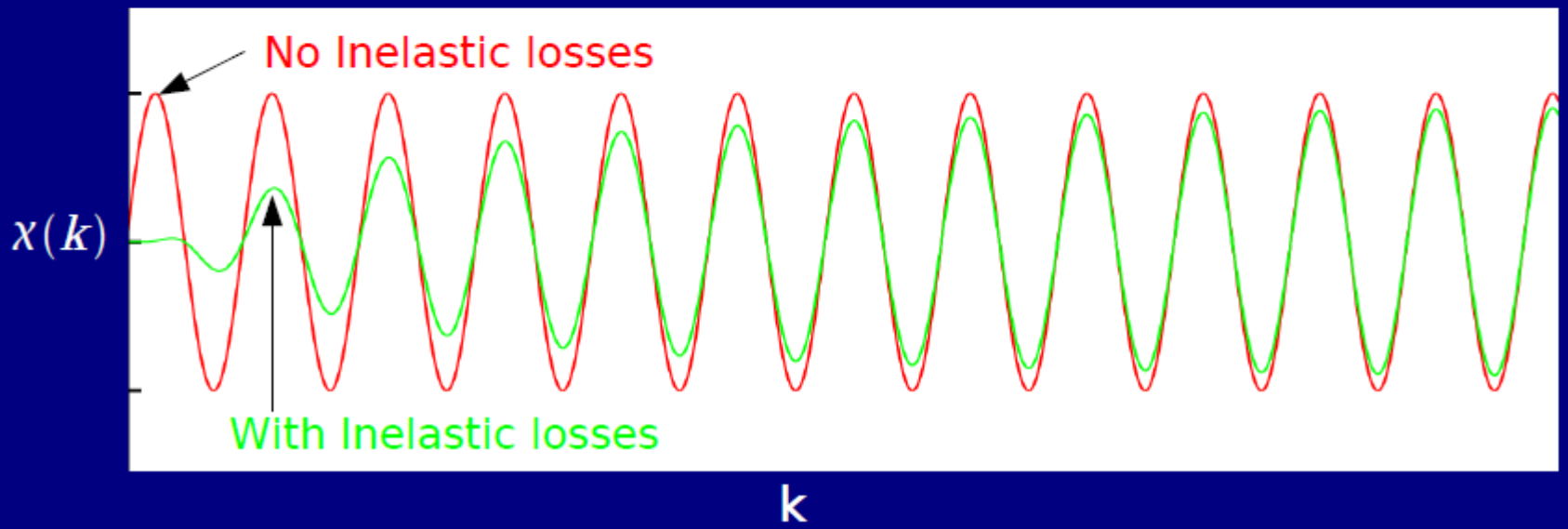


Inelastic losses

$$E_{qp}=\frac{p^2}{2\,\mathrm{m}}+\Sigma(E)+i\Gamma_{ch} \qquad p_{qp}=p'+ip''=p'+\frac{i}{\lambda}$$

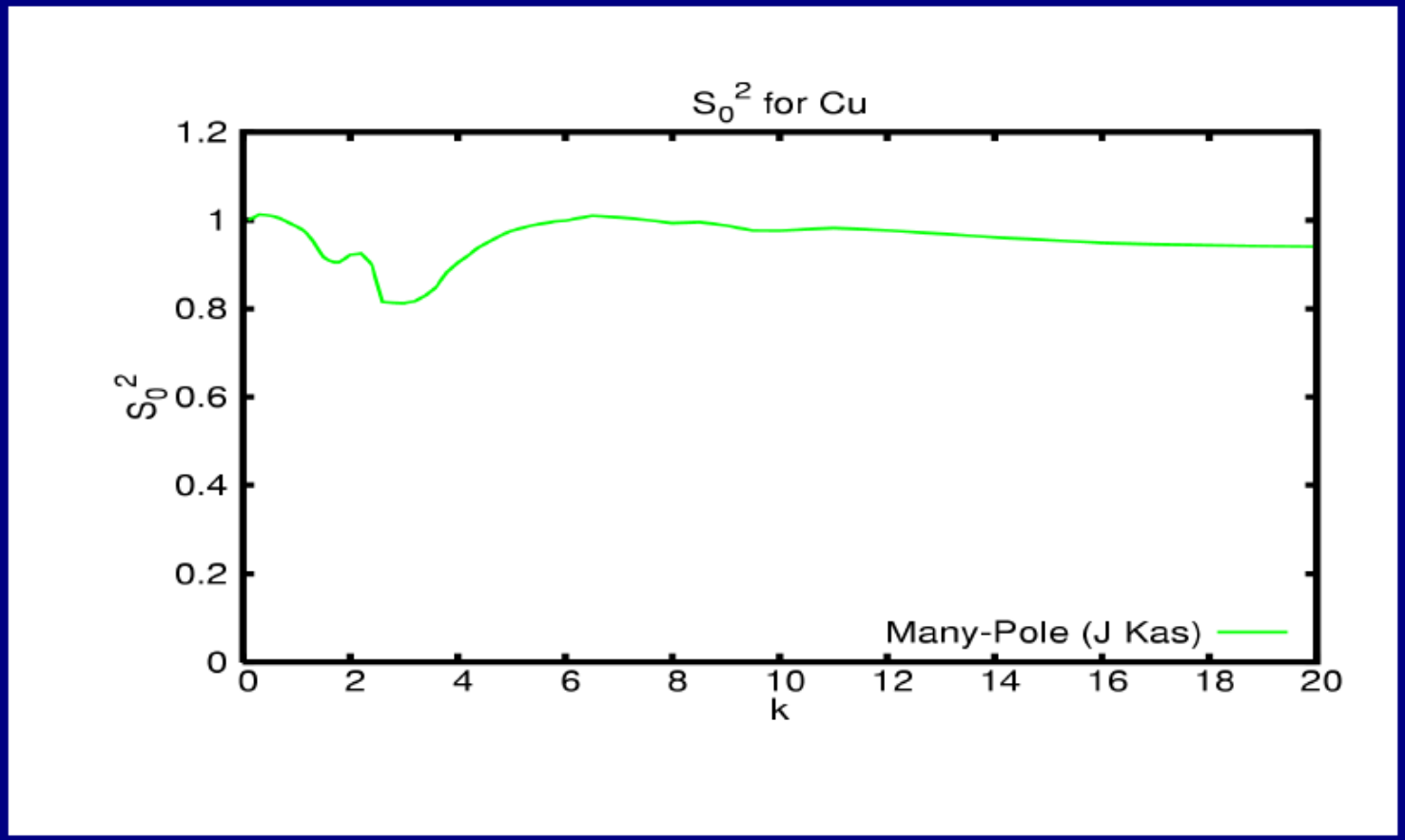
$$\lambda\approx\frac{k}{|\mathrm{Im}\,\Sigma|+\Gamma_{ch}}$$

$$\Rightarrow\ \chi=\sum_i A_i\left|f_i(\pi,k)\right|\frac{\sin(2\mathrm{k}\mathrm{R}_i+\delta_c(k)+\delta_i(k))}{(kR_i)^2}\exp\left(\frac{-R}{\lambda(k)}\right)$$



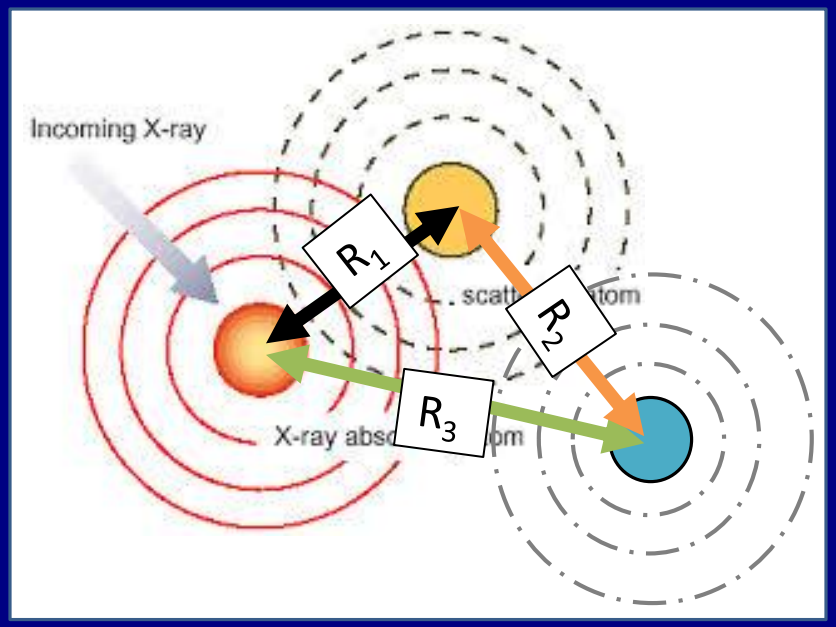
Many-Body Effects S_0^2

$$\Rightarrow \quad \chi = \sum_i N_i S_0^2 \left| f_i(\pi, k) \right| \frac{\sin(2kR_i + \delta_c(k) + \delta_i(k))}{(kR_i)^2} e^{\frac{-R}{\lambda(k)}}$$

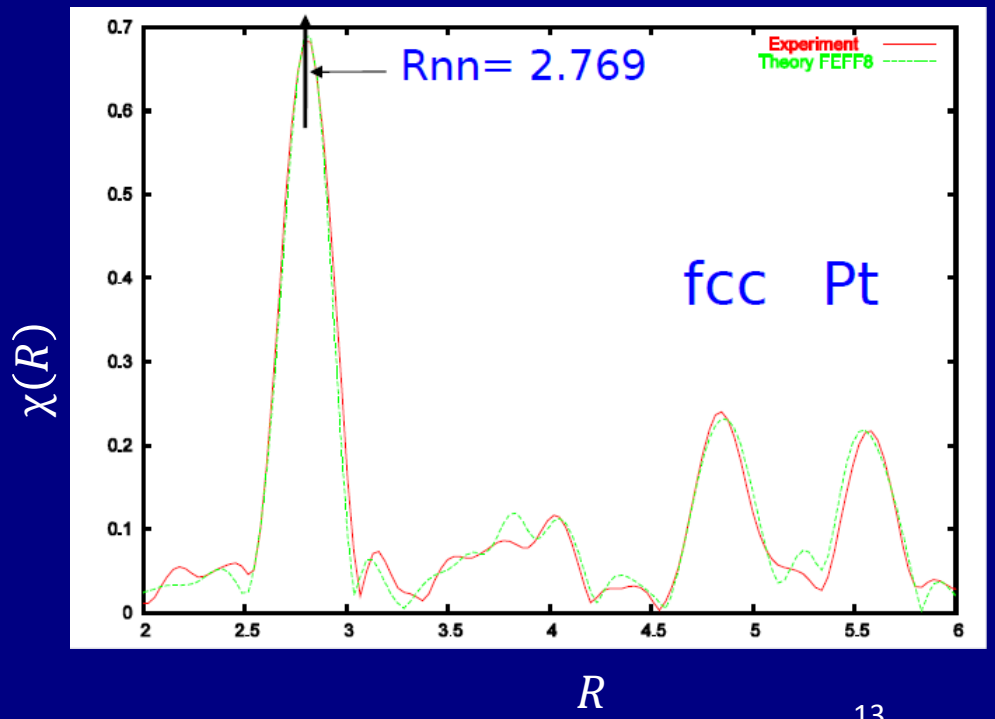


Multiple Scattering and Curved Wave Scattering Amplitudes

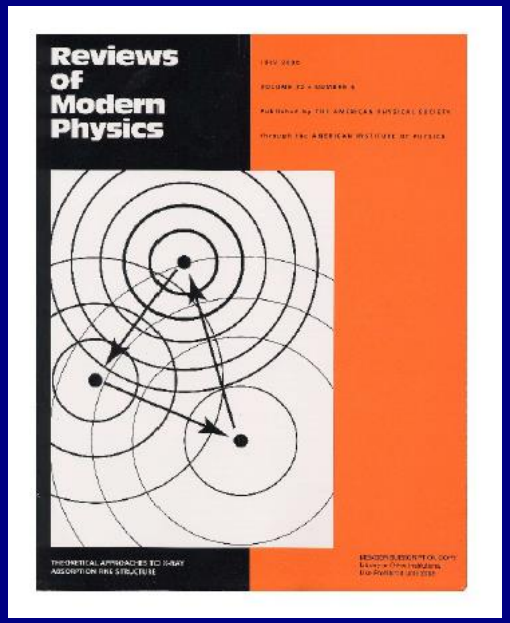
$$\chi(k) = \sum_i N_i S_0^2 |f_i^{eff}(k)| \frac{\sin[2k\,R_i + \delta_c(k) + \delta_i(k)]}{(kR_i)^2} e^{-\frac{R_i}{\lambda(k)}} e^{-2\sigma_i^2 k^2}$$



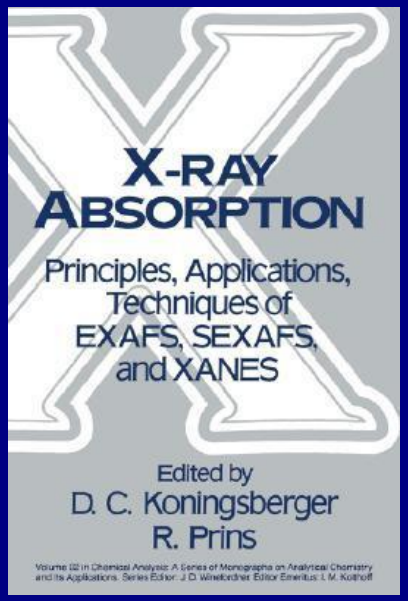
Phase corrected EXAFS FT – RDF



References



Quantitative Theory of EXAFS
J. J. Rehr and R. C. Albers
Rev. Mod. Phys. 72, 621 (2000)



X-Ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS and XANES
D. C. Koningsberger and R Prins (Editors)
Chapter 1 – Theory of EXAFS, E. A. Stern

Theory of XANES

- Back to Fermi's Golden Rule

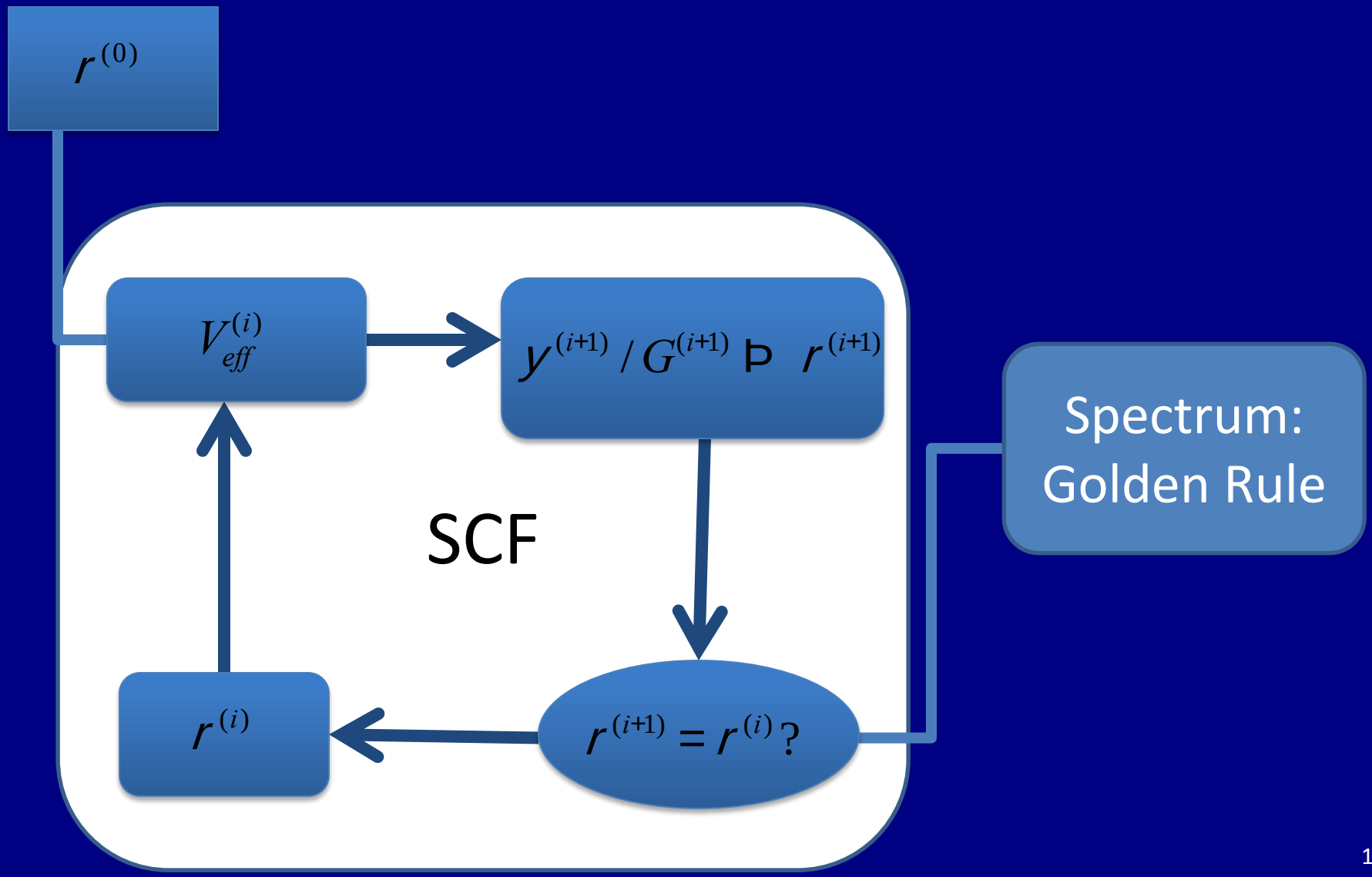
$$\mu \propto \sum_f \left|\langle i|d|f\rangle\right|^2 \delta(E_f - E_i - \hbar\omega)$$

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

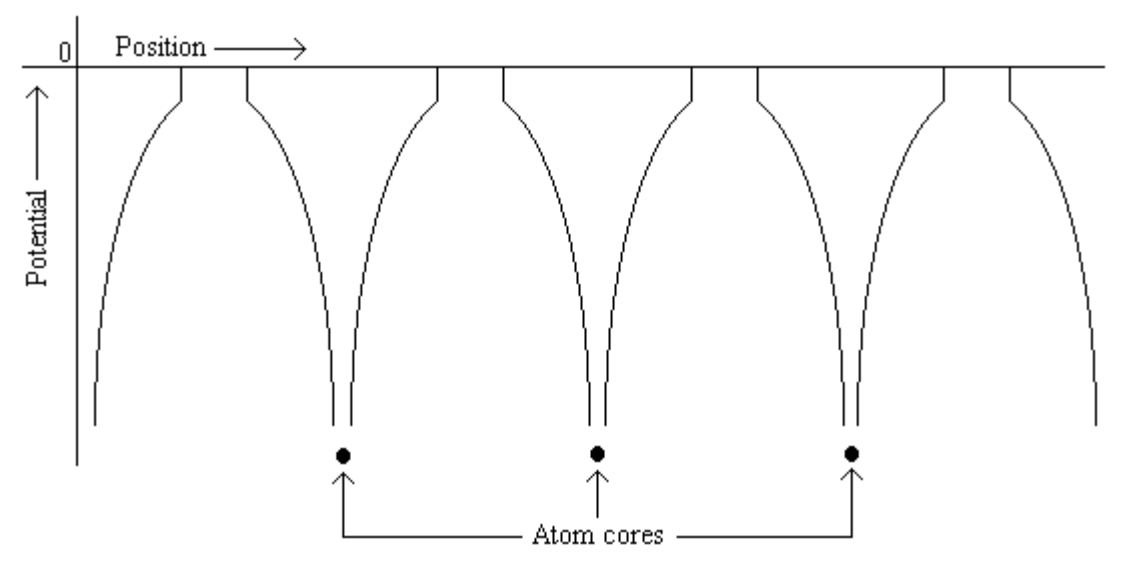
3) $$\mu \propto -\frac{1}{\pi}\mathrm{Im}\langle i|d\, G(\omega)\, d^\dagger|i\rangle$$

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

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

$$V = \sum_i v_i$$

Real-Space Multiple Scattering

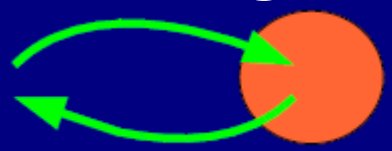
- $G = [E - H]^{-1} = G^0 + G^0 V G^0 + G^0 V G^0 V G^0 + \cdots$
-

$$V = \sum_i v_i$$

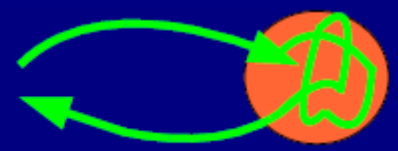
Real-Space Multiple Scattering

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

- 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

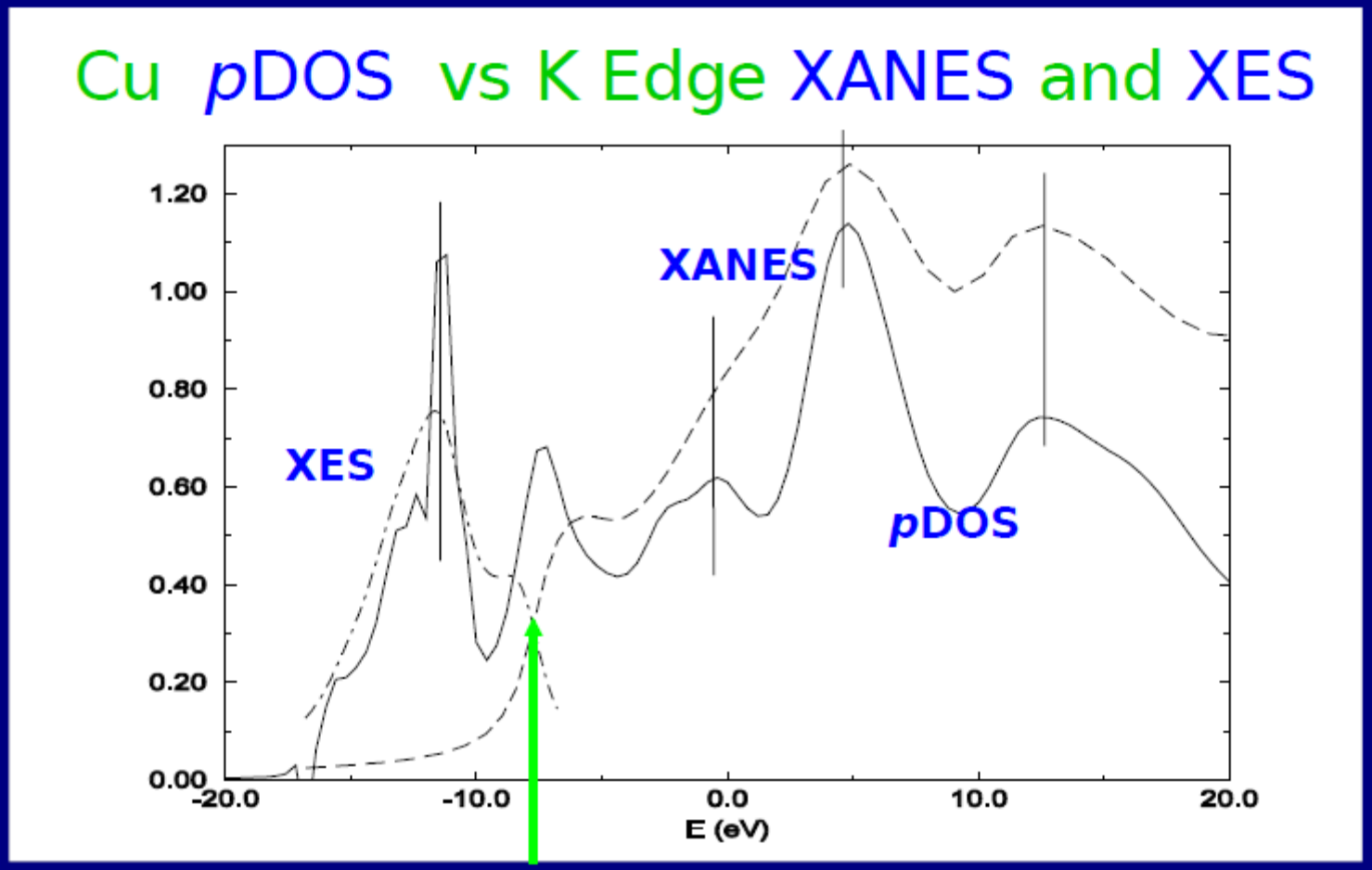
$$G = G_0 + G_0 T G_0 + G_0 T G_0 T G_0 + \ldots$$

- 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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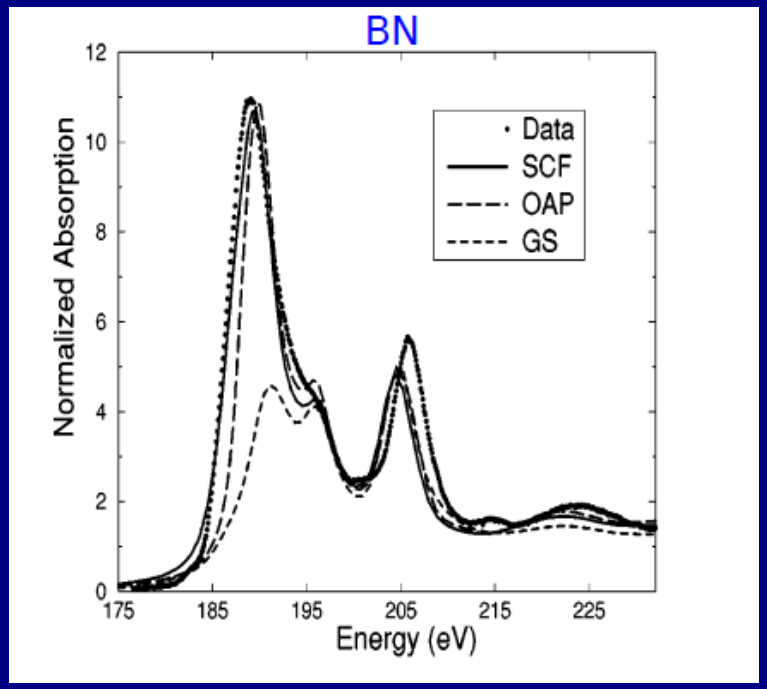


FEFF: Key Approximations

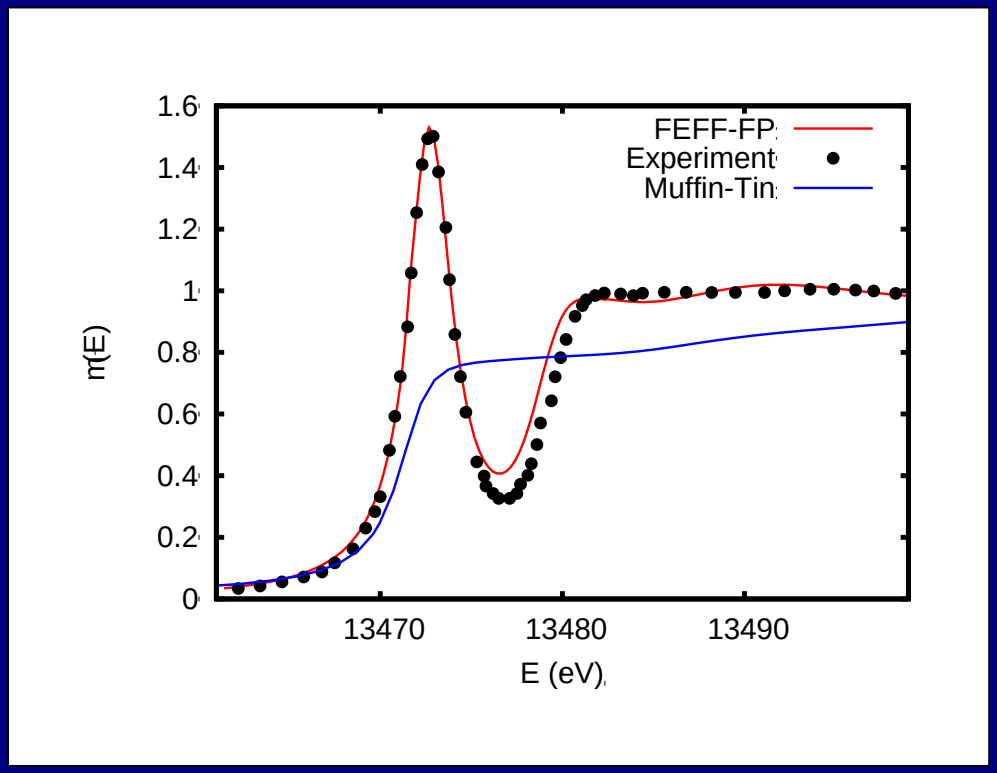
- Spherical muffin-tin potentials
- Local Density approximation
- Quasi-particle approximation
- Core-hole treatment

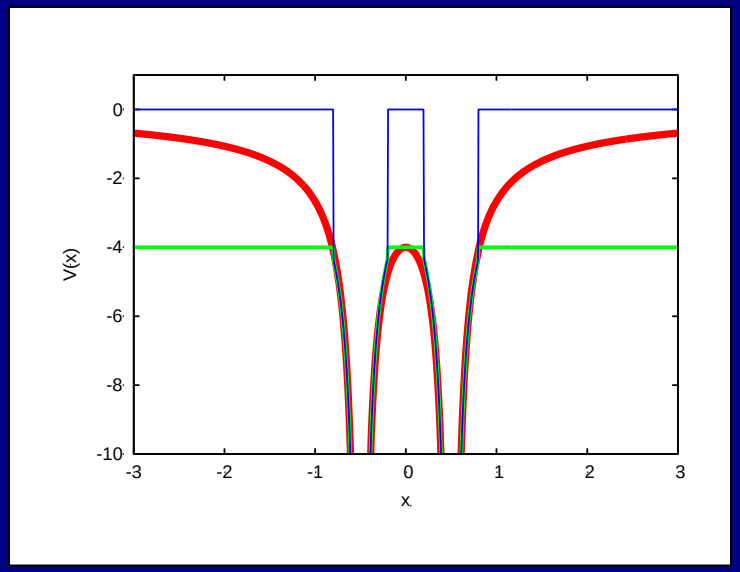
When might approximations break down?

- 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

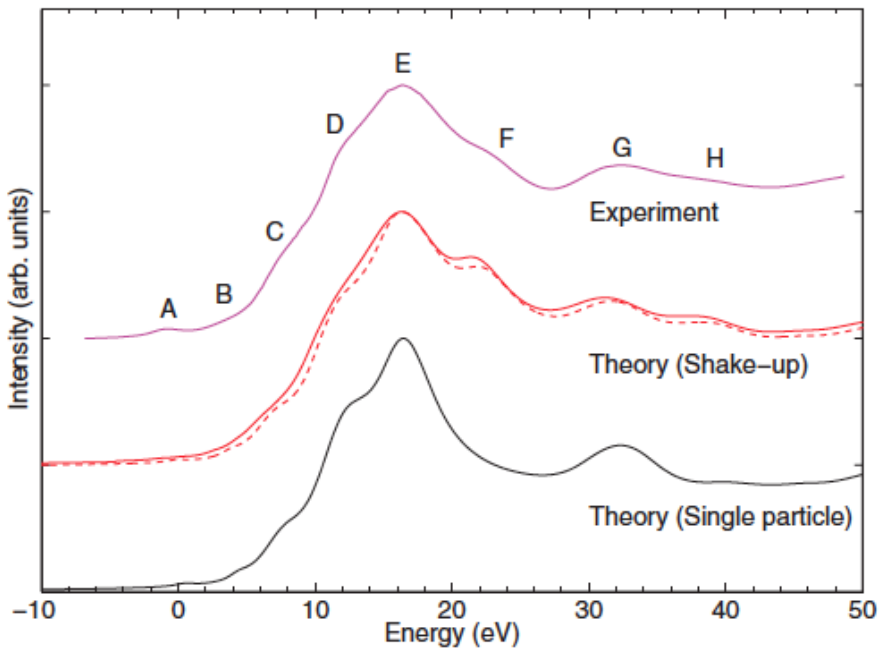
Br_2



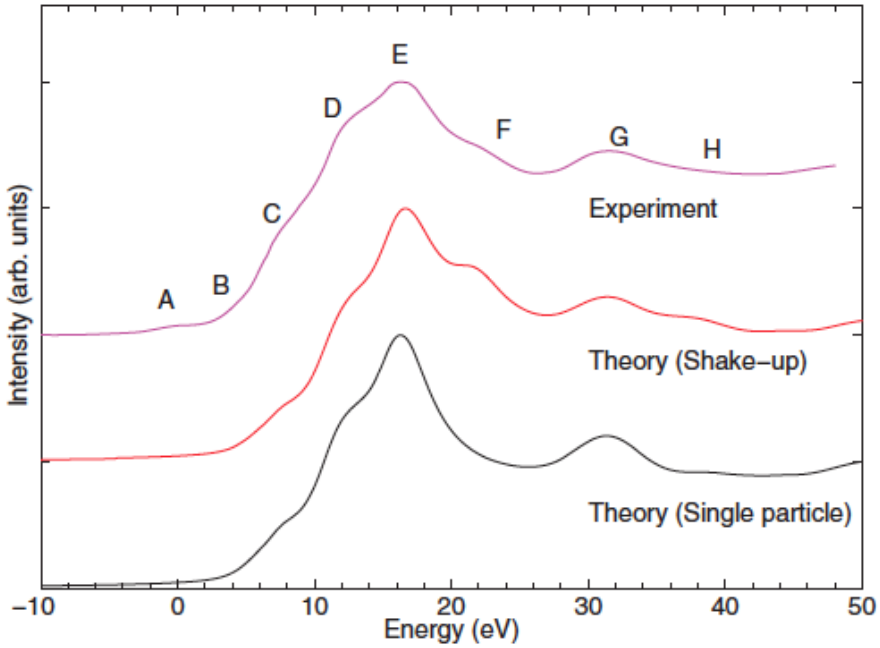


Many-Body Effects: Charge Transfer

NiO



CoO



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

Conclusions

- RSGF method
  - Pros
    - No restriction on symmetry
    - Large systems
    - Wide energy range
    - Relativistic/All electron
    - Can include self-energy effects
    - Easy to use
  - Cons
    - Spherical muffin tin approximation
    - Difficult to incorporate many-body effects

Thank You!

- Rehr group members
  - John Rehr
  - Fernando Vila
  - Kevin Jorrissen
  - Egor Clevac
  - Andrew Lee
  - Shauna Story

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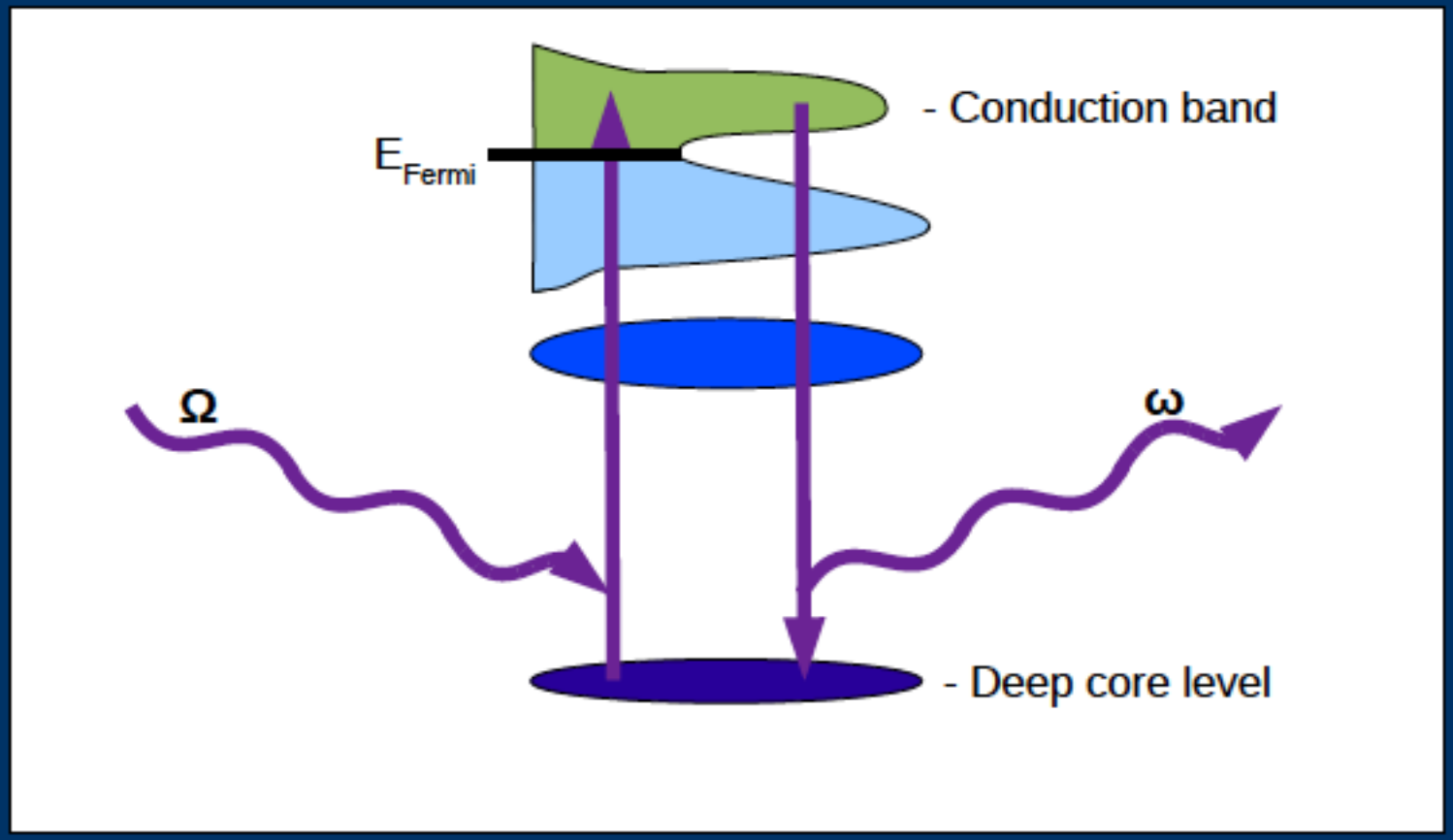
Workshop

- http://leonardo.phys.washington.edu/feff/BNL_XANES_WORKSHOP_2014.zip

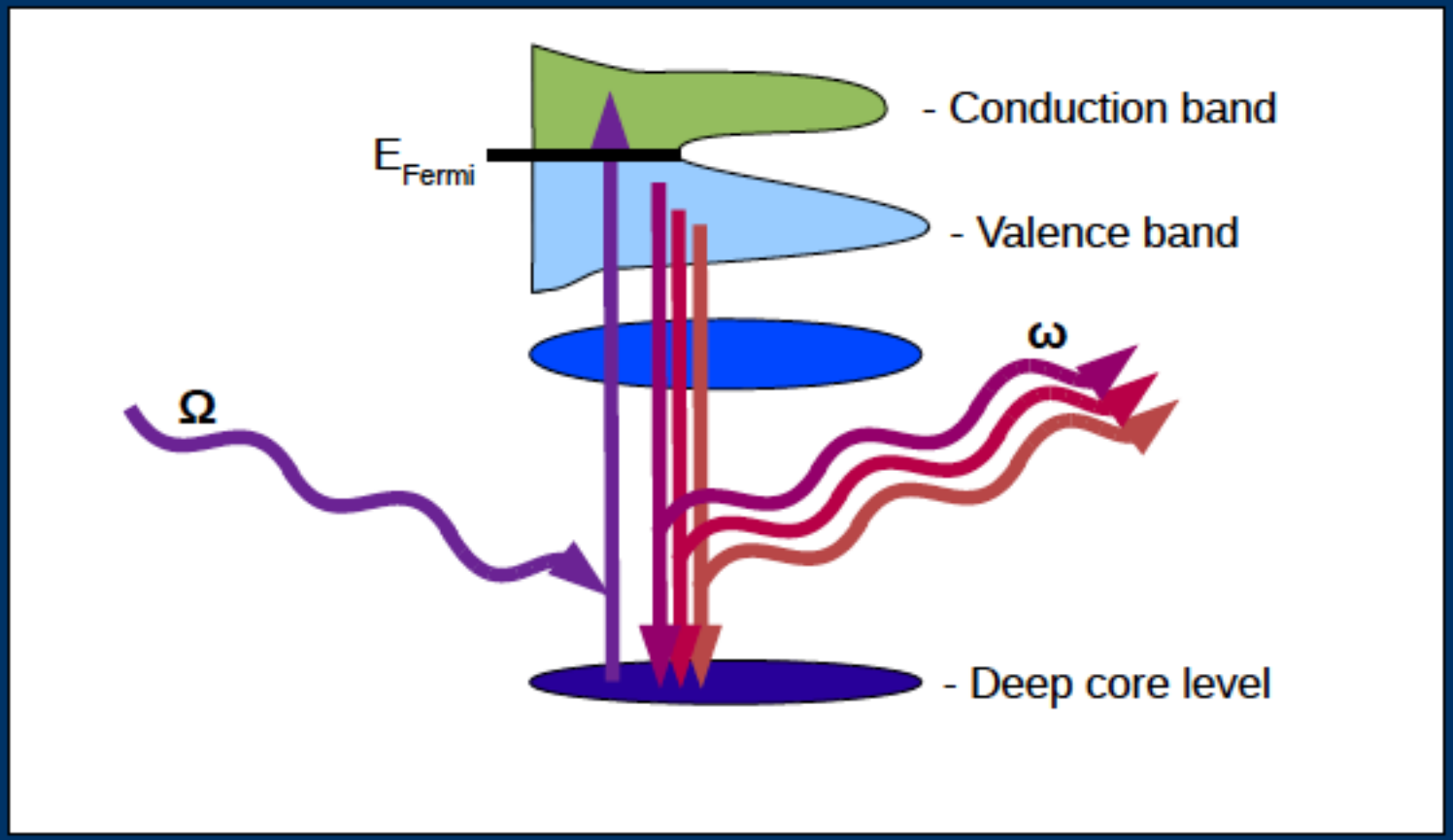
Theory of RIXS

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

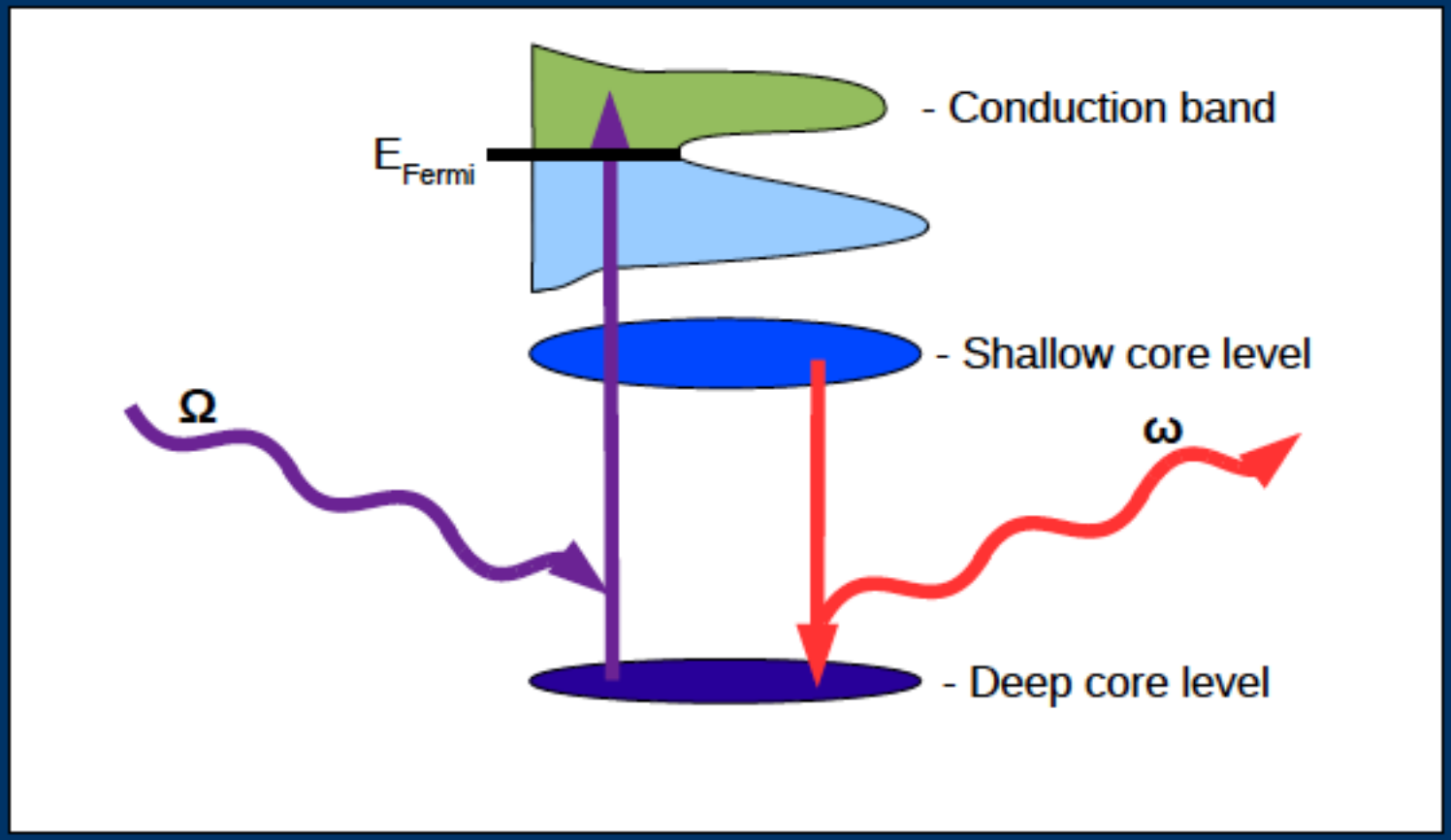
I. "Indirect" RIXS



I. "Direct" RIXS or RXES



I. "Direct" RIXS or RXES



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)

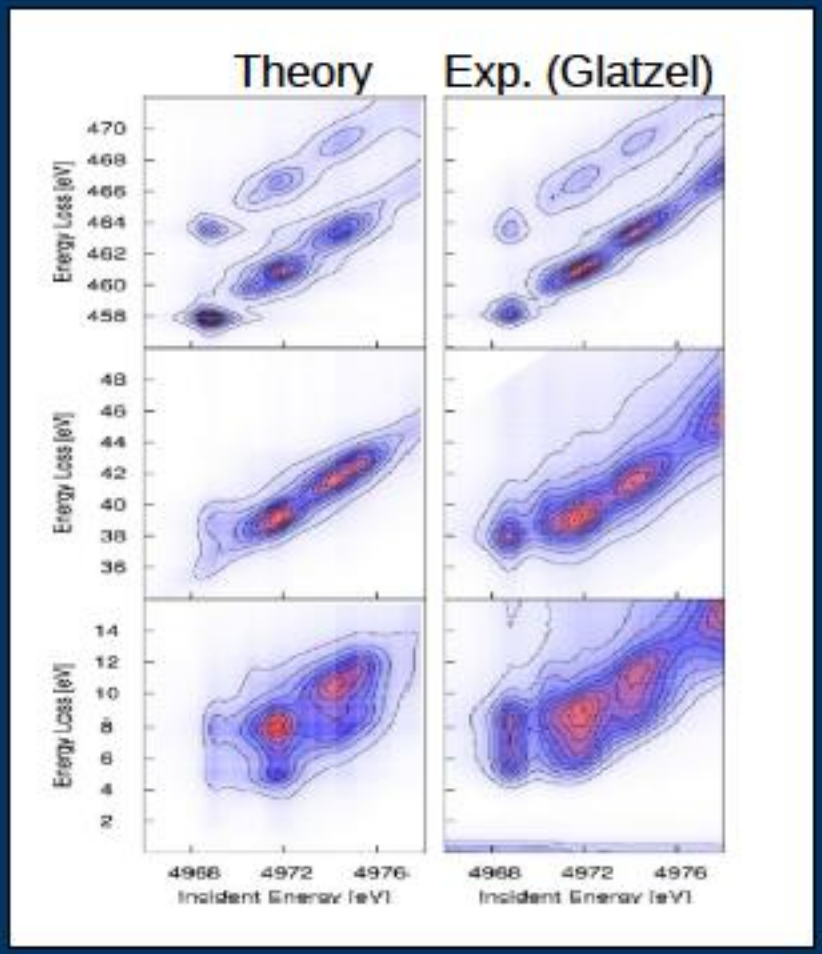
[2]Fujikawa et al., J. Electron Spectrosc. Relat. Phenom. 134, p 195 (2004)

III. Ti K RIXS: TiO_2 - Anatase

Progression with strength of ΔV

Quadrupole peak: Localized state

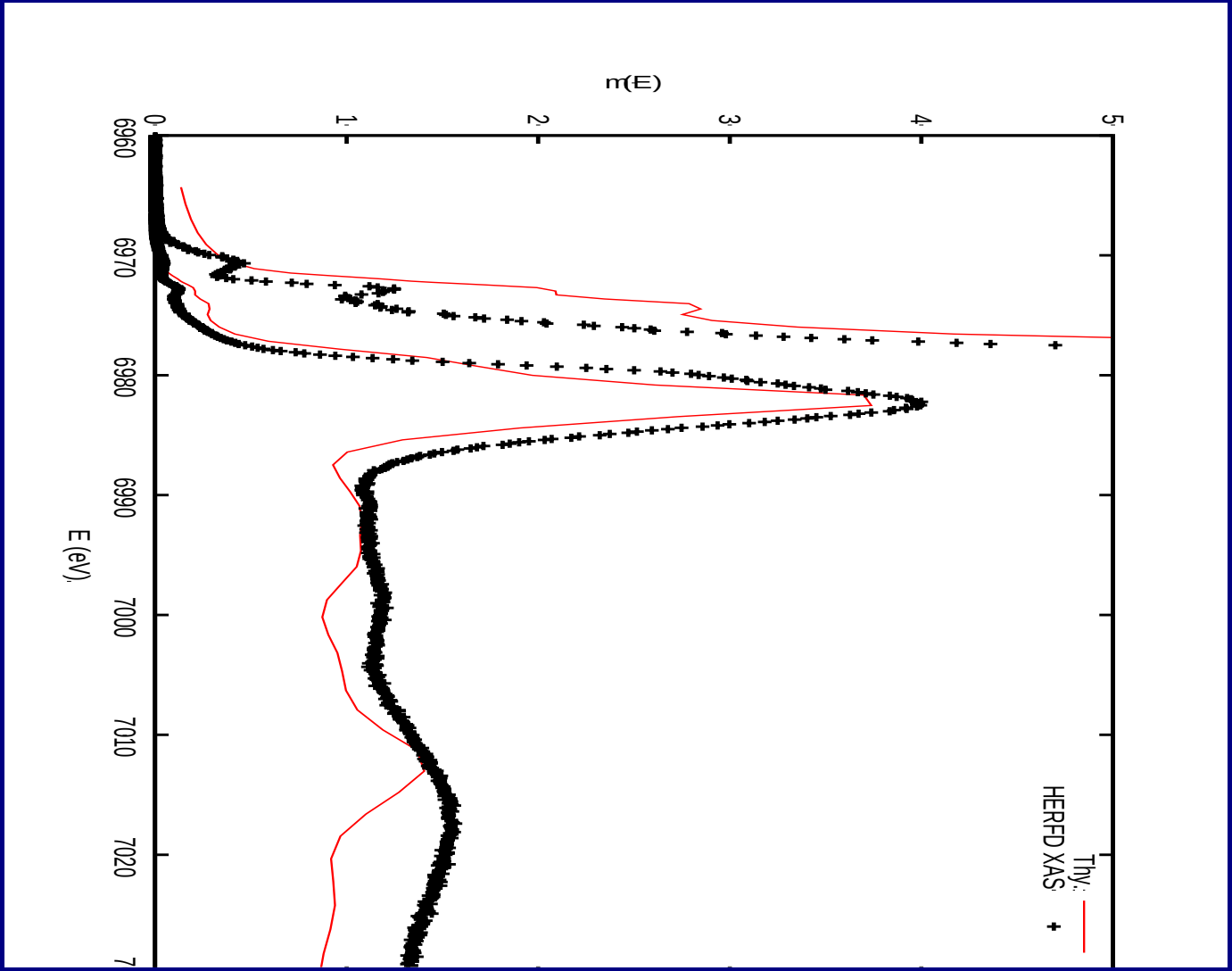
Qualitative behavior reproduced



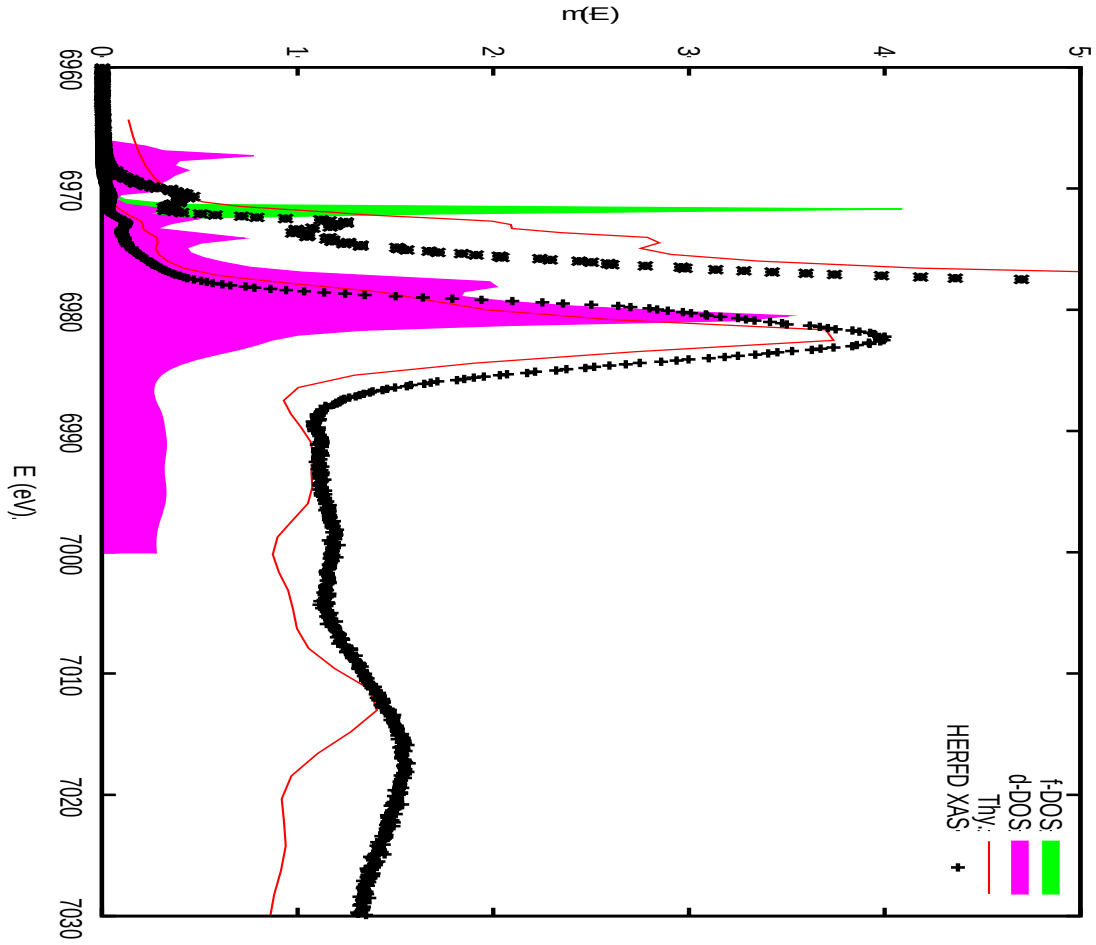
XANES is sensitive to …

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

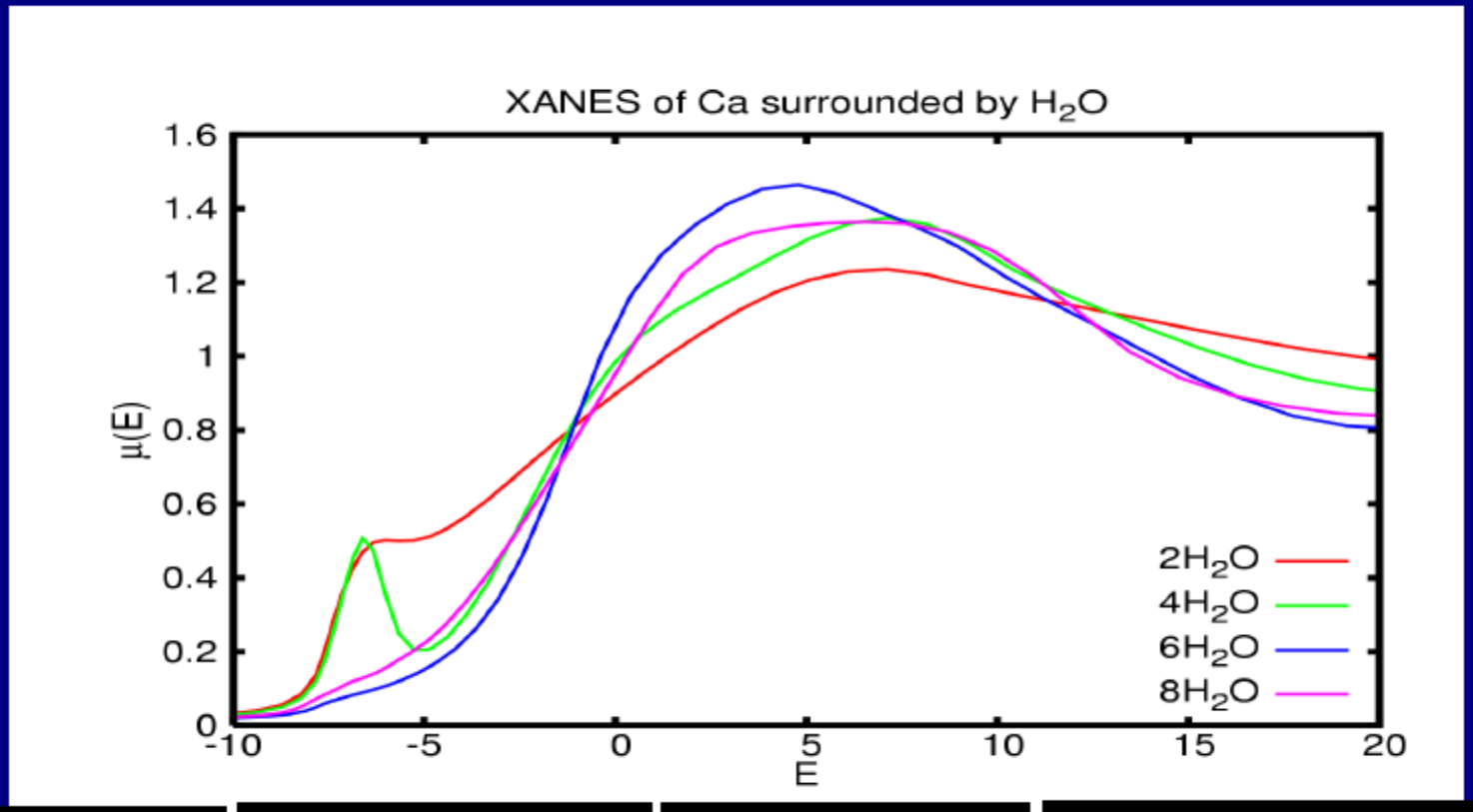
Eu_2O_3 L3 XANES

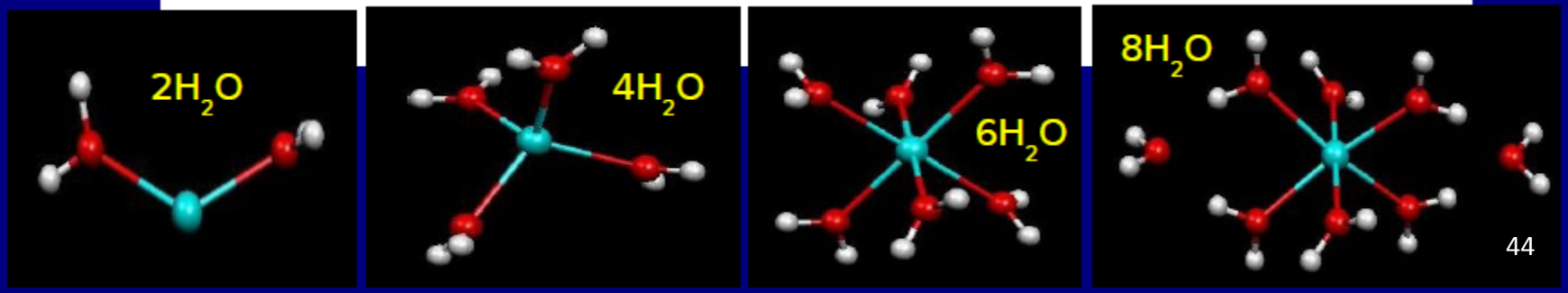


Eu_2O_3 L3 XANES

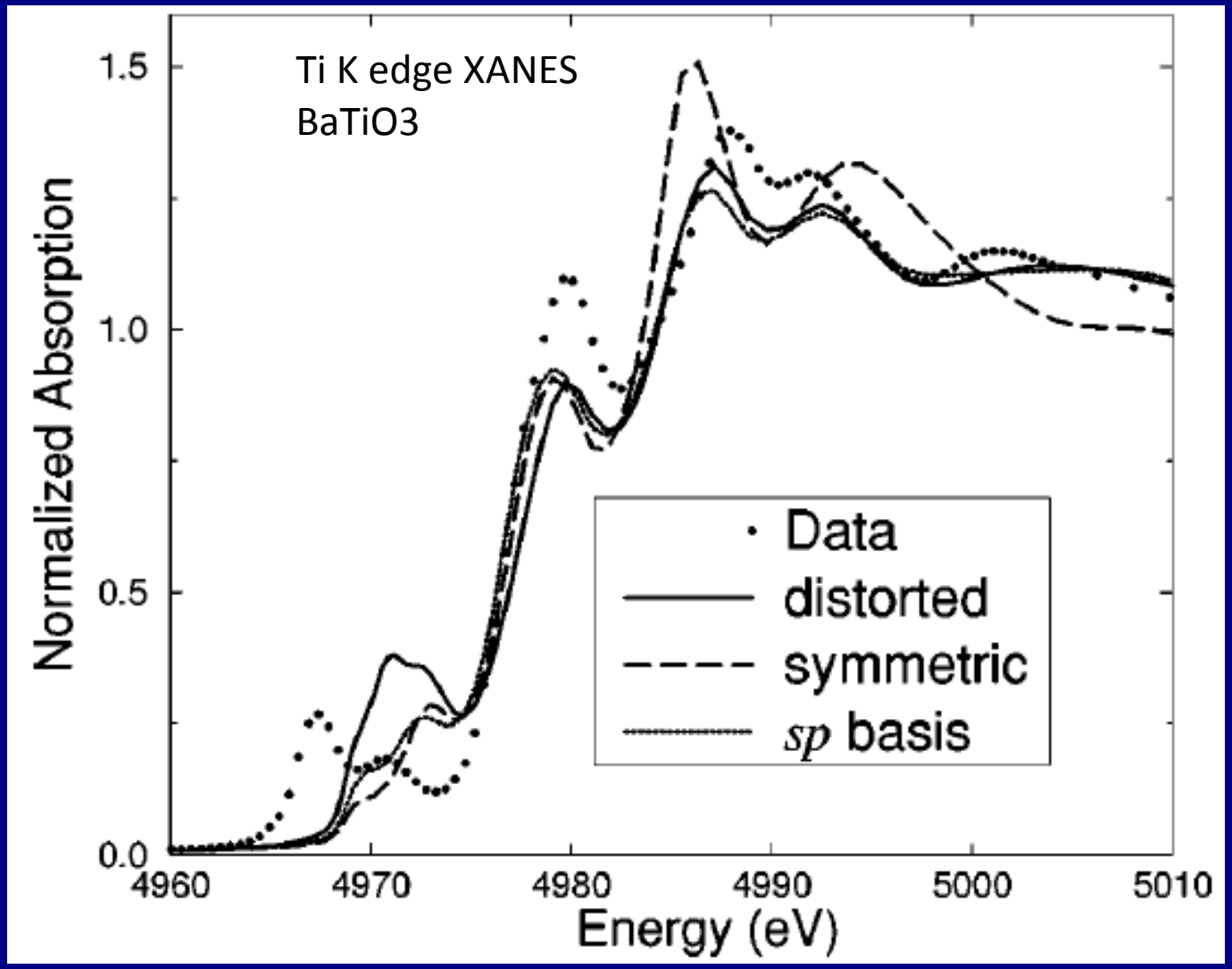


Symmetry and Pre/Near-Edge Features

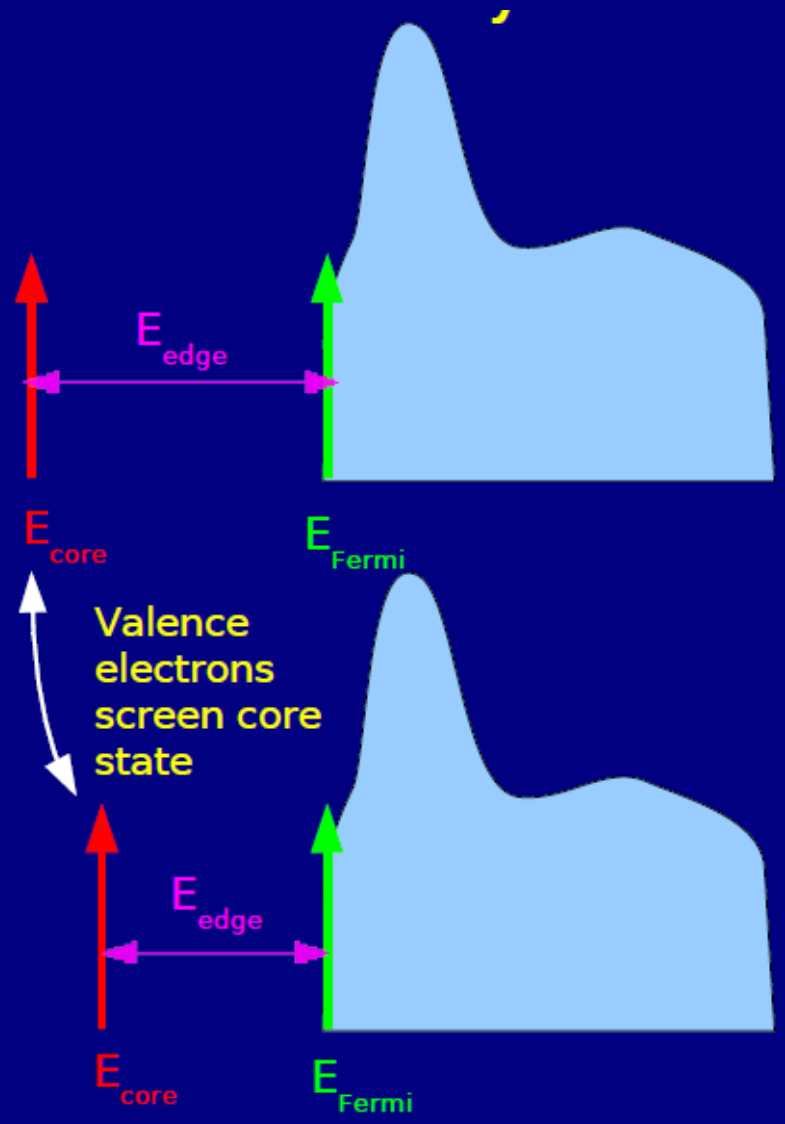


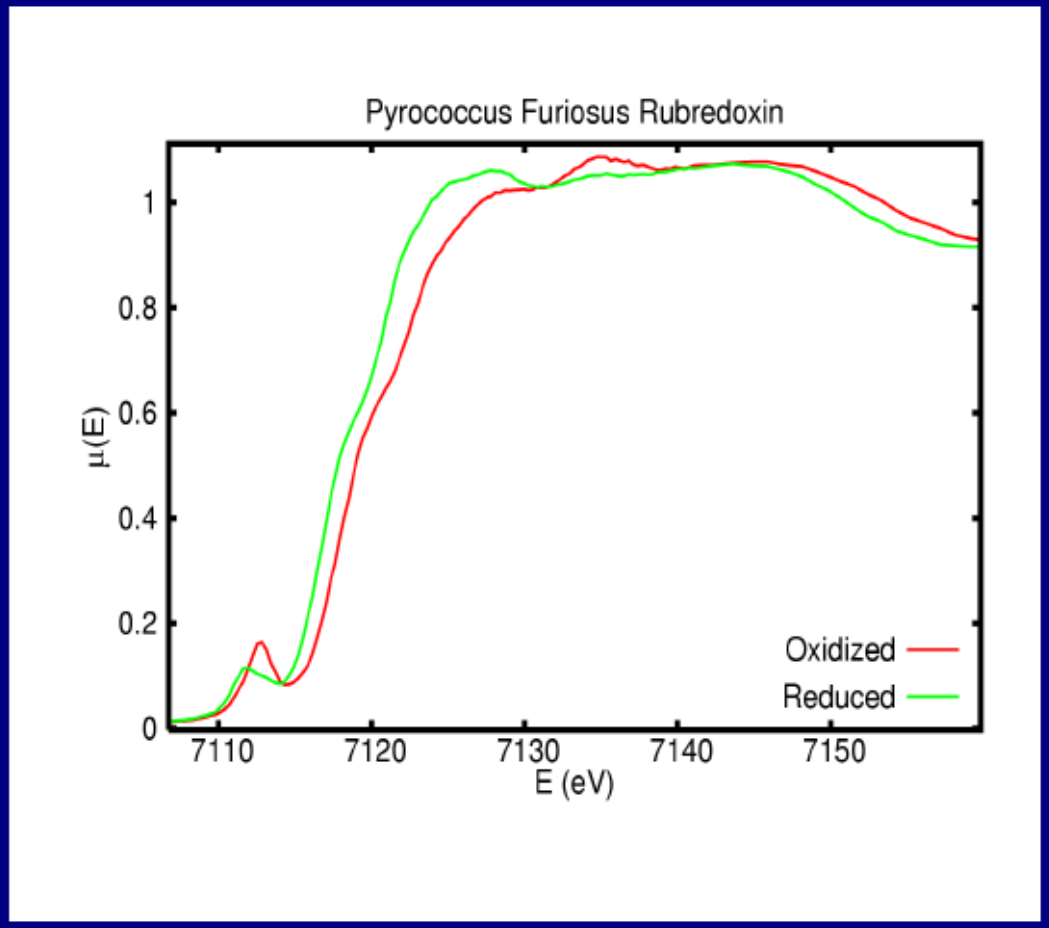


Symmetry and Pre/Near-Edge Features

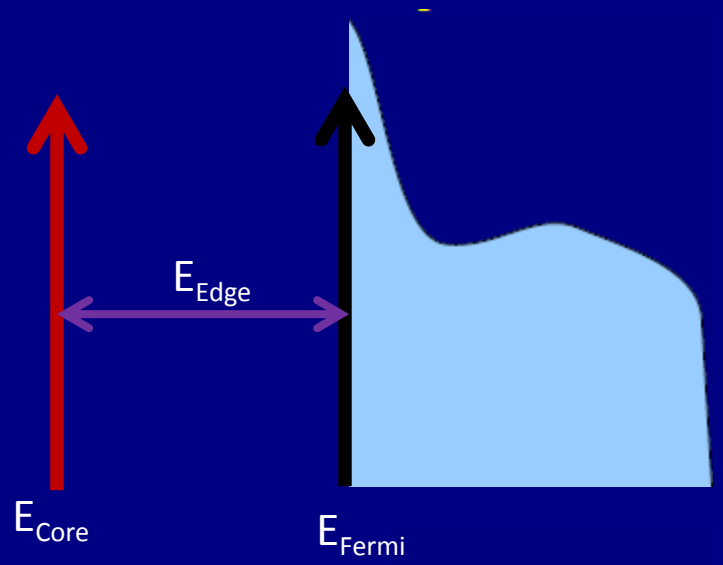


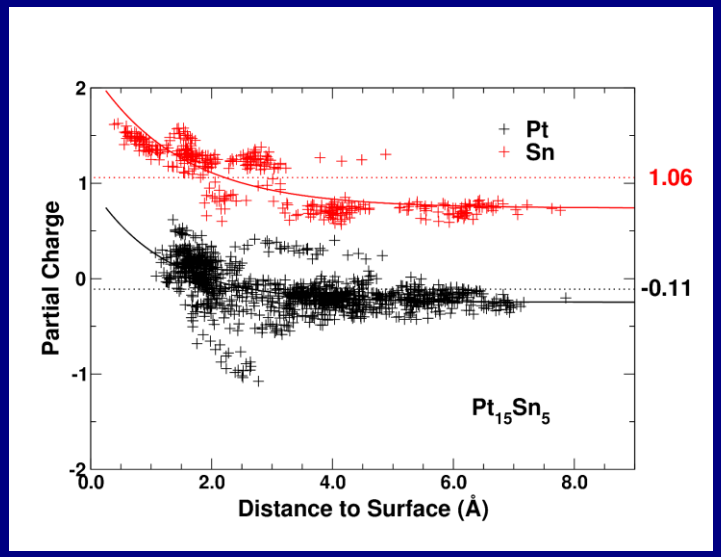
Edge Position and Charge Transfer

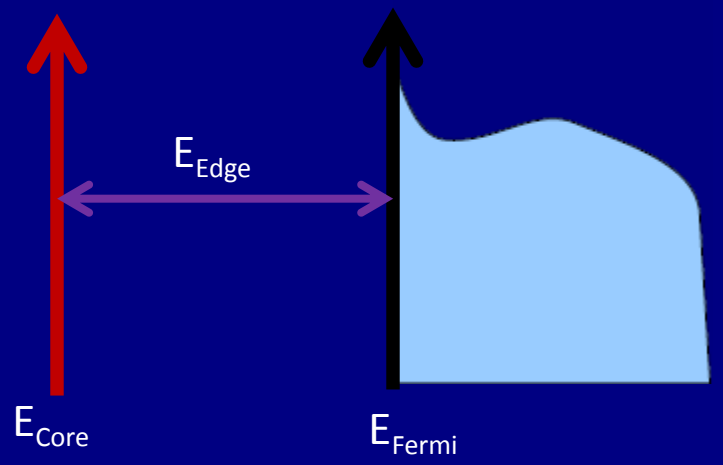


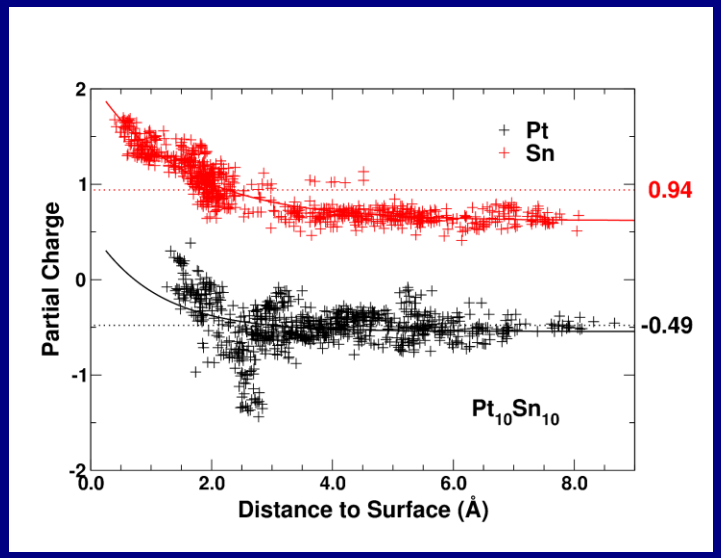


Edge Position and Charge Transfer

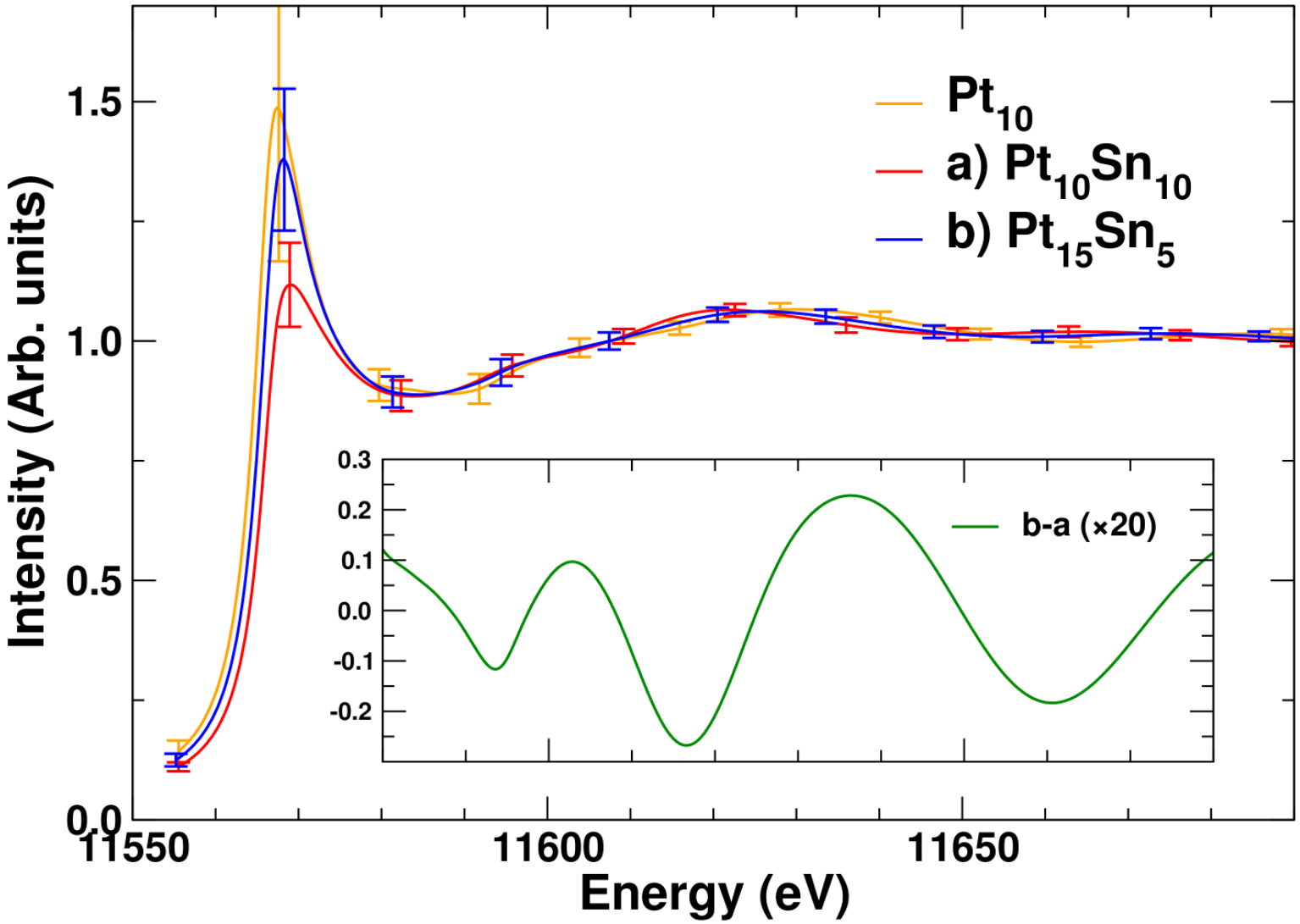








F. D. Vila

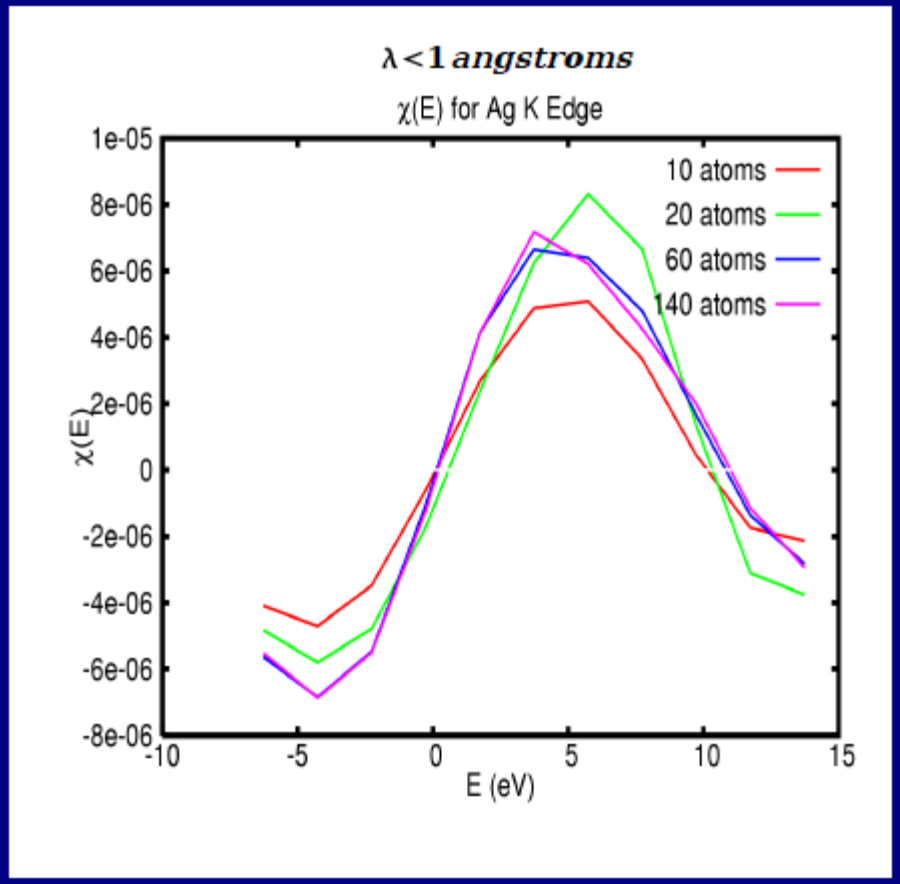

Pt10
a) Pt10Sn10
b) Pt15Sn5
b-a (×20)
Intensity (Arb. units)
Energy (eV)
0.0
0.5
1.0
1.5
11550
11600
11650
0.3
0.2
0.1
0.0
-0.1
-0.2

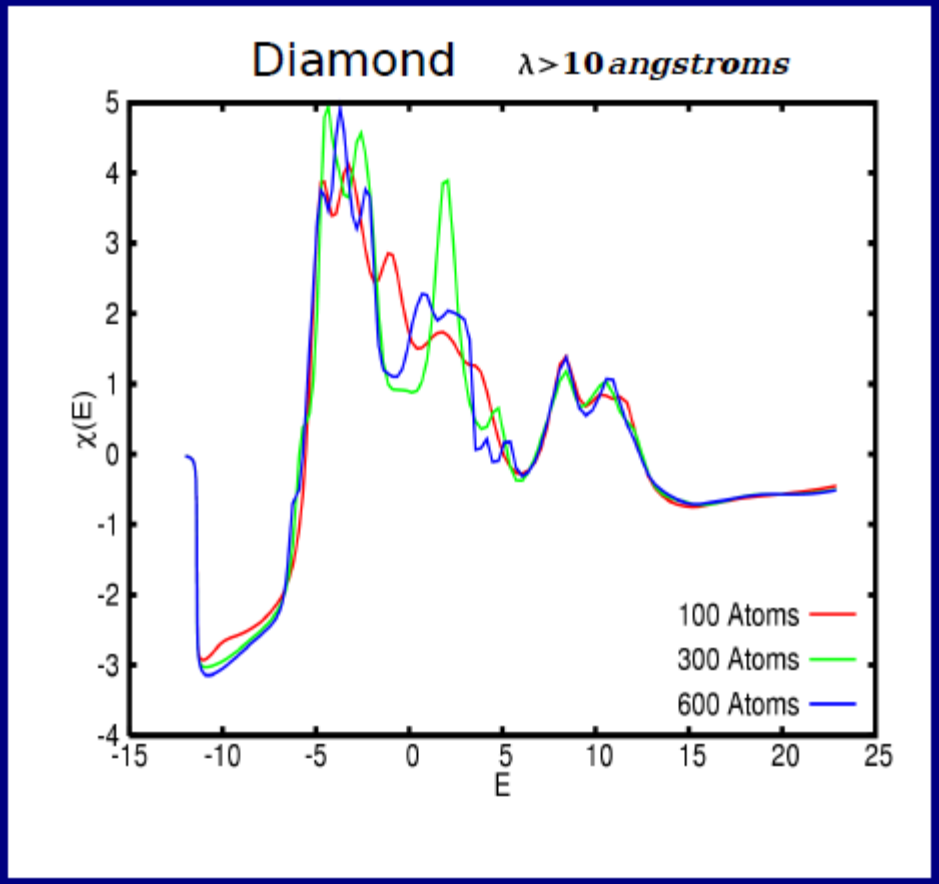
Simulation of XANES with FEFF

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

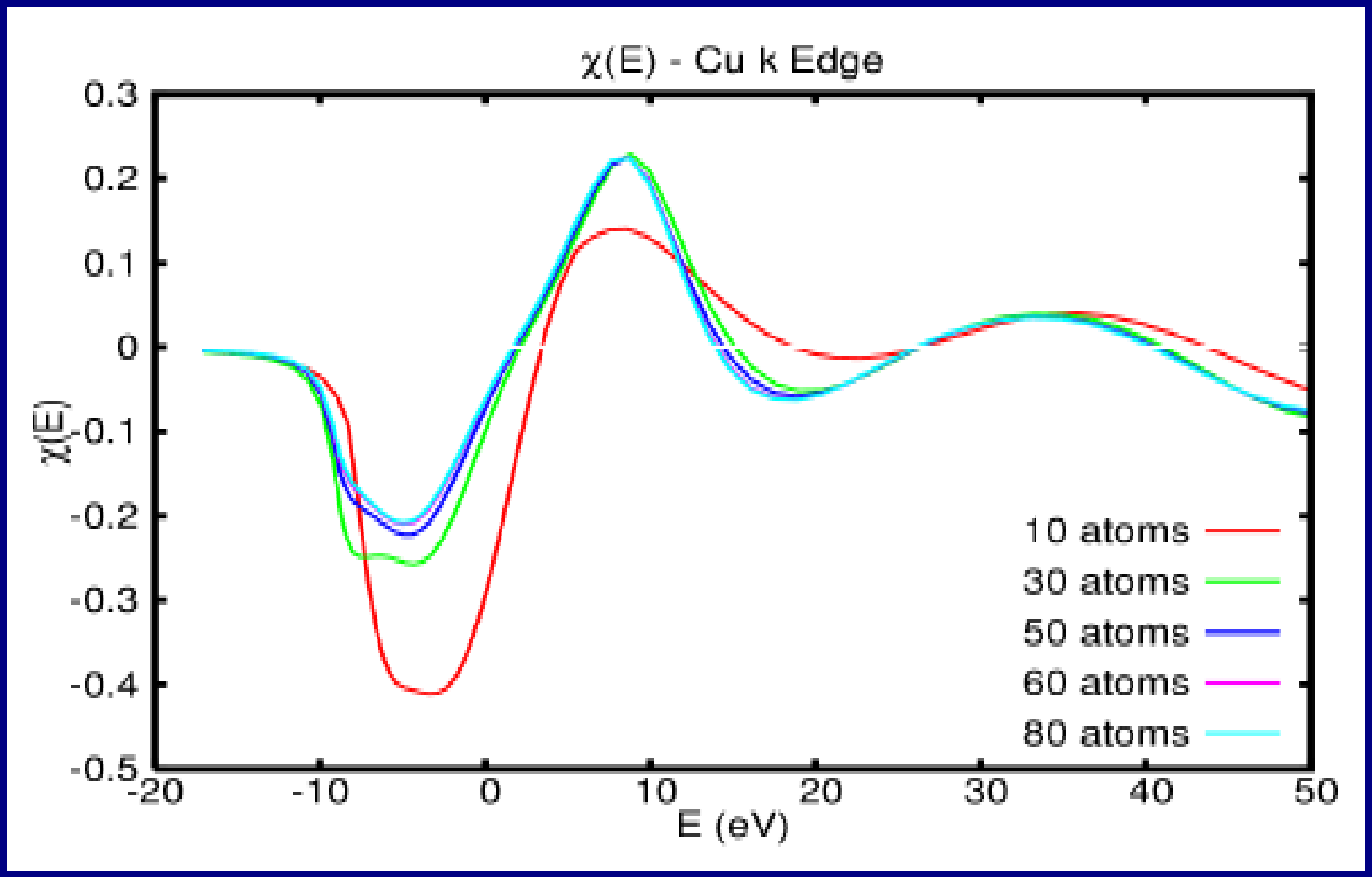
FMS Convergence

- Guess: Inelastic mean free path

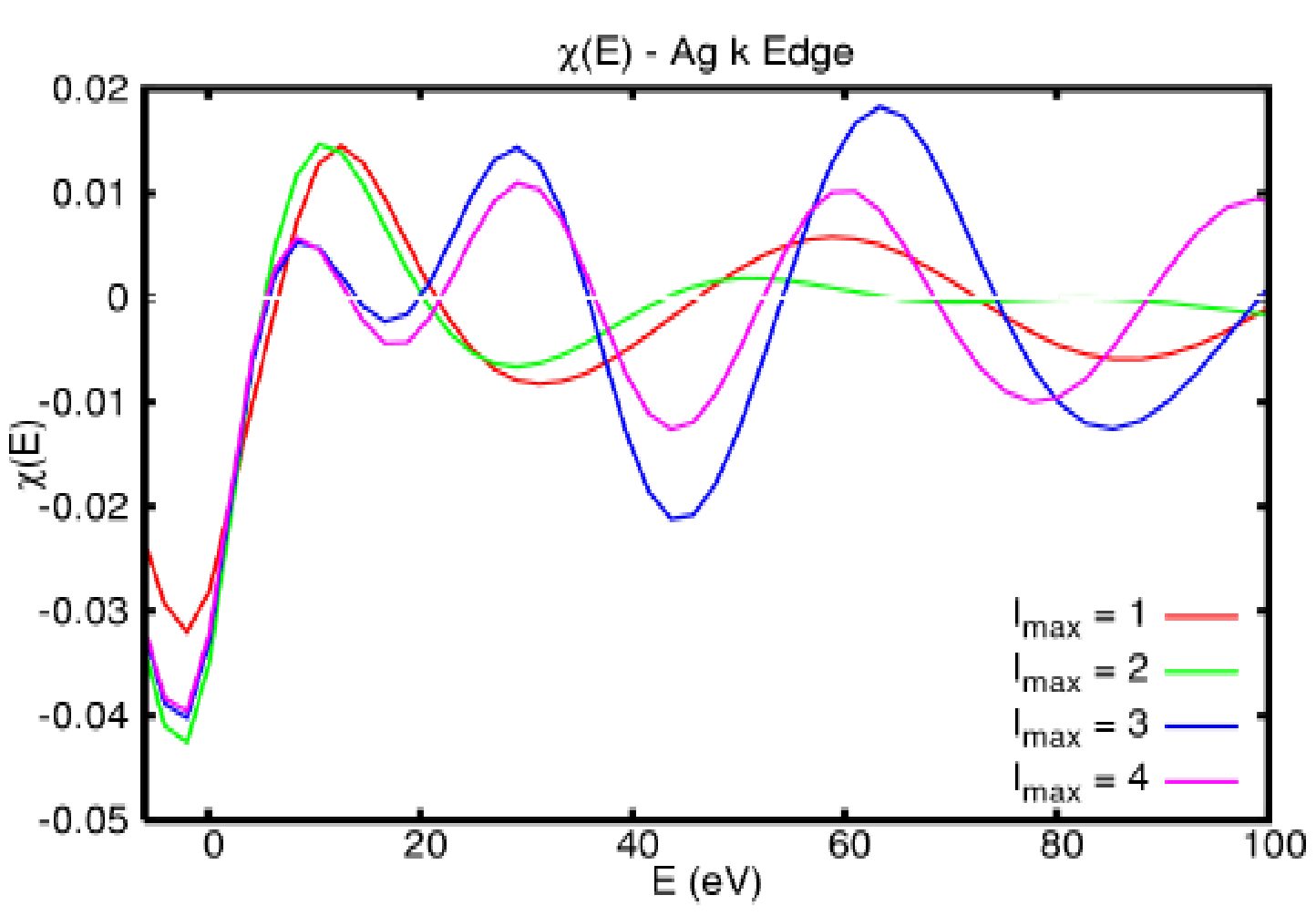




SCF Convergence



L_{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