Advances in Theory and Analysis of EXAFS

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†*Supported by NIH/SSRL, DOE and CMSN*

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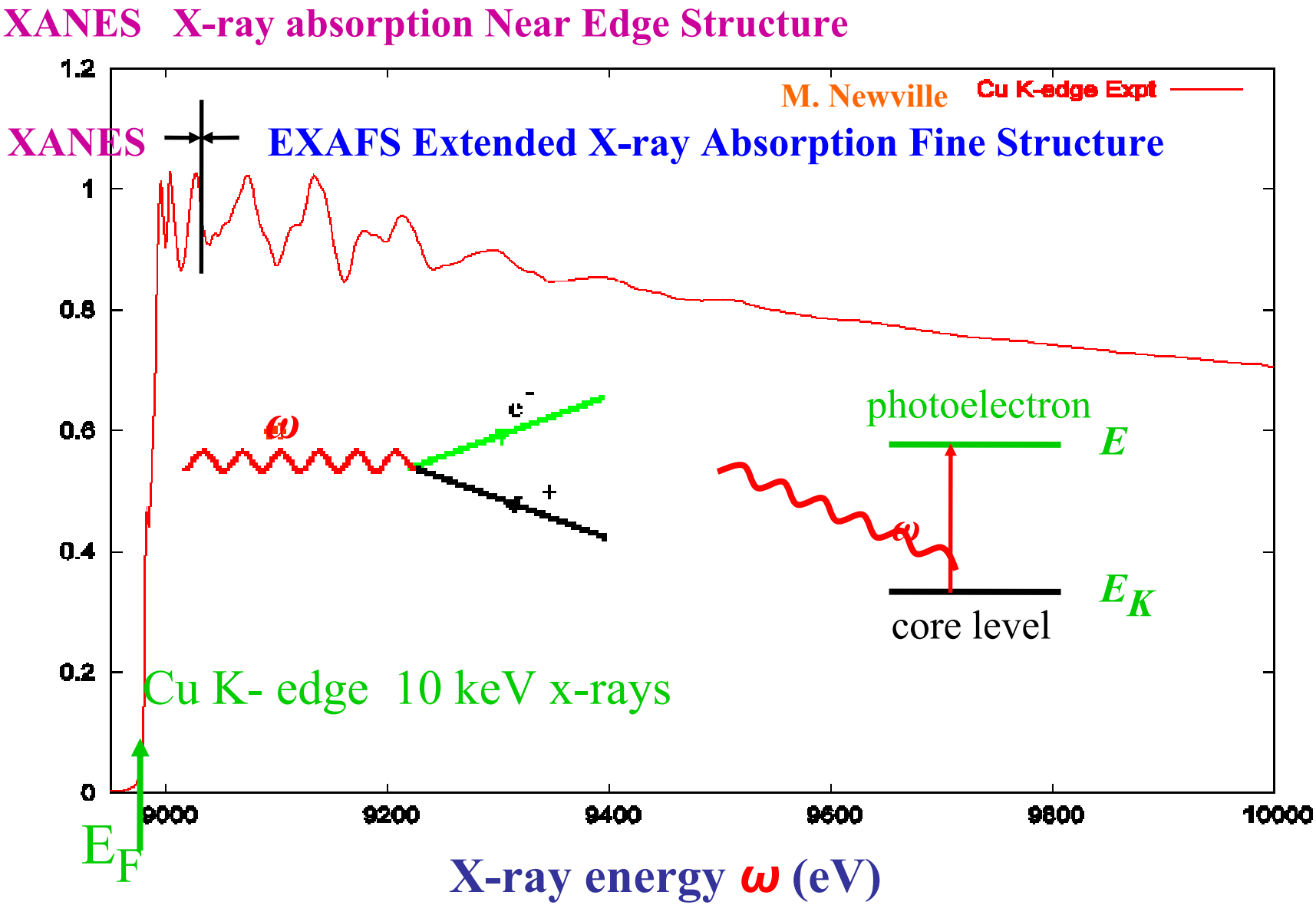
*Supported by NIH/SSRL, DOE, CMSN

- **GOAL**: *ab initio* Theory of *XAS, EELS, ···*
- *No* adjustable parameters
- Accuracy ~ experiment
- **GOAL**: Quantitative interpretation
- Inverse problem: What's in a spectrum?
- Atomic structure, chemistry, ···
- **TALK**:

1. EXAFS and XANES — Theory, History
2. NEW Interpretation — Bayesian Analysis

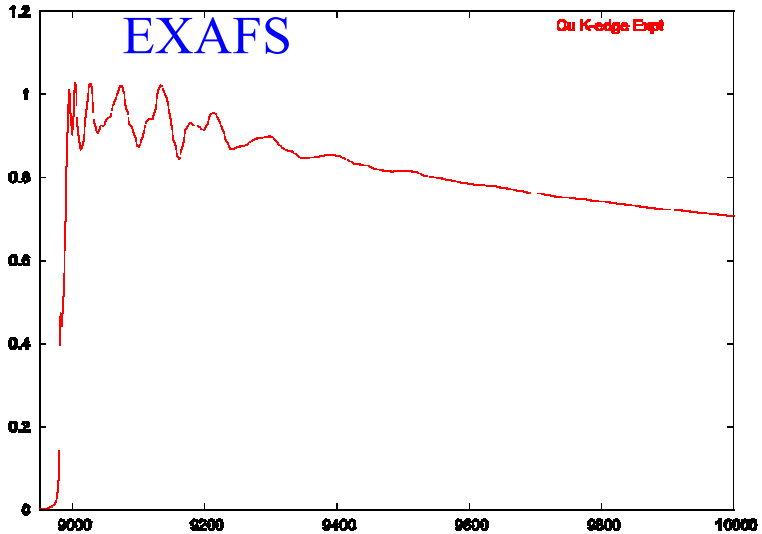
Experiment: X-ray Absorption Spectra



Qualitative Interpretation of EXAFS

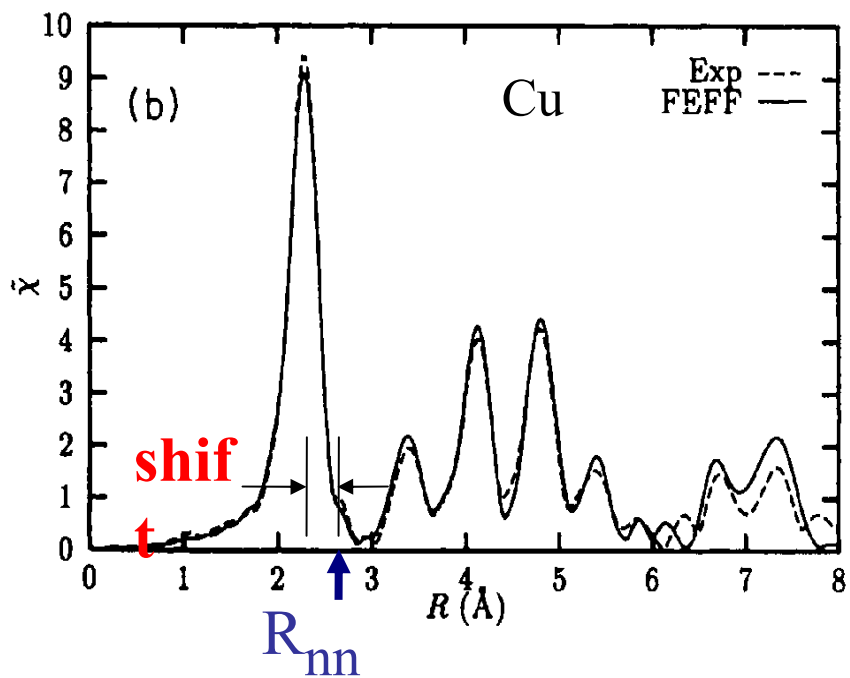
D.Sayers Stern & Lytle 1970

Short range order theory



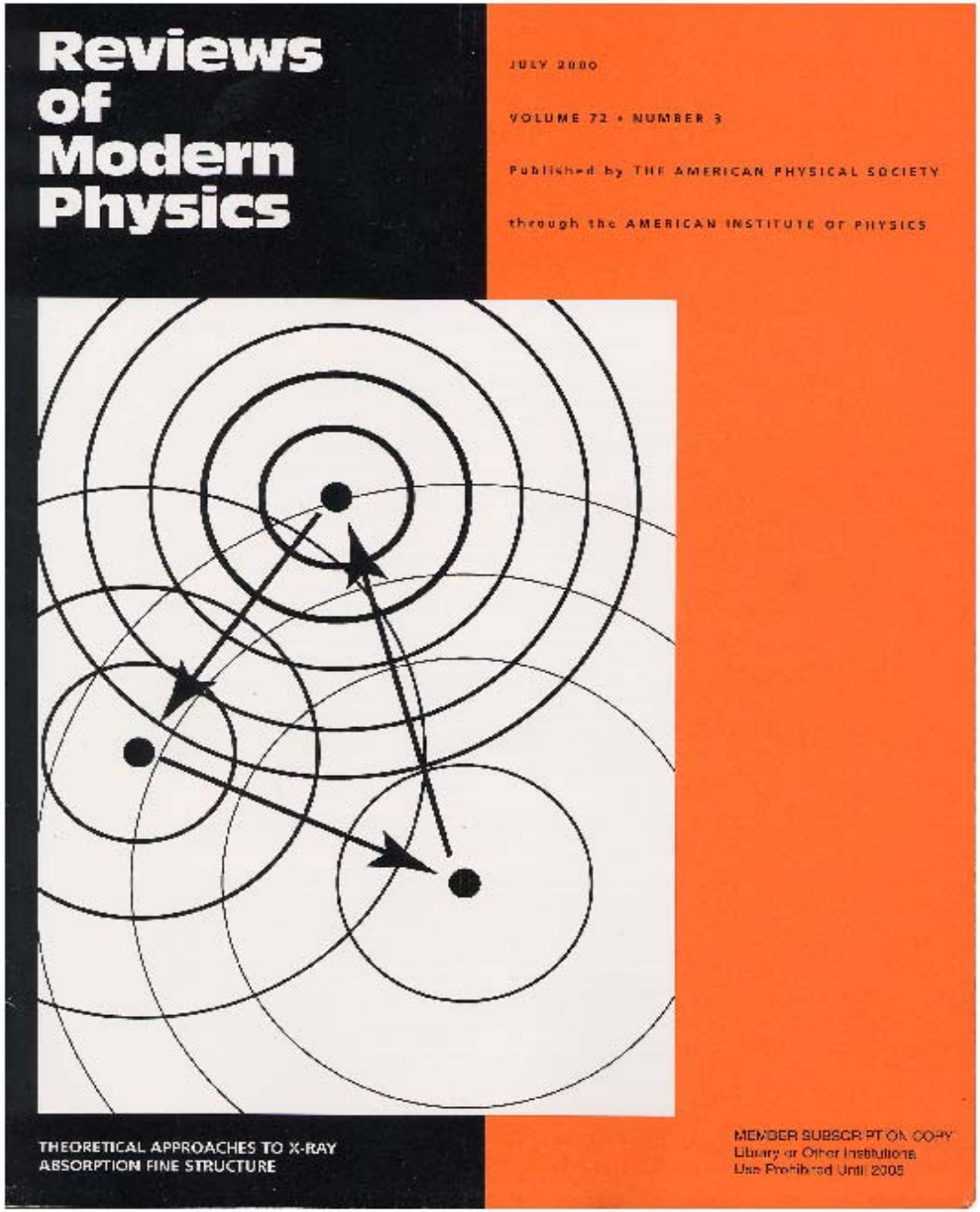
Sayers EXAFS Fourier Transform

→ **Shifted** Radial Distribution



→ **X-ray Microscope!**

BUT need to calibrate experiment with "Standard"



Quantitative

Theory of EXAFS

J. J. Rehr & R.C. Albers

Rev. Mod. Phys. **72**, 621 (2000)

Quantitative EXAFS Theory

Three Key Developments

Curved Wave Scattering Theory f_{eff}

Inelastic Losses $\Sigma(E)$

EXAFS *Debye Waller Factors* σ^2

Must extend ground state methods!

REVISED Stern-Sayers-Lytle XAFS Formula

Multiple Scattering Expansion: sum over paths Γ

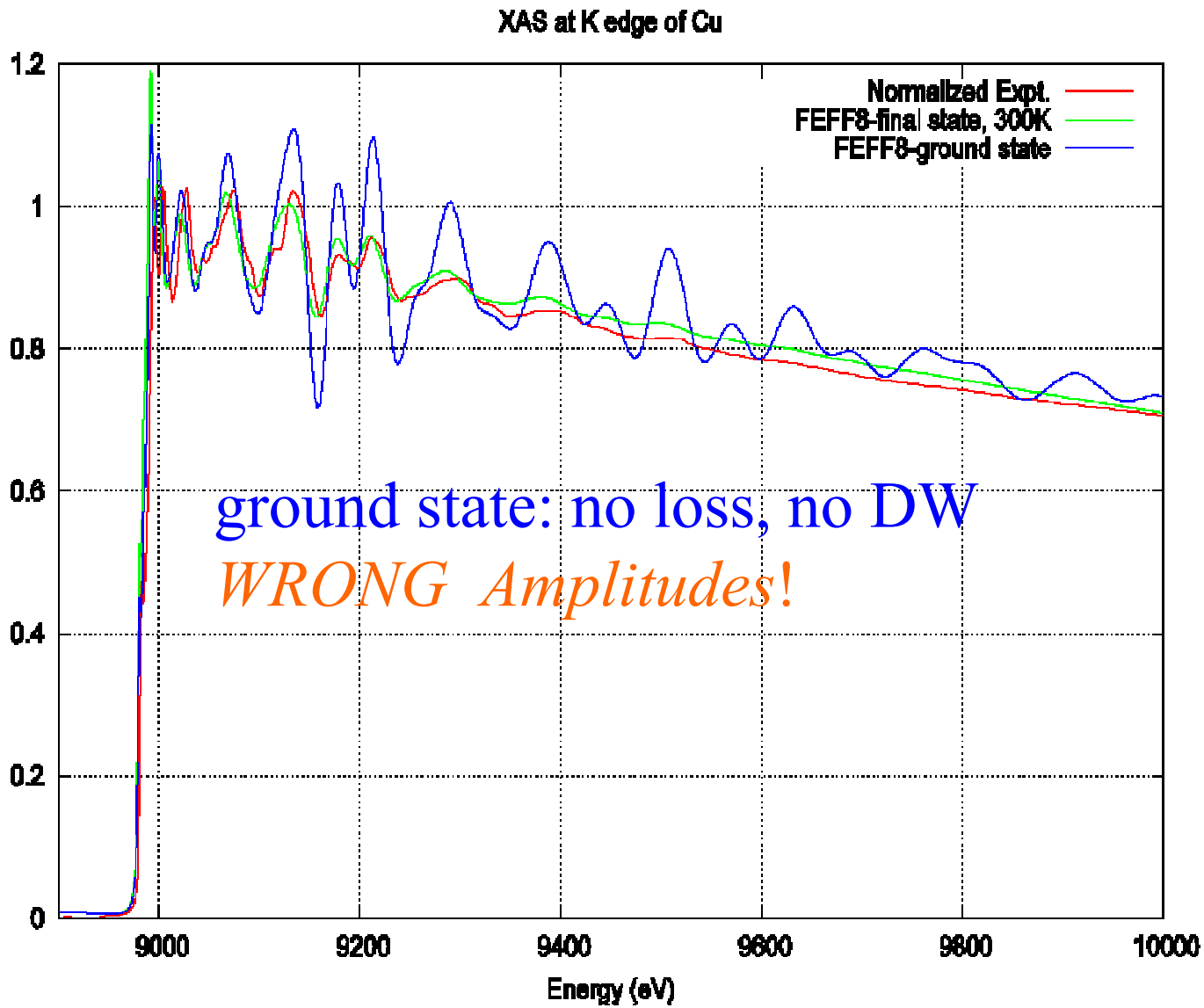
$$\chi_\Gamma(E) = S_0^2(E)\, N \frac{\left|f_{eff}(k)\right|}{kR^2}.\sin(2kR + 2\delta_c(k) + \phi(k))e^{-2R/\lambda(k)}e^{-2\sigma^2k^2}$$

N = coordination number R = ½ path length

Same form as Stern-Sayers-Lytle ***BUT***

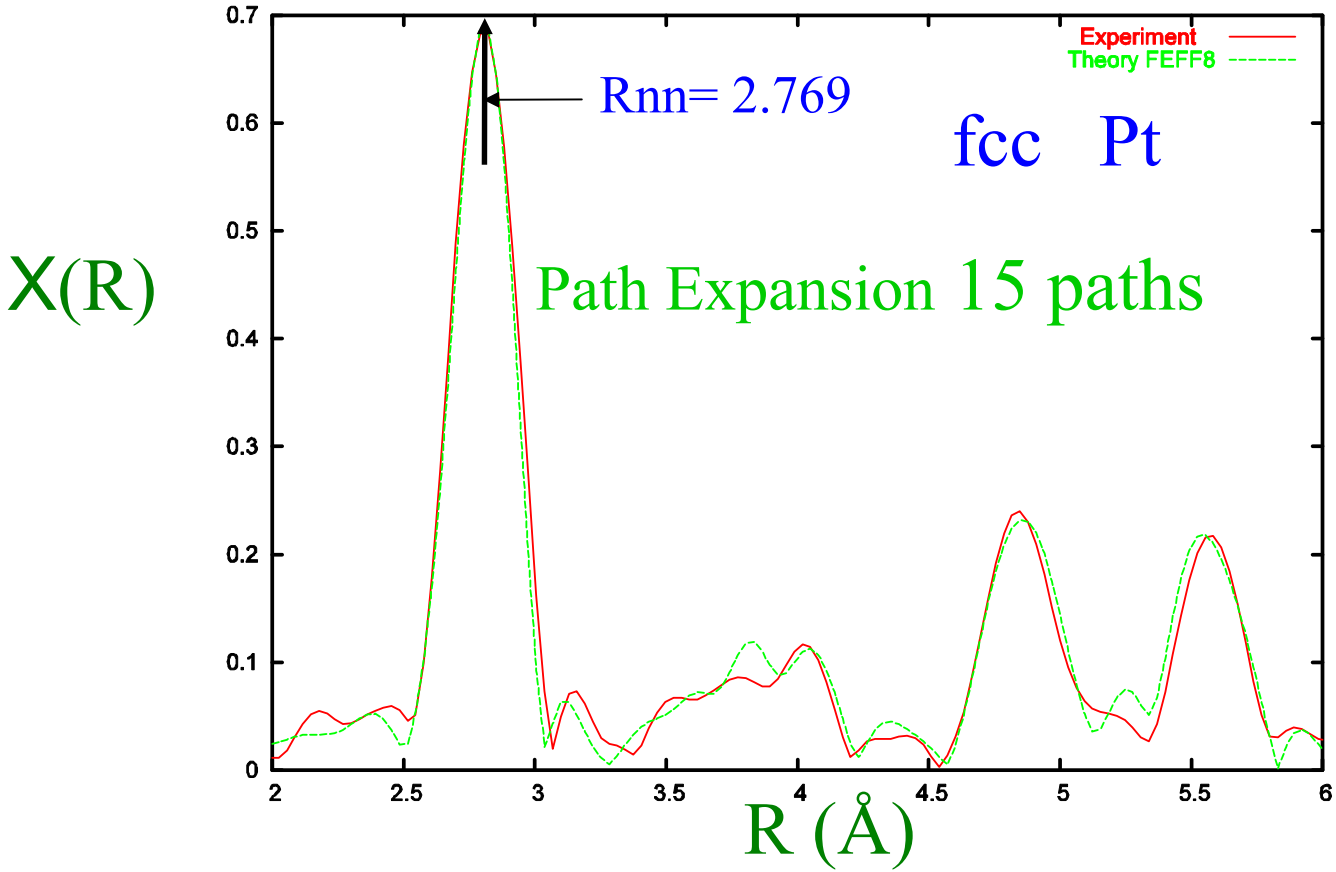
ALL PARAMETERS RENORMALIZED !

Ground-state vs FEFF vs Expt



Phase Corrected EXAFS Fourier Transform

No shift! Accurate distances to < 0.01 Å



Modern EXAFS Theory: FEFF6 Code

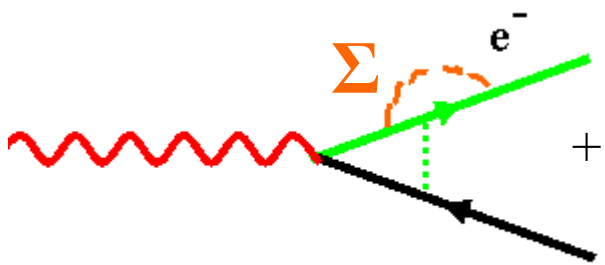
XANES Theory Key Developments

Quasi-particle **Theory**

- Beyond Ground State Density Functional Theory

- Inelastic losses, self-energy **Σ**

- Core-hole effects



Standard Quasi-particle Theory of XAS

Beyond DFT!

Fermi Golden Rule for XAS $\mu(\omega)$

$$\mu(\omega) \sim \Sigma_f |\langle \psi_f | d | \psi_i \rangle|^2 \delta(E_f - E_i - \hbar\omega)$$

Calculate with *Excted State Electronic Structure*

Quasi-particle *final states* ψ_f - with core hole

$$\left[\frac{p^2}{2m} + V'_{coul} + \Sigma(E)\right] \psi_f = E_f \psi_f \quad (Dyson\ Eq.)$$

Final state rule $V'_{coul} = V_{coul} + V_{core-hole}$

Non-hermitian Self-energy $\Sigma(E) = iGW$

Inelastic Mean free paths $\Sigma(E)$ replaces Vxc !

$$\lambda = k/|\mathrm{Im}\,\Sigma(E)| \approx 5 - 20\ \text{Å}$$

Non-standard Quantum Mechanics !

Wave-function vs Green's functions

Paradigm shift:

Use Green's functions *not* wave functions!

- Golden rule via Wave functions

$$\mu(E) \sim \Sigma_f |\langle i|\hat{\epsilon}\cdot\mathbf{r}|f\rangle|^2 \delta(E-E_f)$$

- Golden rule via Green's functions *Efficient!*

Theorem: $-\frac{1}{\pi}\mathrm{Im}\, G(\mathbf{r}',\mathbf{r},E) = \Sigma_f |f\rangle\delta(E-E_f)\langle f|$

$$\boxed{\mu(E) \sim -\frac{1}{\pi}\mathrm{Im}\,\langle \mathrm{i}|\,\hat{\epsilon}\cdot\mathbf{r}'\,\mathrm{G}(\mathbf{r}',\mathbf{r},\mathrm{E})\,\hat{\epsilon}\cdot\mathbf{r}\,|\mathrm{i}\rangle}$$

Real-space Green's Function Formalism

not k-space!

- $$\mu(E) \sim -\frac{1}{\pi}\mathrm{Im}\,\langle \mathrm{i}|\,\hat{\epsilon}\cdot\mathbf{r}'\,\mathrm{G}(\mathbf{r}',\mathbf{r},\mathrm{E})\,\hat{\epsilon}\cdot\mathbf{r}\,|\mathrm{i}\rangle$$

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

(MS path expansion - geometric series)

$$= [1 - G^0 t]^{-1} G^0$$ "full MS" "Real-space KKR"

Matrix inversion sums all paths implicitly!

- Separation $G = G^c + G^{scatt}$

$$\rightarrow \qquad \mu(E) \sim \mu_0(E)[1 + \chi(E)]$$

$\mu_0(E)$ Atomic background

$\chi(E)$ Fine structure

FEFF8 *ab initio*, Relativistic, Self-consistent, Full Multiple Scattering XANES Code

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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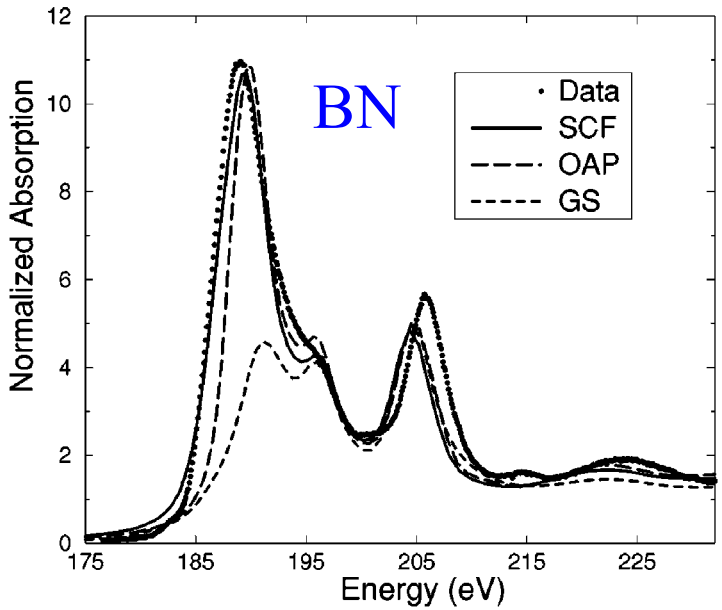
89 atom cluster

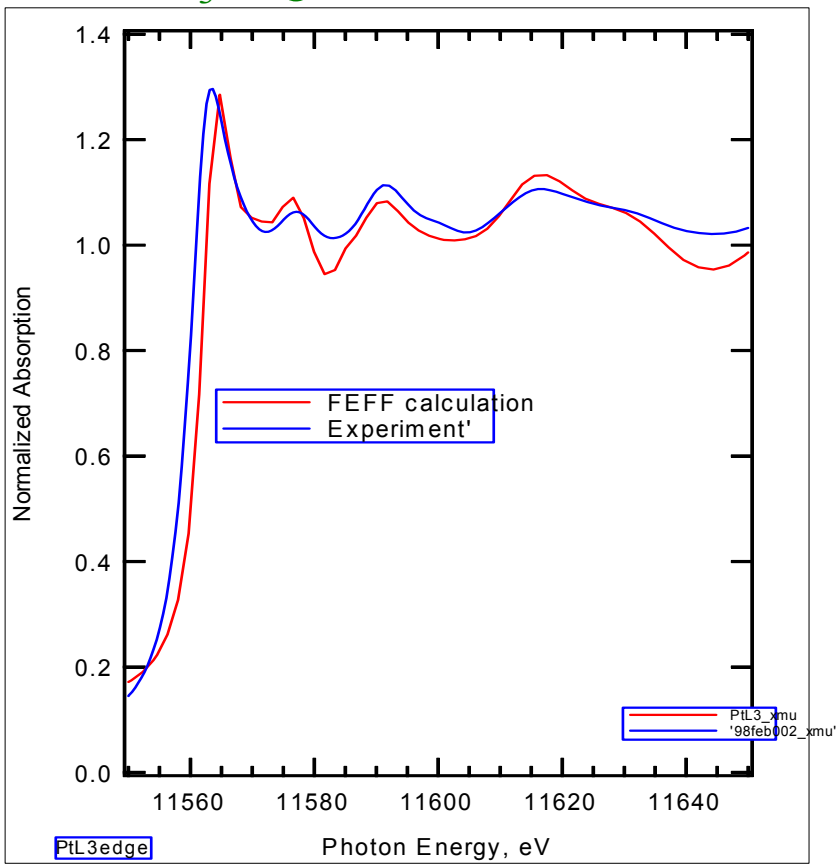


Core-hole, SCF potentials

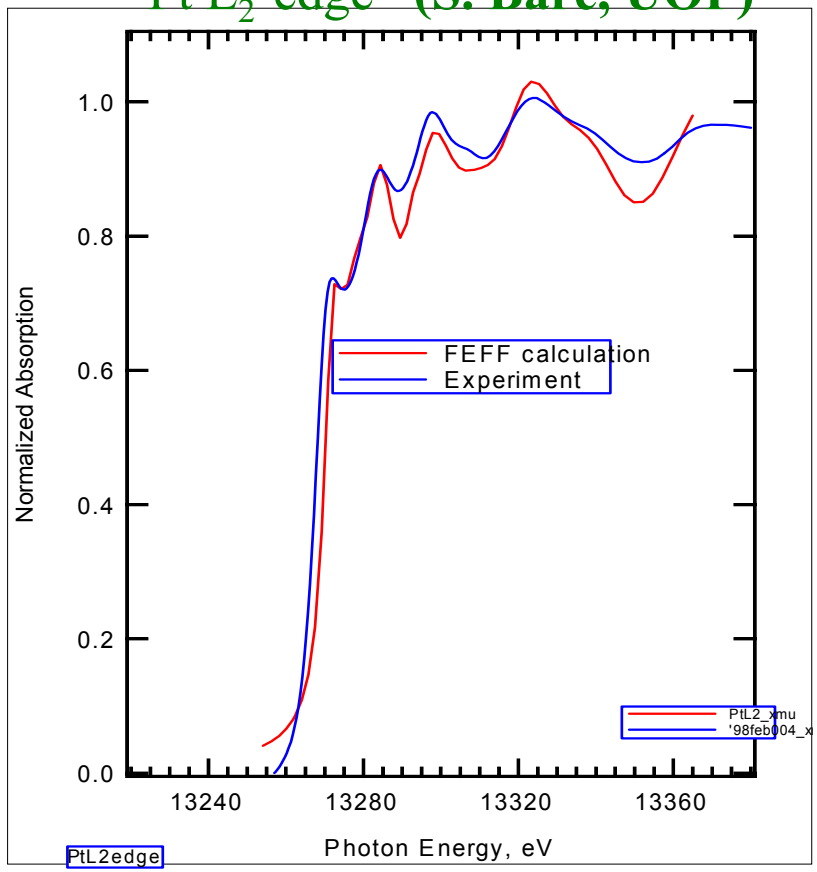
Essential!

XAS and Pt Catalysts: FEFF8 vs. experiment

Pt L_3-edge



Pt L_2-edge **(S. Bare, UOP)**



- Very good agreement: *Relativistic* FEFF8 code reproduces all spectral features, ***including absence of white line at L_2-edge***.
- Self-consistency essential: small changes in position of Fermi level strongly affect white line intensity.

FAST! Parallel Computation FEFFMPI

PHYSICAL REVIEW B, VOLUME 65, 104107

Parallel calculation of electron multiple scattering using Lanczos algorithms

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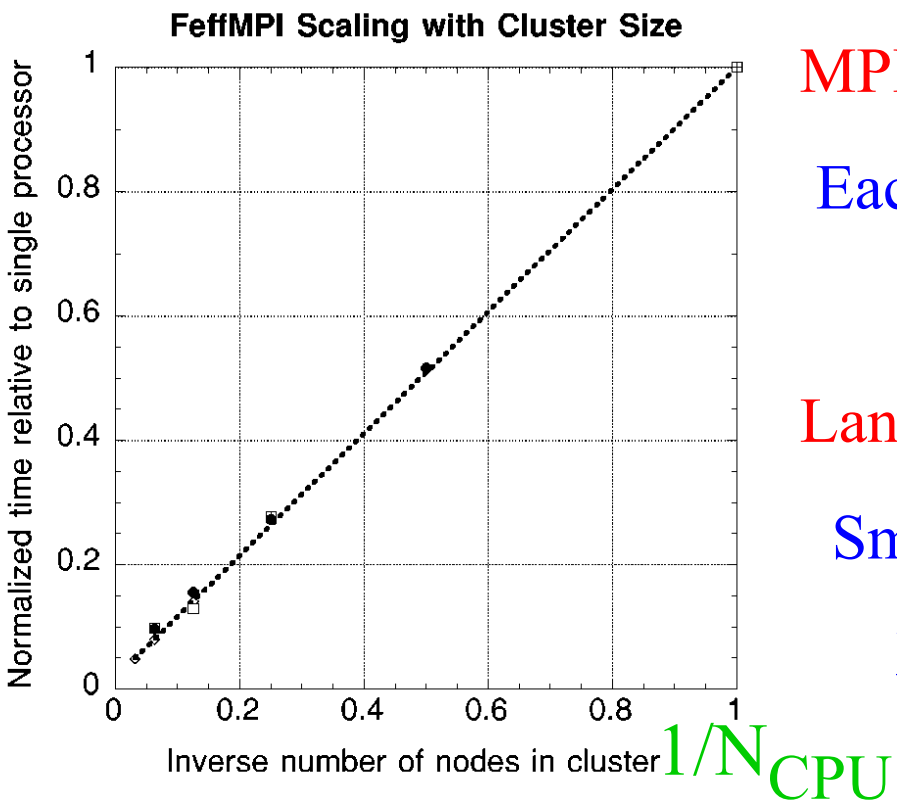


MPI: "Natural parallelization"

Each CPU does few energies

Lanczos: Iterative matrix inverse

Smooth crossover between

XANES and EXAFS!

2. Interpretation of XAS

- EXAFS measures structure

  → distances, coordination numbers, disorder and vibrations, …

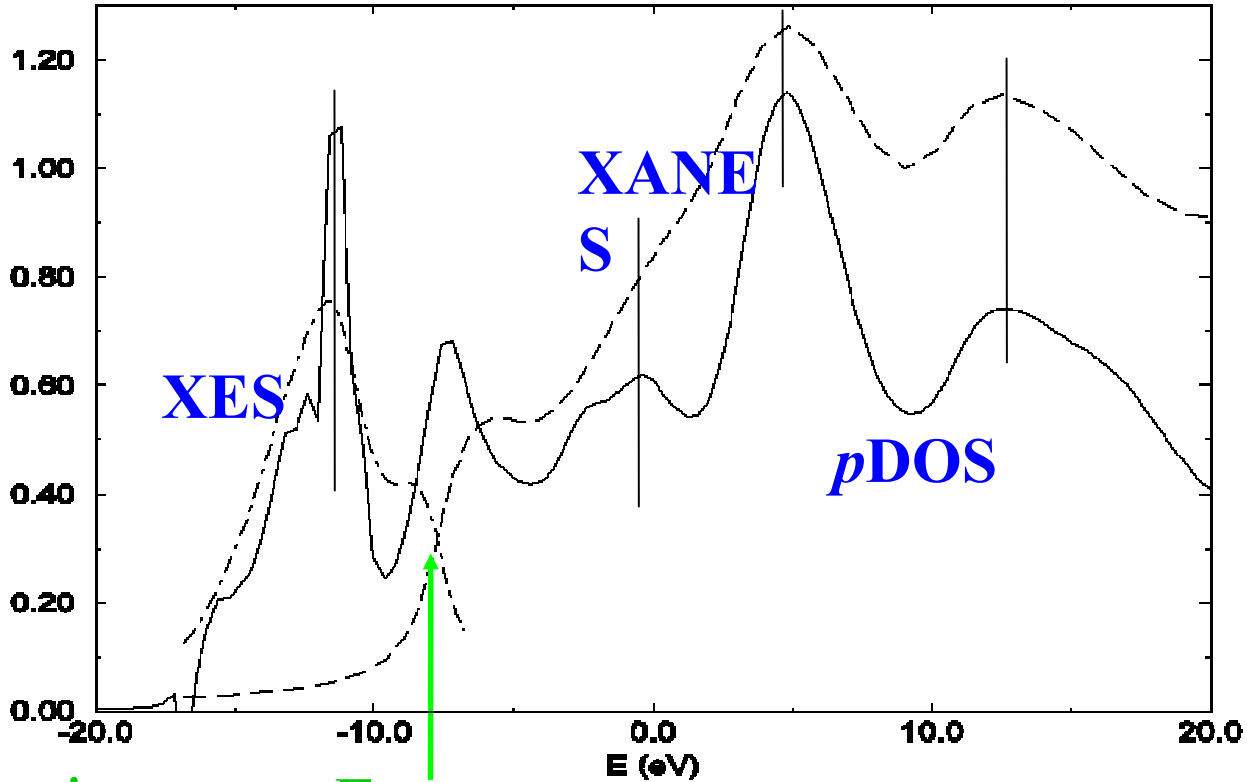
- XANES electronic structure $\rho(E) = -\,\mathrm{Im}\, G \sim \mu(E)$

  → LDOS, charge counts, valence ···

- Need to analyze XANES!

XANES vs Projected Density of States (*LDOS*)

Cu *p*DOS vs XANES and XES



Fermi energy E_F

Final state energy E_f

Difficulty – not easy to fit XANES!

too many parameters, too little bandwidth!

→ Least squares fits are ***ill-conditioned***

FIX: Bayesian Analysis (H. Krappe & H. Rossner)

- include ***a priori*** **knowledge**

Stabilizes fits!
Improves statistical error estimates!
Can use all data – XANES and EXAFS

Bayesian-Turchin XAS Analysis

J. J. Rehr, U. Washington Supported by DOE and SSRL/NIH

H. J. Krappe, H. Rossner, Hahn-Meitner Institute

Questions:

- What is the information content in XAS Expt?

  Experimental data: $\mu_k, \quad k = 1 \cdots K$

  Ans: $\mu_k = \mu^0(\vec{x}, \omega_k), \ \vec{x} = R, N, \sigma^2, \cdots.$

- How can it be extracted?

  Std. Ans: least squares fits in k or R space

  min $\chi^2 \equiv \Sigma_k[(\mu_k - \mu^0(\vec{x}, \omega_k))/\Delta\mu_k]^2$

Problem: ILL-CONDITIONED equations

Not obvious which x_k are important

Effects of noise not treated explicitly

- FIX: add *a prior* information - Bayesian analysis

TALK

"Standard" Approach

Bayesian-Turchin Approach

Application to XAS,XAFS,XANES

Standard χ^2 Analysis

- $\chi^2 = \Sigma_{k=1}^{K} \left|(\mu_k - \mu^0(\vec{x}, \omega_k))/\Delta\mu_k\right|^2$

  $\mu_k^0(\vec{x}) = \mu_k^0(\vec{x}_0) + \Sigma_i(\partial\mu_k^0/\partial x_i)x_i$

  $\chi^2 = |\vec{\Delta} - \Sigma_i^N \vec{g}_i x_i|^2$

  "Signal components" $\Delta_k = [\mu_k - \mu_k^0]/\Delta\mu_k$
  "Gradient of model" $g_{ki} = (\partial\mu_k^0/\partial x_i)/\Delta\mu_k$

- min χ^2 with respect to x_i

  $\longrightarrow$ Linear eq. $\Sigma_j Q_{ij} x_j = b_i \quad i = 1 \cdots N.$

  "Information matrix" $Q_{ij} = \vec{g}_i \cdot \vec{g}_j$
  "Signal components" $b_i = \vec{\Delta} \cdot \vec{g}_i$

- ILL-CONDITIONED solutions

  Very large conditioning number $z = q_1/q_N$

  $\longrightarrow$ Eigen-components unstable: $x_\alpha = (b_\alpha/q_\alpha)$

  (q_α: Eigenvalues of Q)

Bayesian-Turchin Regularization

- FIX: Use known *a priori* information on $\vec{x}$

$$P_{\text{prior}}(\vec{x}) = Ne^{-\chi^2_{\text{prior}}}$$

$$\chi^2_{\text{prior}} = \Sigma_{ij} A_{ij} x_i x_j, \quad A^{-1}_{ij} = \langle x_i x_j \rangle.$$

- $\longrightarrow$ Aposteriori distribution

$$P_{\text{post}} = N P_{\text{prior}} P_{\text{conditional}}(\vec{\mu}|\vec{x}) = e^{-\chi^2_{\text{post}}}$$

$$\chi^2_{\text{post}} = \mathbf{xAx} + (\mathbf{\Delta} - \mathbf{Gx})\mathbf{C}(\mathbf{\Delta} - \mathbf{Gx})$$

$$\mathbf{C} \approx [\mathbf{1} + \mathbf{B^{-1}} + \mathbf{TD^{-1}T}]^{-1}, \;\; G_{ki} = \vec{g}_i$$

- min χ^2_{post} with respect to x_i

$\longrightarrow$ Linear eq. $\Sigma_j [Q_{ij} + A_{ij}] x_j = b_i, i = 1 \cdots N.$

$$\mathbf{Q} = \mathbf{G^{\dagger}CG} \quad b_i = \Delta C \vec{g}$$

- Stable $x_\alpha = b_\alpha/(q_\alpha + a_\alpha)$

$$x_\alpha = b_\alpha/q_\alpha, \quad \alpha \epsilon R \quad \text{(Relevant subspace)}$$

$$x_\alpha = b_\alpha/a_\alpha, \quad \alpha \epsilon P \quad \text{(Prior subspace)}$$

XANES Experiment

- Application to Ge XAS $\mu = \mu_0(1+\chi)$

  Model parameters

  $\vec{x} = (R_1, R_2, \ldots R_7,$ near neighbor distances

  $\kappa_1, \kappa_2, \kappa_3$ spring constants

  $\sigma_1^{(3)}, \sigma_2^{(3)} \ldots \sigma_1^{(3)}$ third cumulants

  S_0^2 many-body amplitude factor

  E_0, E_i edge energy shift, broadening

  $\delta\mu_1, \delta\mu_2, \ldots \delta\mu_{21})$ spline parameters

  in $\mu_0 = \mu_0^0 + \delta\mu_0[\vec{\delta}\mu]$

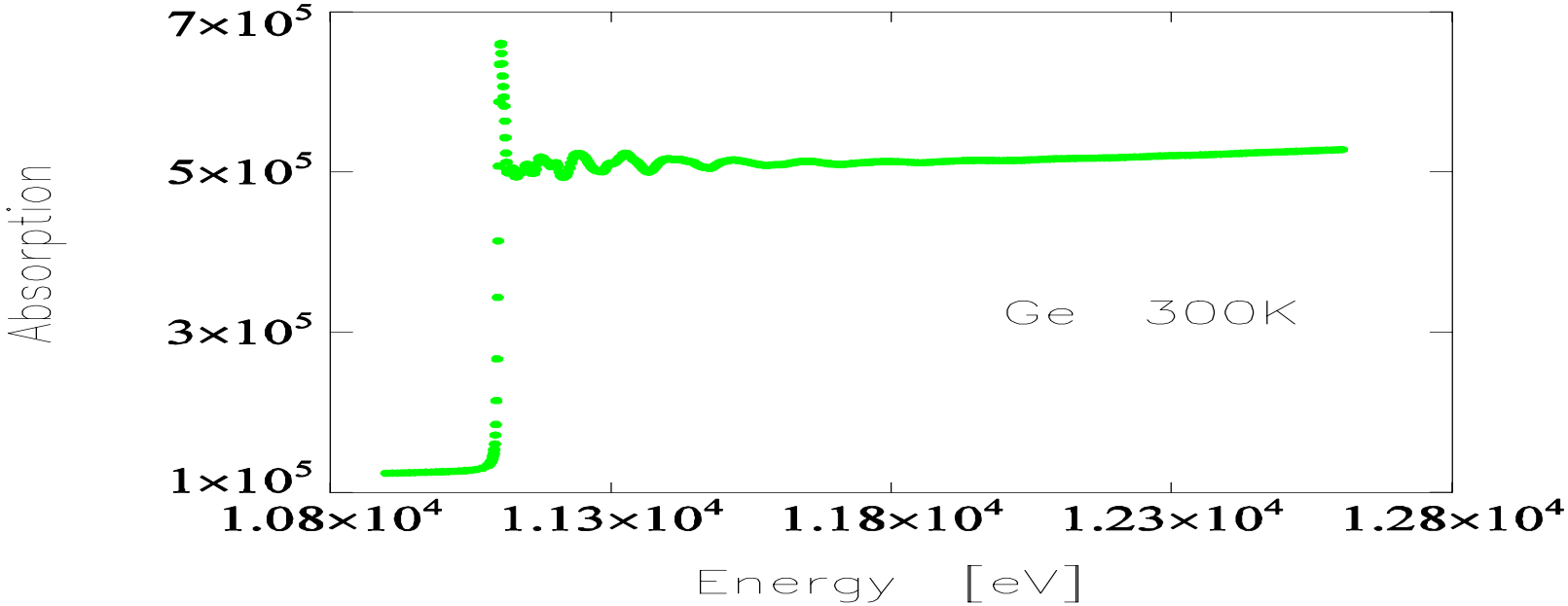
- Modification for XANES analysis

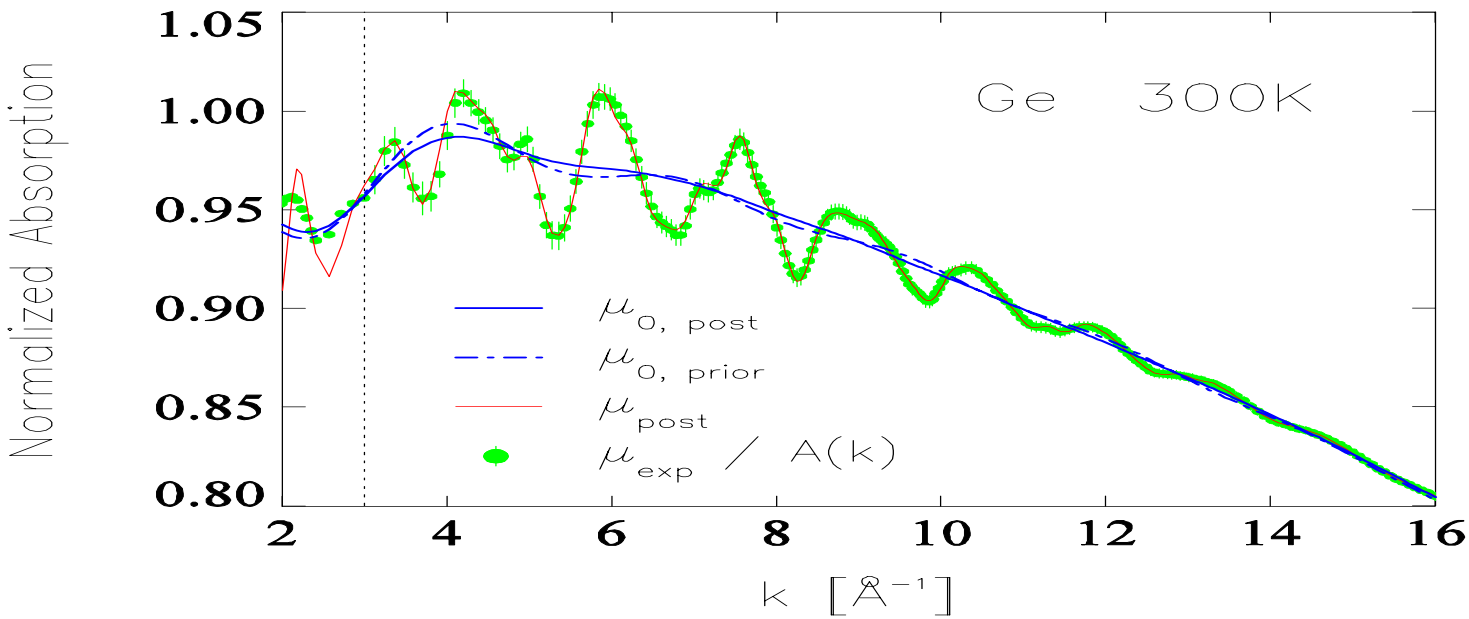
  Model: FMS FEFF8MPI fast parallel code

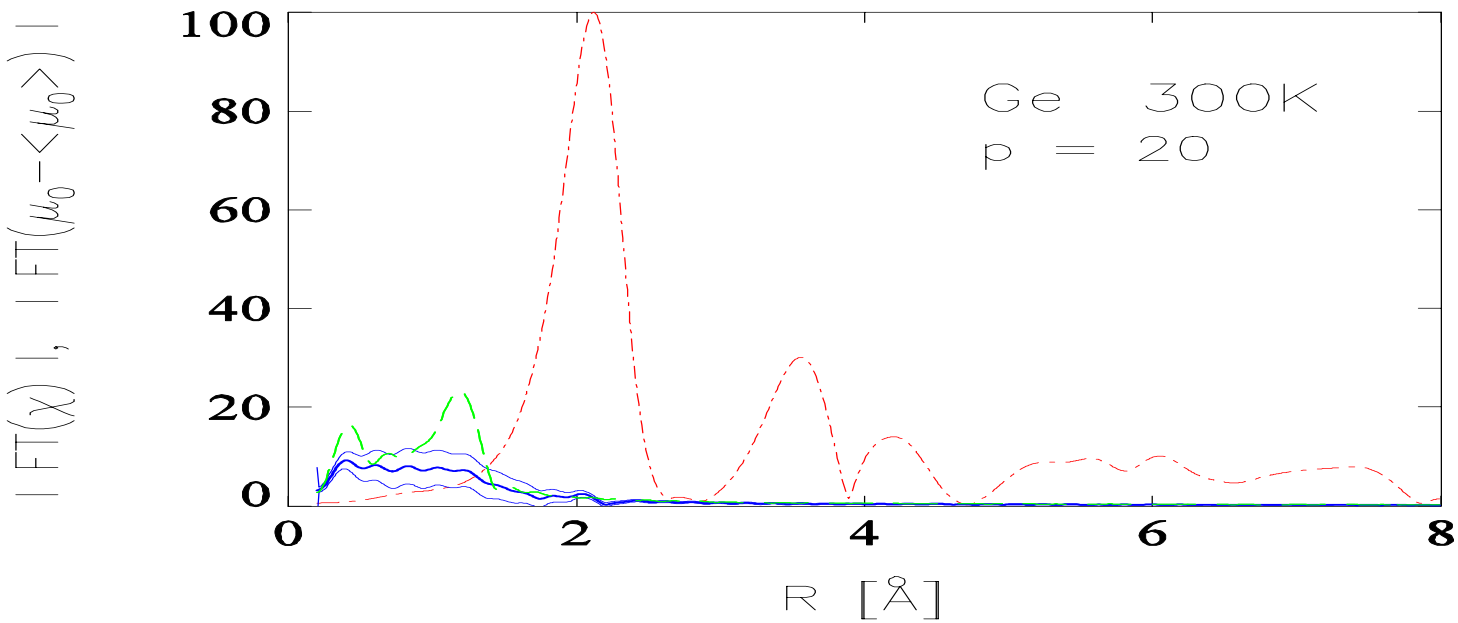
  XANES parameters, e.g., charge counts,

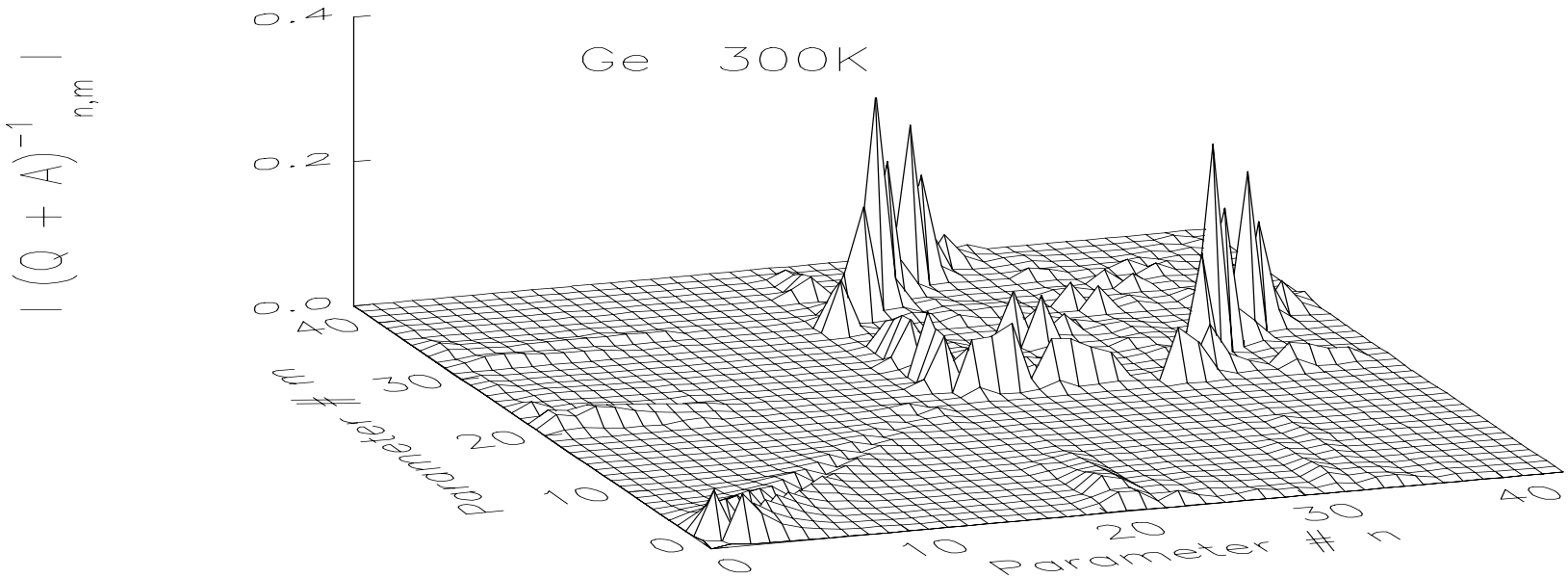
  Numerical model gradients:

$$\frac{\partial\vec{\mu}(\vec{x})}{\partial x_i} = \frac{1}{2\delta x_i}[\mu(\vec{x} + \delta x_i \hat{x}_i) - \mu(\vec{x} - \delta x_i \hat{x}_i)]$$


7×10^5
5×10^5
3×10^5
1×10^5
Absorption
Ge 300K
1.08×10^4
1.13×10^4
1.18×10^4
1.23×10^4
1.28×10^4
Energy [eV]

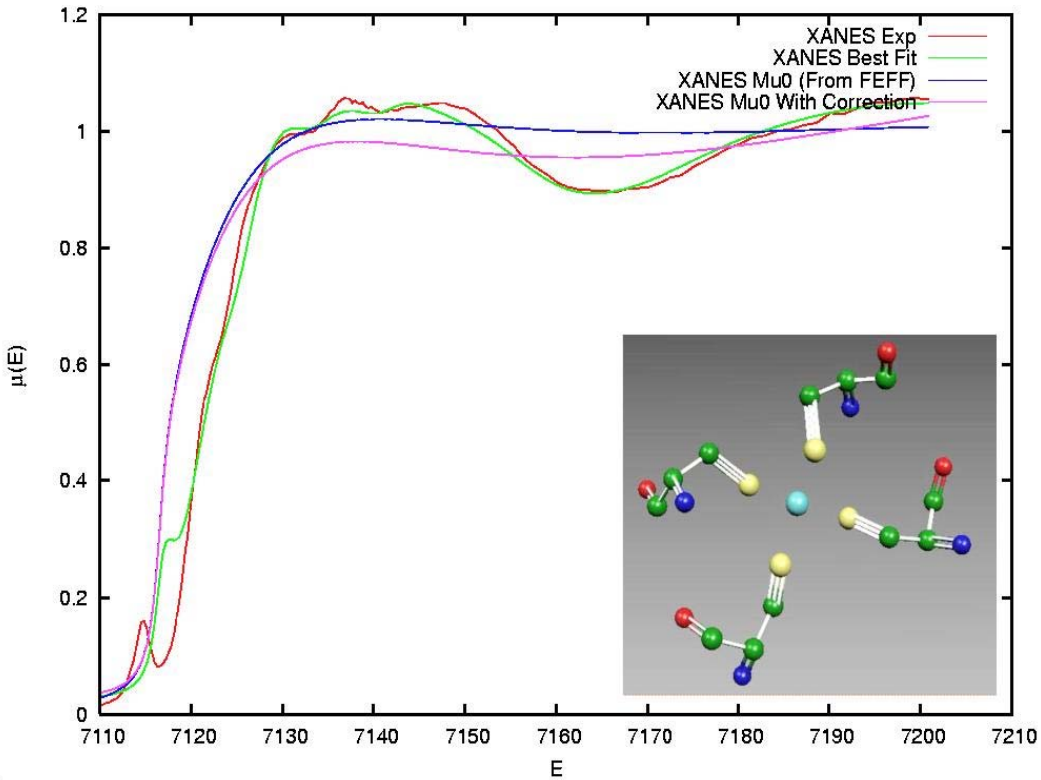

Ge 300K
Normalized Absorption
1.05
1.00
0.95
0.90
0.85
0.80
2
4
6
8
10
12
14
16
k [Å⁻¹]
μ0, post
μ0, prior
μpost
μexp / A(k)


Ge 300K
p = 20
100
80
60
40
20
0
0
2
4
6
8
R [Å]
| FT(χ) |, | FT(μ0−<μ0>) |


Ge 300K
0.4
0.2
0.0
$|(Q+A)^{-1}_{n,m}|$
0
10
20
30
40
parameter # m
0
10
20
30
40
parameter # n

Application to Bio-XAS*

Oxidized Pyrococcus Furious Rubredoxin



Combined Bayesian XANES & EXAFS Analysis Code

(add-on to FEFFIT)

Fits: R_n, distortions, atomic background, etc

Data: G. George SSRL

*Supported by SSRL-NIH

CONCLUSIONS

- EXAFS – Quantitative! Reliable.
- XANES – Semi-quantitative
- New: Many body corrections – Semi-quantitative
- New: Bayesian EXAFS/XANES analysis codes
  SMART BLACK BOX

GOALS – Achieved or within sight!

Acknowledgments

Collaborators

- A.L. Ankudinov (UW)
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- Y. Takimoto (UW)
- J. Kas (UW)
- M. Prange (UW)
- E. Shirley (NIST)
- A. Soininen (U. Helsinki)
- C. Bouldin (NSF)
- G. Hug (ONERA/CNRS)
- M. Jaouen (U. Poitiers)
- S.R. Bare (UOP)
- H. Krappe (HMI)
- H. Rossner (HMI)
- L. Hedin – still a major influence!

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DOE BES

DOE-CMSN

NIH-SSRL