Introduction to XAS Theory

J. J. Rehr, U. Washington Supported by DOE

GOAL: *ab initio* Theory

- *No* adjustable parameters
- Accuracy $\sim$ experiment

GOAL: Quantitative Interpretation

"Inverse Problem" What's in a spectrum?

- Atomic Structure - Interatomic distances
- Chemistry

"Theory without Experiment is empty."

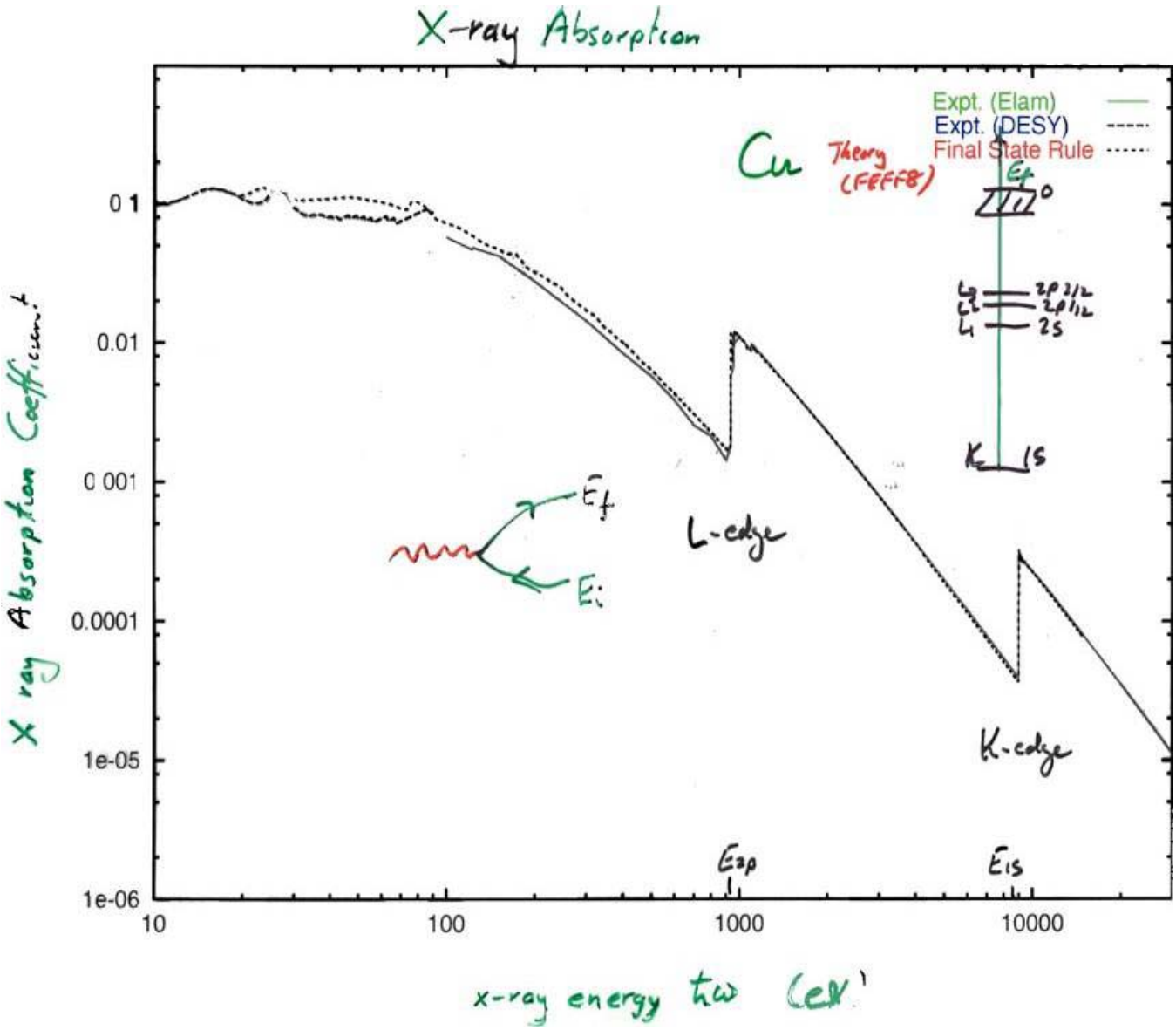
"Experiment without Theory is blind."

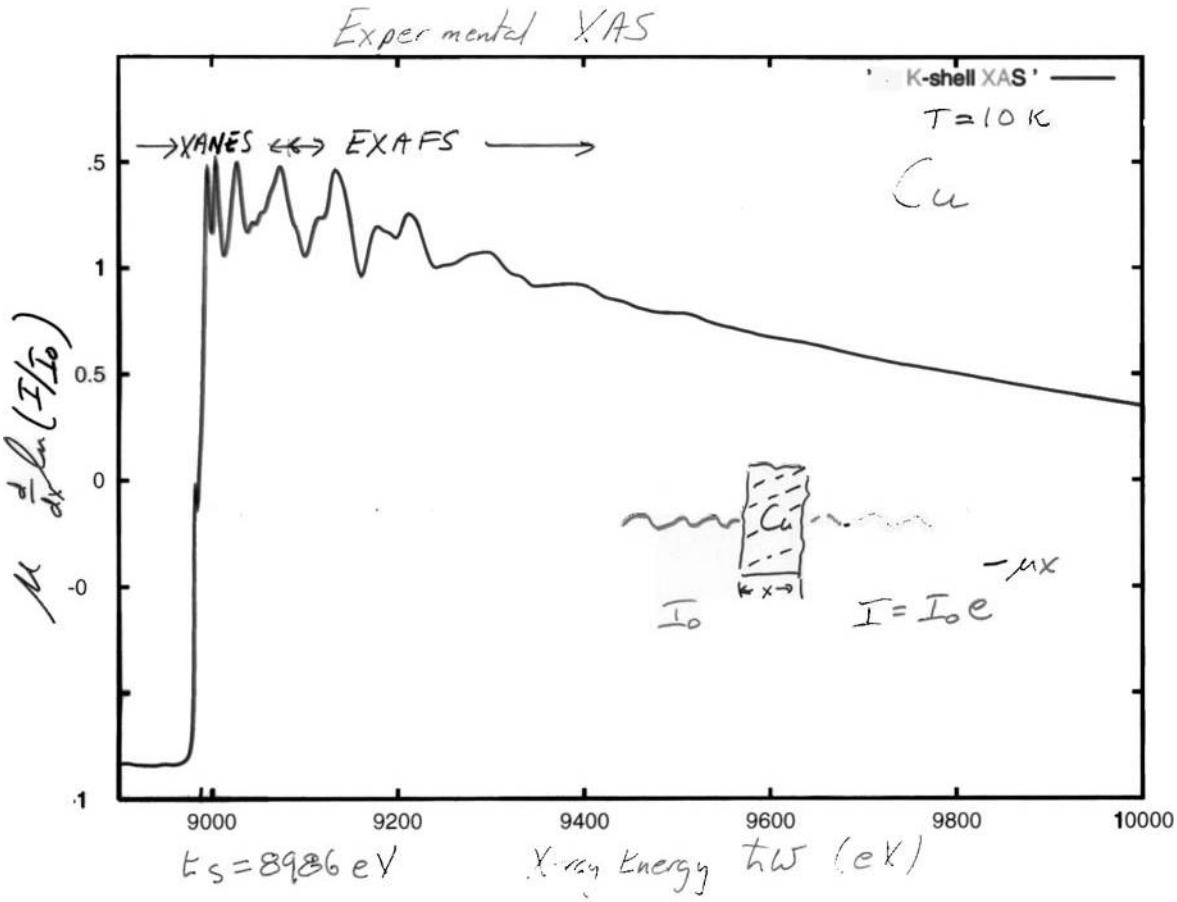
H. Pagels

"Theory or Experiment without

Computation is old-fashioned."

J. J. R.


X-ray Absorption
Cu
Theory (FEFF8)
Expt. (Elam)
Expt. (DESY)
Final State Rule
Ef
0
L3 2p 3/2
L2 2p 1/2
L1 2s
K 1s
Ef
Ei
L-edge
K-edge
E2p
E1s
X ray Absorption Coefficient
0 1
0.01
0 001
0.0001
1e-05
1e-06
10
100
1000
10000
x-ray energy ħω (eV)


Experimental XAS
K-shell XAS
T = 10 K
Cu
→XANES ⟷ EXAFS →
μ d/dx ln(I/I0)
.5
1
0.5
0
-0
-1
9000
9200
9400
9600
9800
10000
Es = 8986 eV
X-ray Energy ħω (eV)
Cu
x
I0
I = I0 e^-μx

Qualitative Theory

Fermi Golden Rule

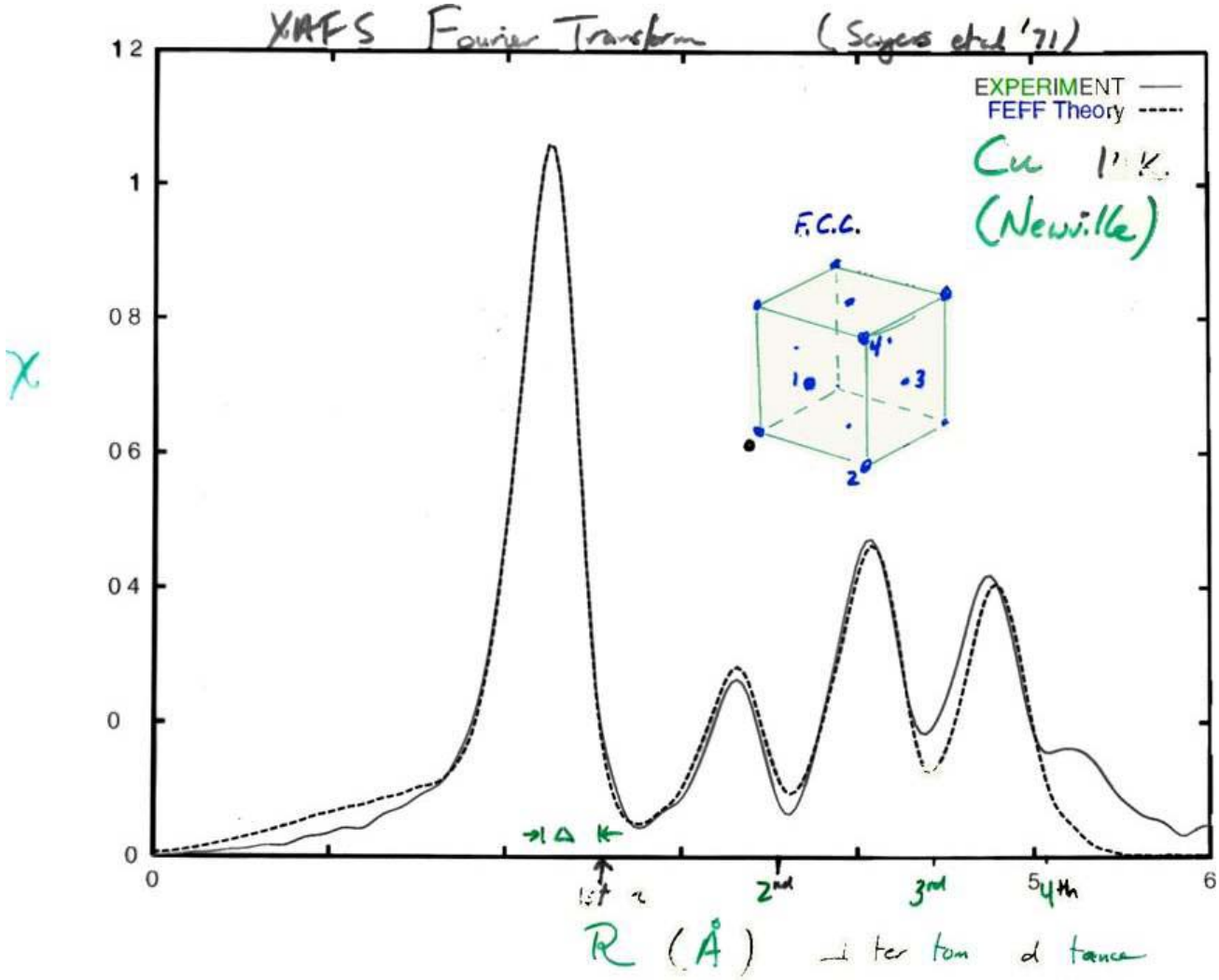
$$\mu \sim |\langle \psi_{core} | \hat{\epsilon} \cdot \vec{r} | \psi_f \rangle|^2 \sim |\psi_f(0)|^2$$

$$\psi_f(0) \sim \psi_f^{out} + \psi_f^{scatt}$$

$$\psi_f^{scatt} \sim \frac{e^{ikR+\delta}}{kR} f(\pi) \frac{e^{ikR+\delta}}{kR}$$

- $\Rightarrow$ XAFS (Quantum Interference)

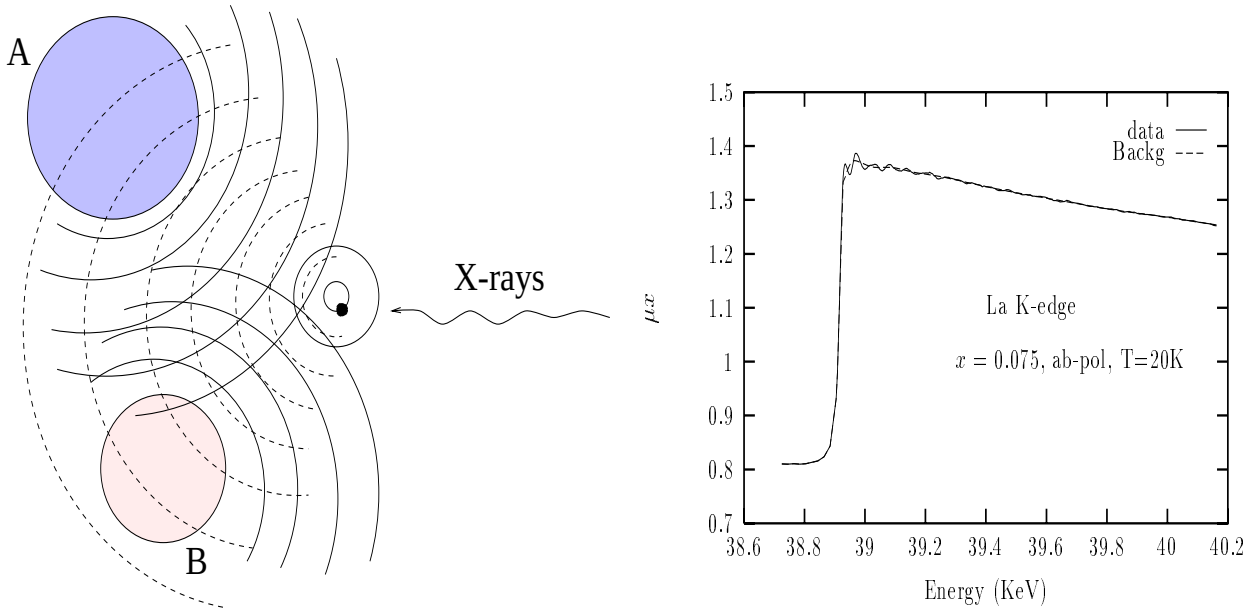
$$\mu \sim \mu_0 \left[1 + \mathrm{Im} \frac{f(\pi)}{(kR)^2} e^{2ikR+2i\delta} \right]$$


XAFS Fourier Transform (Sayers et al '71)
EXPERIMENT
FEFF Theory
Cu 11 K
(Newville)
F.C.C.
χ
12
1
0.8
0.6
0.4
0
0
0
1st
2nd
3rd
4th
5th
6
R (Å) interatomic distance

X-ray Absorption Fine Structure

- Modulation in X-ray absorption coefficient due to presence of condensed matter.

$$\mu \propto |\langle f \,|\, \vec{p}\cdot\vec{E} \,|\, i\rangle|^2 \equiv \mu_0(1+\chi)$$



$$\chi(k) = \sum_j 3\,(\hat{\epsilon}\cdot\hat{r}_j)^2 \frac{N_j\, S_0^2 F_j(k)}{k r_j^{\,2}} e^{-2k^2\sigma_j^2}\, e^{-2r_j/\lambda(k)} \sin(2kr_j + \delta_j(k))$$

k Photoelectron wave number

$\hat{\epsilon}$ Polarization direction

N_j Coordination number

S_0^2 Many body correction

σ_j^2 Debye-Waller factor

$\lambda(k)$ Photoelectron mean free path

$\delta_j(k) = 2\,\delta_c(k) + \delta_b(k)$ Phase shifts

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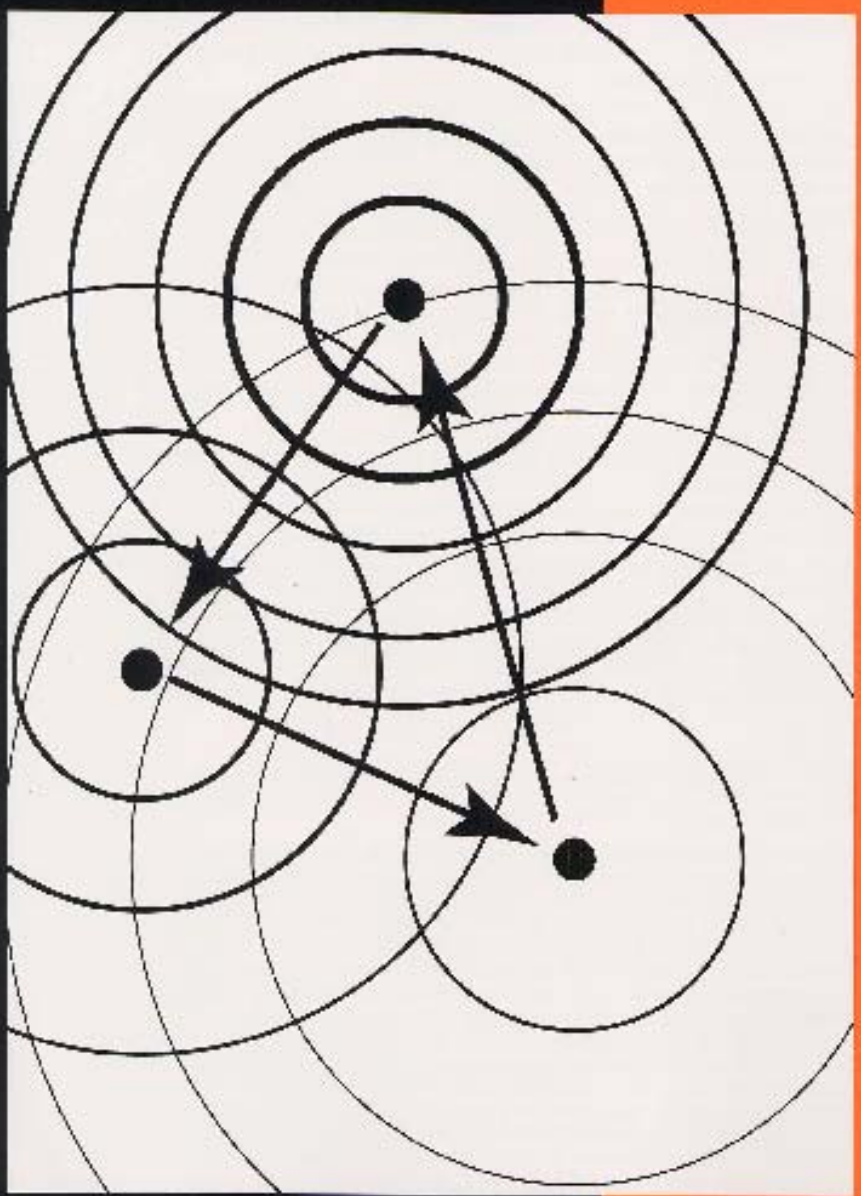

THEORETICAL APPROACHES TO X-RAY ABSORPTION FINE STRUCTURE

Key Developments

Curved-wave Scattering Theory

- "Plane-wave" scattering theory f INVALID
- $f \longrightarrow$ Effective scattering amplitude $f_{\rm eff}$ FEFF

$$f_{\rm eff}(\pi; k) \cong \Sigma_l (-1)^l (2l+1) e^{i\delta_l} \sin\delta_l \quad C_l(k)$$

- Curved wave factor $C_l(k) \cong e^{il(l+1)/2kR}$

Inelastic Losses

Must account for various LOSSES

- Extrinsic Losses

  Mean free paths $\lambda = k/[|\mathrm{Im}\,\Sigma(E)| + \Gamma]$

  $\Sigma(E)$ Photoelectron Self-energy

  Γ Core-hole lifetime

- Intrinsic Losses

  $S_0^2 = |\langle \Psi'_{N-1} | \Psi_{N-1} \rangle|^2 \approx 0.9$

EXAFS Debye-Waller Factors

Damping of EXAFS from Disorder and Vibrations

$$\langle \chi(R) \rangle = \chi(\bar{R}) e^{-W)}$$

$W = 2k^2\sigma^2 - \frac{4}{3} i k^3 \sigma^{(3)} + \cdots$ "Debye-Waller factor"

$\sigma^2 = \langle |(\vec{u}_0 - \vec{u}_R) \cdot \hat{R}|^2 \rangle$ "MSRD"

$\sigma^{(3)}$ "3rd cumulant"

Explains anomalous length contraction!

Approximation: Correlated Debye-Model

Relation: $\sigma^{(1)}\sigma^2/\sigma^{(3)} = 1/[2 - (4/3)(\sigma_0^2/\sigma^2)^2]$

Automated FEFF code (FEFF 3)

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Theoretical X-ray Absorption Fine Structure Standards

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Contribution from the Department of Physics, FM-15, University of Washington, Seattle, Washington 98195, and Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545. *Received November 13, 1990*

Abstract: Theoretical X-ray absorption fine structure (XAFS) standards are developed for arbitrary pairs of atoms throughout the periodic table ($Z \leq 94$). These standard XAFS spectra are obtained from *ab initio* single-scattering XAFS calculations, using an automated code, FEFF, which takes into account the most important features in current theories: (i) an exact treatment of curved-wave effects; (ii) approximate molecular potentials derived from relativistic atoms, (iii) a complex, energy-dependent self-energy; (iv) a well defined energy reference. FEFF also yields tables of XAFS phases and amplitudes as well as mean-free paths. Sample results are presented and compared with experimental results and with earlier work. We find that these theoretical standards are competitive with experimental standards, permitting XAFS analysis at lower wavenumbers and yielding distance determinations typically better than 0.02 Å and coordination numbers typically better than 20%. These standards also provide theoretical tests of chemical transferability in XAFS.

i)
iii)

Theory vs Experiment

Phase Shifts

XAFS

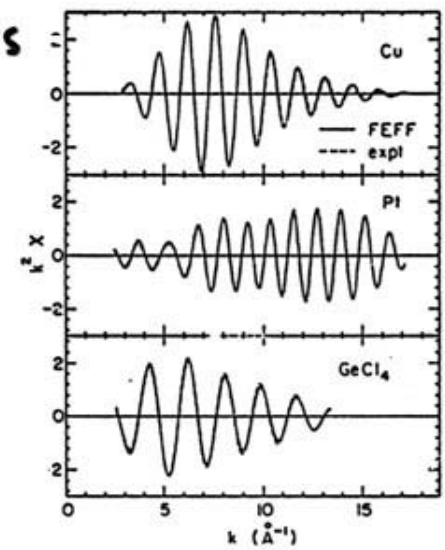


Figure 2. Filtered XAFS data $k^2\chi(k)$ for the first coordination shell of Cu, Pt, and $GeCl_4$ from FEFF (solid lines) and from similarly filtered experimental data[29,30] (dashed lines).

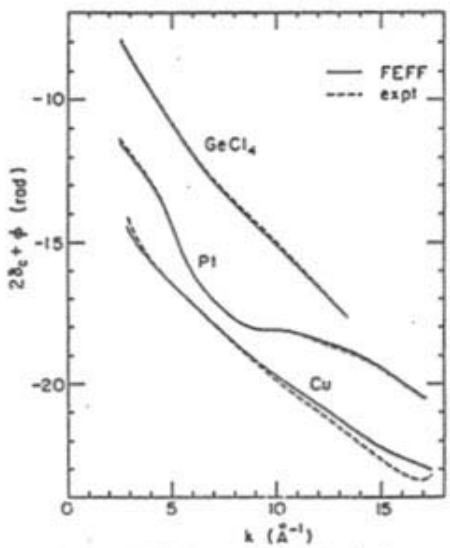


Figure 3. Filtered total XAFS phase ($2\delta_c + \Phi$) for the first coordination shell of Cu, Pt, and $GeCl_4$ from FEFF (solid lines) and from similarly filtered experimental data[30,29] (dashed lines).

XAFS from 1st shell

Expt: Stern Heald Boulding

Standard Quasi-particle Theory of XAS

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

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

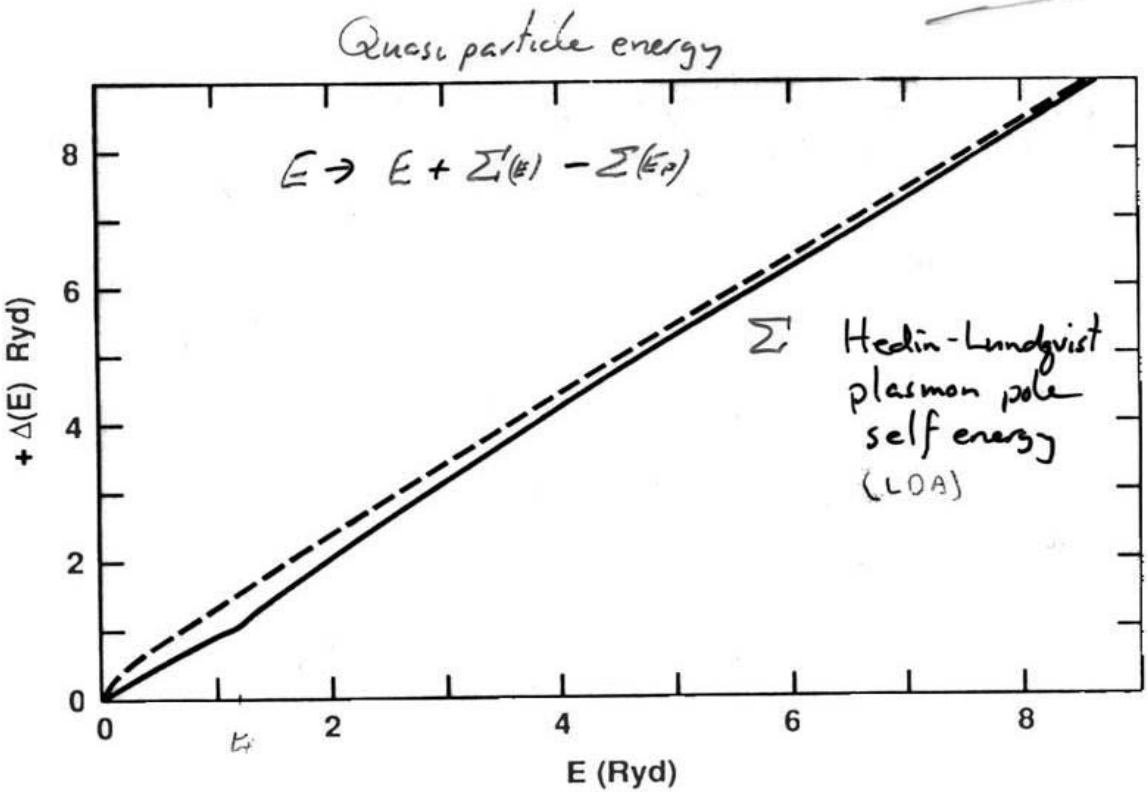
Final state rule $V'_{coul} = V_{coul} + V_{core-hole}$

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

Inelastic Mean free paths

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

Non-standard Quantum Mechanics !


Quasi particle energy
$E \rightarrow E + \Sigma'(E) - \Sigma(E_F)$
Σ Hedin-Lundqvist plasmon pole self energy (LDA)
+ Δ(E) Ryd)
E (Ryd)
0
2
4
6
8

Wave-function vs Green's 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

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

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

Real-space Green's Function Formalism

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

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

(MS path expansion - geometric series)

$$= [1 - G^0 t]^{-1} G^0 \qquad \text{"full MS"}$$

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

High-order Multiple-scattering Theory

- Multiple-scattering Path Expansion

$$\chi = \Sigma_{\text{MS paths}} \\ = GtG + GtGtG + GtGtGtG + \cdots$$

- Separable-Propagators (Rehr-Albers 1990)

$$G_{L,L'}(kR) = \frac{e^{ikR}}{kR} \Sigma_n \tilde{Y}_{Ln} Y_{L'n} \quad (6 \times 6)$$

$\rightarrow$ Modern EXAFS Equation

$$\chi = \Sigma_{\text{paths}} \frac{N S_0^2 f_{\text{eff}}}{kR^2} \sin(2kR + \Phi) e^{-2R/\lambda} e^{-2k^2\sigma^2}$$

RESULT: MS Series converges with $10^2 - 10^3$ paths

High-Order Multiple-Scattering Calculations of X-Ray-Absorption Fine Structure

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FEFF

(Received 29 May 1992)

High-order scattering is found to be essential for the convergence of the multiple-scattering (MS) theory of x-ray-absorption fine structure, both in the near-edge and the extended regimes. These contributions are calculated using an *ab initio* curved-wave scattering-matrix formalism. Convergence to full MS accuracy is demonstrated for fcc Cu, as well as for molecular O_2 and N_2, where our approach provides a high-order MS interpretation of the σ^* shape resonances.

PACS numbers: 78.70.Dm, 71.10.+x, 79.60.-i

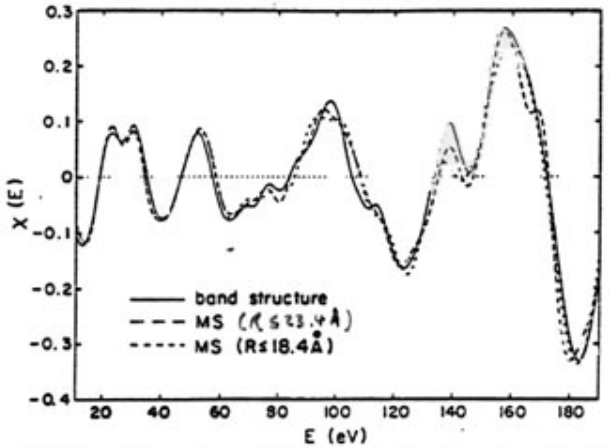


FIG. 1. Comparison of 8-eV Lorentzian broadened band-structure calculations of Cu XAFS (solid line) with high-order MS calculations of χ from this work: (long dashes) subset of MS paths with length $R_t \leq 23.4$ Å and single-scattering paths to 53.1 Å, and (short dashes) subset of SS and MS paths with $R_t \leq 18.4$ Å.

Band-structure vs High-order M.S. 10^6 paths

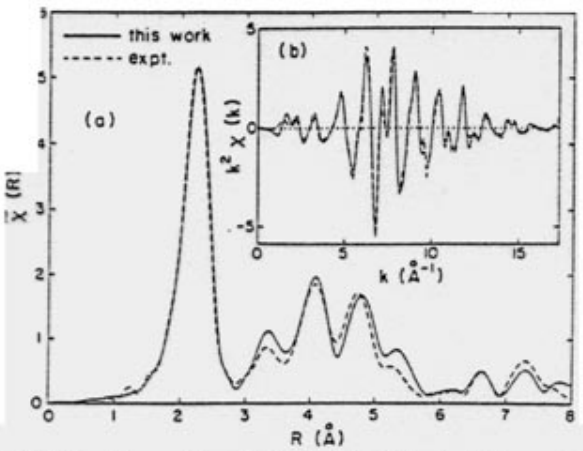
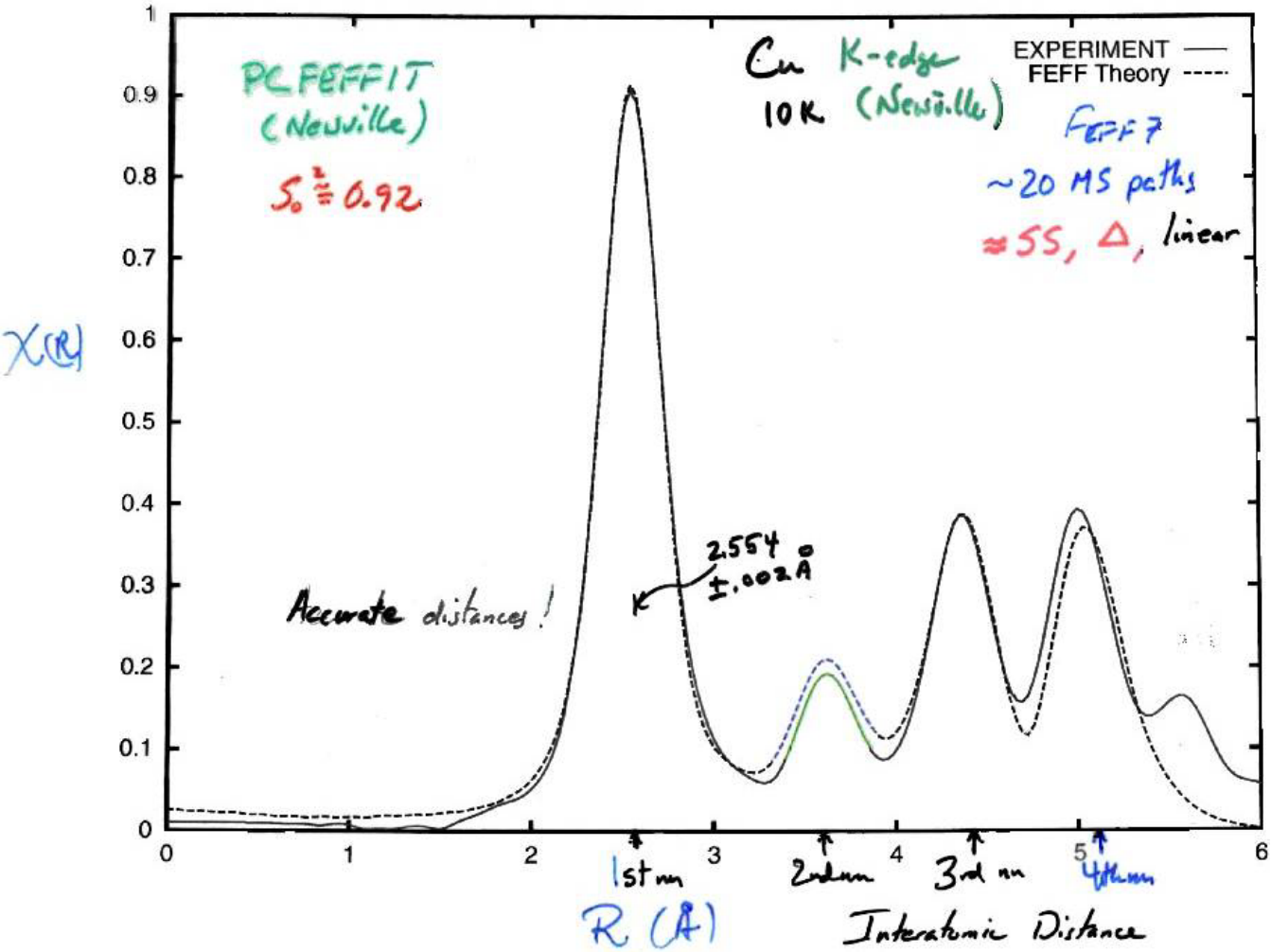


FIG. 2. Comparison of high-order MS calculations of Cu XAFS from this work with $S_0^2 = 0.906$ (solid line) and from XAFS experiment at 190 K (dashed line): (a) position space Fourier transform $\tilde{\chi}(R)$ and (b) in momentum space, $k^2\chi(k)$. Here k is defined with respect to the Fermi energy, $k = \sqrt{E - E_F}$.

56 paths


PC FEFFIT
(Neville)
$S_0^2 \approx 0.92$
Cu K-edge
10K (Neville)
EXPERIMENT
FEFF Theory
FEFF 7
~20 MS paths
≈ SS, Δ, linear
χ(R)
2.554 Å ±.002 Å
Accurate distances!
1st nn
2nd nn
3rd nn
4th nn
R (Å)
Interatomic Distance

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

FEFF8

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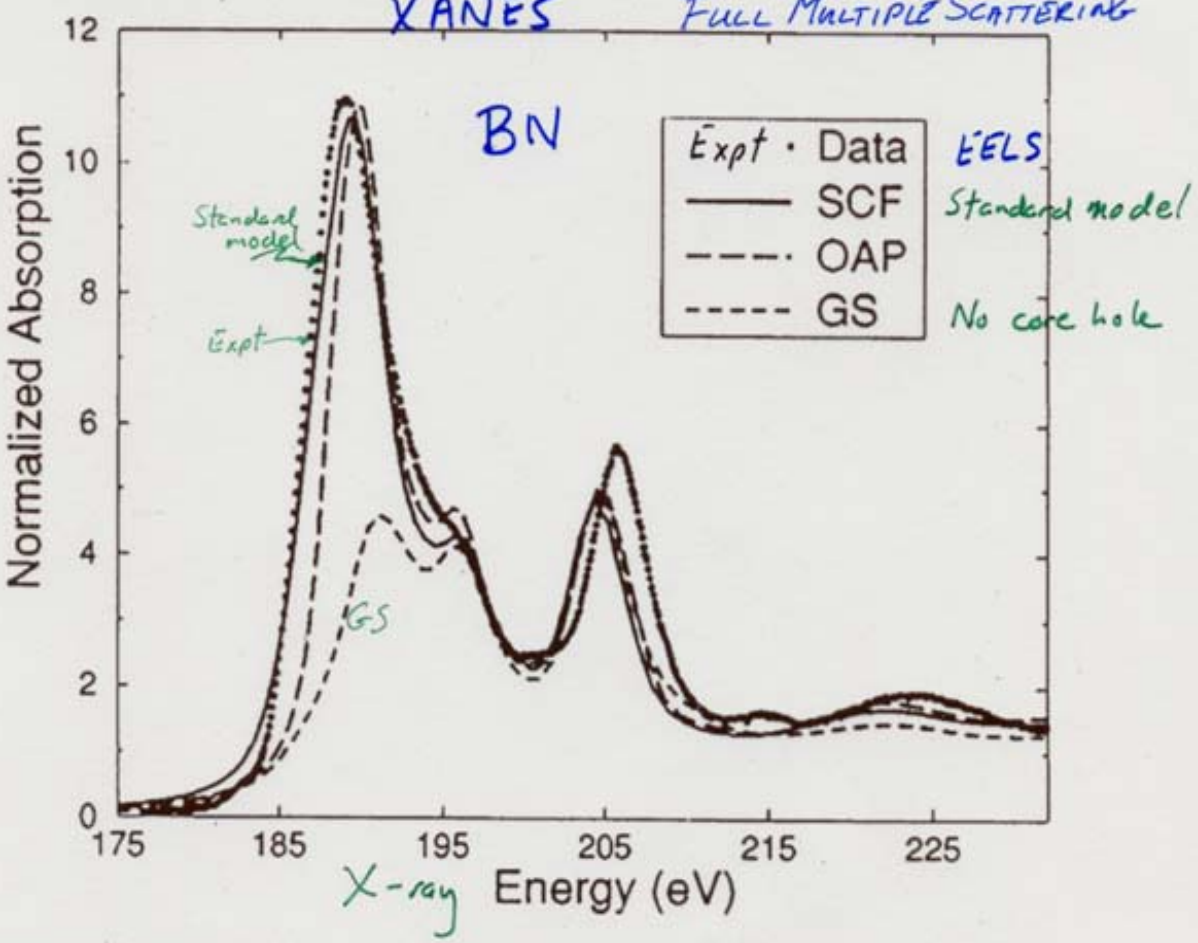
(Received 26 September 1997; revised manuscript received 14 April 1998)

A self-consistent real-space multiple-scattering (RSMS) approach for calculations of x-ray-absorption near-edge structure (XANES) is presented and implemented in an *ab initio* code applicable to arbitrary aperiodic or periodic systems. This approach yields a quantitative interpretation of XANES based on simultaneous, self-consistent-field (SCF) calculations of local electronic structure and x-ray absorption spectra, which include full multiple scattering from atoms within a small cluster and the contributions of high-order MS from scatterers outside that cluster. In addition, the code includes a SCF estimate of the Fermi energy and an account of orbital occupancy and charge transfer. We also present a qualitative, scattering-theoretic interpretation of XANES. Sample applications are presented for cubic BN, UF_6, Pu hydrates, and distorted $PbTiO_3$. Limitations and various extensions are also discussed. [S0163-1829(98)03736-9]

XANES FULL MULTIPLE SCATTERING



Interpretation of XAS

M.O. Interpretation of XANES

PHYSICAL REVIEW B VOLUME 27, NUMBER 4 15 FEBRUARY 1983

Study of the K edges of $3d$ transition metals in pure and oxide form by x-ray-absorption spectroscopy

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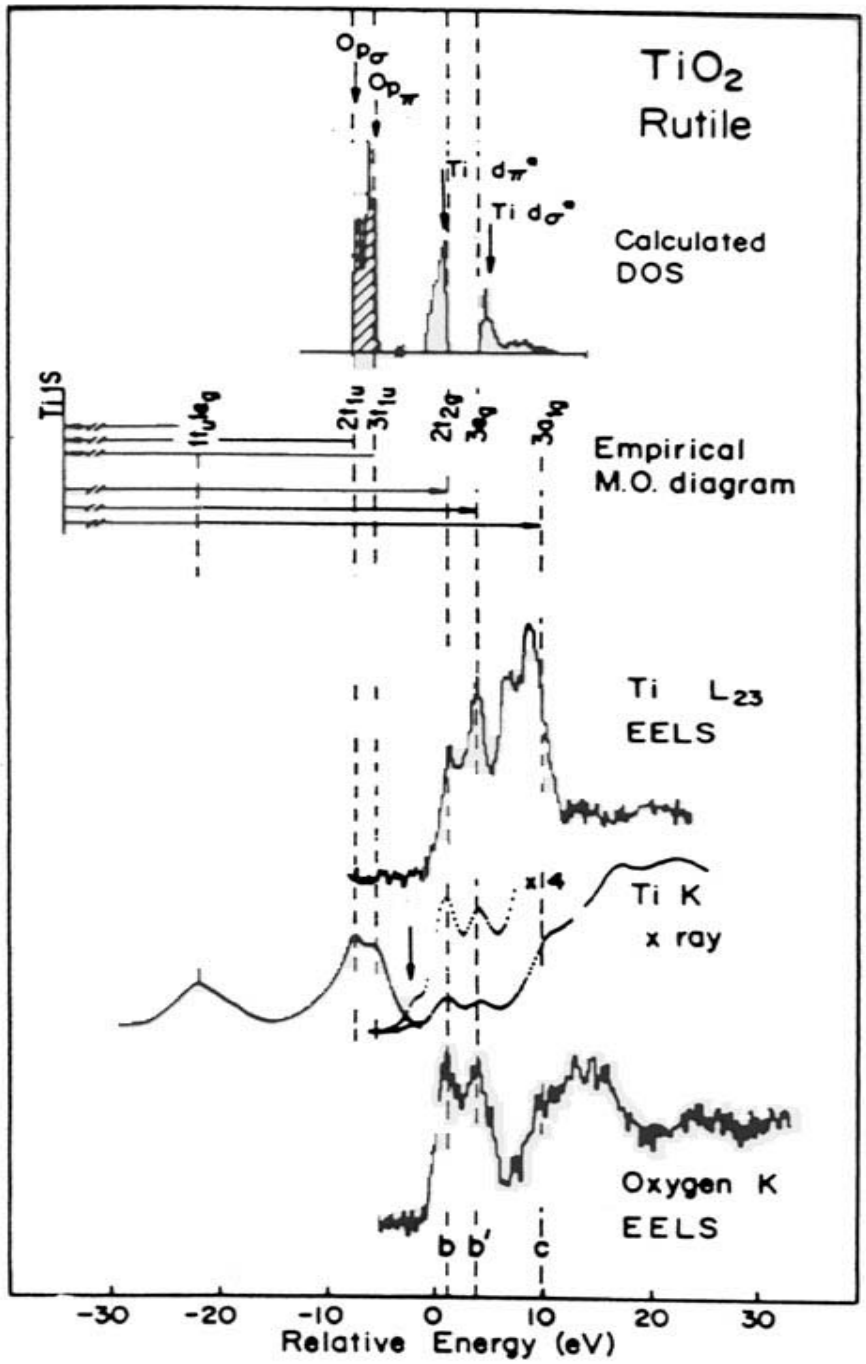
(Received 9 September 1982)



Normalization and convergence of x-ray absorption sum rules

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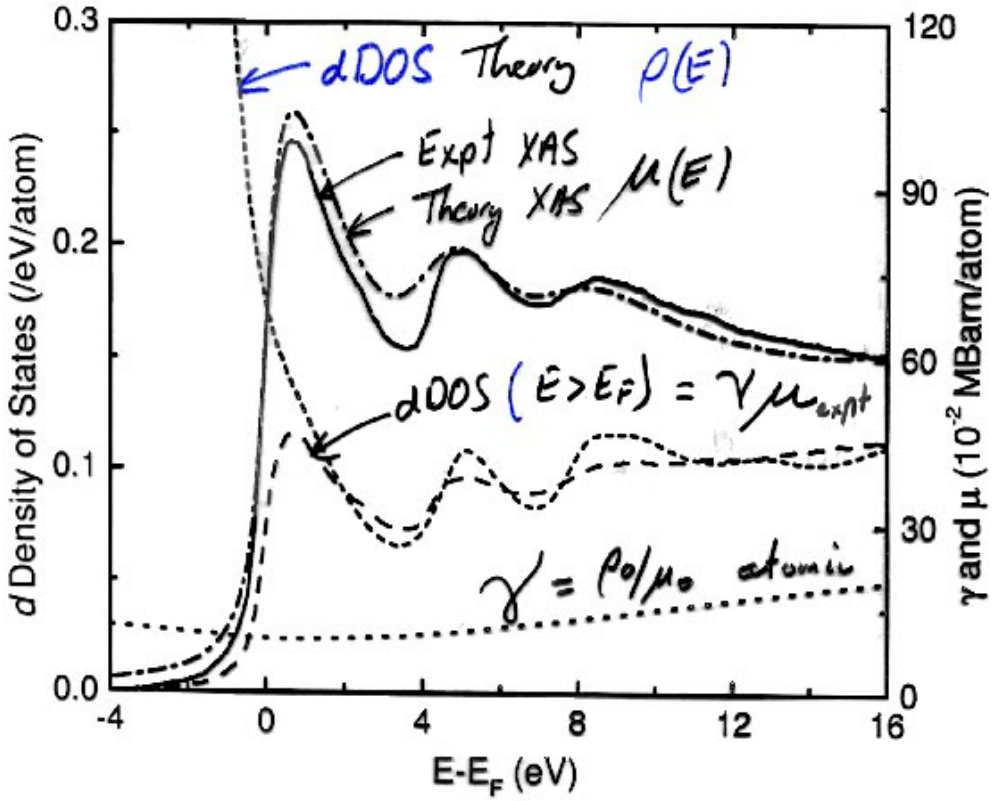
Dept. of Physics, Box 351560, University of Washington, Seattle, Washington 98195
(January 12, 2000)

(2000)
Phys Rev B 63
p. 094 412

Unoccupied LDOS XAS

$\rho(E) \cong \gamma(E)\,\mu(E)$

Cu L



$\mu(E) = \mu_0 (1 + \chi)$ $\sim I_m$

$\rho(E) = \rho_0 (1 + \chi)$ $\sim I_m$

$\Rightarrow$ LDOS ~ XAS

What is S_0^2

- Many body effects in XAS
- Multi-electron excitations

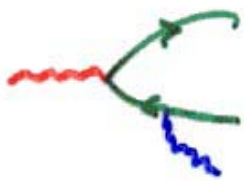
Failure of Quasiparticle Theory of XAS

? What is S_0^2 - Many-body loss factor?

Observe

Quasi-particle theory works *pretty well* but

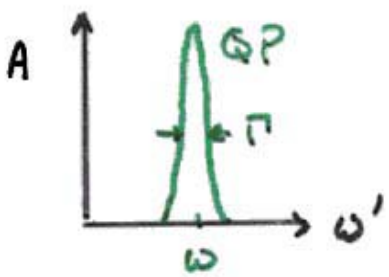
- Includes only "extrinsic" losses $\chi(E)$
- Neglects *satellites*, e.g. shake-up

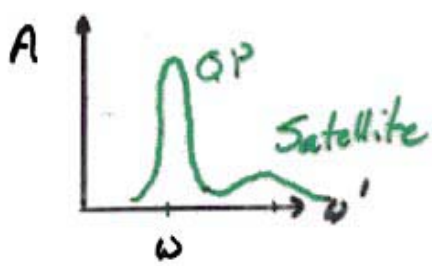


- EXAFS amplitudes too high: $S_0^2 \approx 0.9$

Fix: Theory beyond quasi-particle approximation

quasi-particle $\rightarrow$ *spectral function* $A(\omega, \omega')$





Interference between Extrinsic and Intrinsic Losses in XAFS

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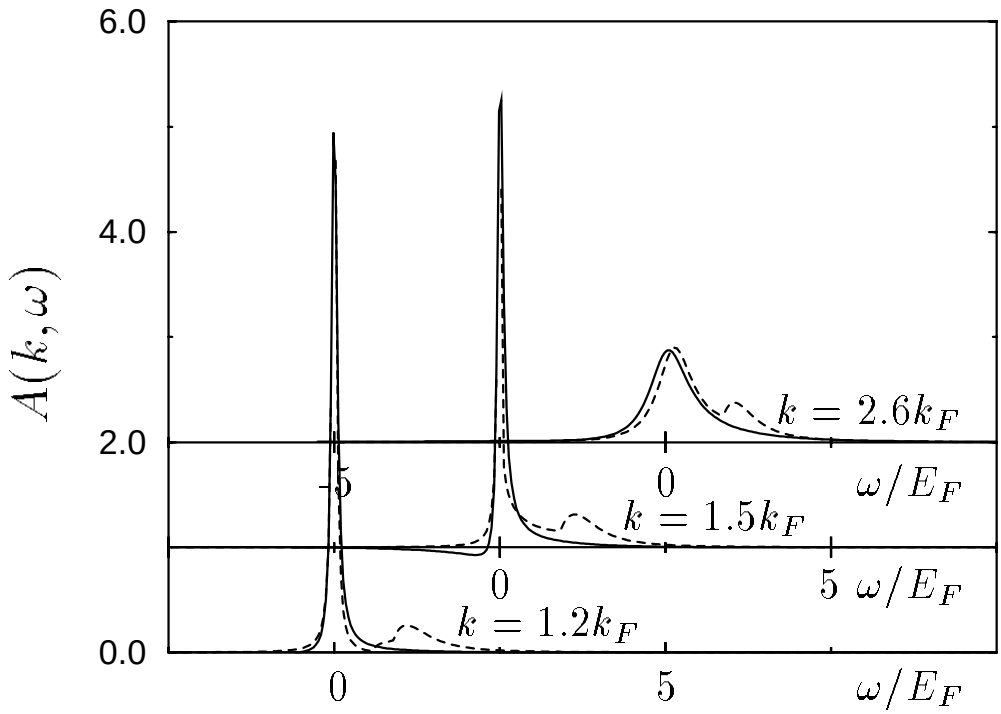
[3] *Dept. of Physics, Univ. of Warsaw, Warsaw, Poland*
(Dated: November 20, 2002)

The interference between extrinsic and intrinsic losses in x-ray absorption fine structure (XAFS) is treated within a Green's function formalism, without explicit reference to final states. The approach makes use of a quasi-boson representation of excitations and perturbation theory in the interaction potential between electrons and quasi-bosons. These losses lead to an asymmetric broadening of the main quasi-particle peak plus an energy-dependent satellite in the spectral function. The x-ray absorption spectra (XAS) is then given by a convolution of an effective spectral function over a one-electron cross-section. It is shown that extrinsic and intrinsic losses tend to cancel near excitation thresholds, and correspondingly, the strength in the main peak increases. At high energies, the theory crosses-over to the sudden approximation. These results thus explain the observed weakness of multi-electron excitations in XAS. The approach is applied to estimate the many-body corrections to XAFS, beyond the usual mean-free-path, using a phasor summation over the spectral function. The asymmetry of the spectral function gives rise to an additional many-body phase shift in the XAFS formula.

PACS numbers: 71.10.-w 78.70.Dm

$$\mu(\omega - E_c) = \int d\omega' A_{\rm eff}(\omega, \omega')\, \mu_{qp}(\omega - \omega'), \qquad (1)$$



Calculation of S_0^2