Caltech Workshop on Scattering Science Pasadena, CA Jan 31-Feb 2

The Evolution of FEFF and ab initio X-ray Spectroscopy Codes

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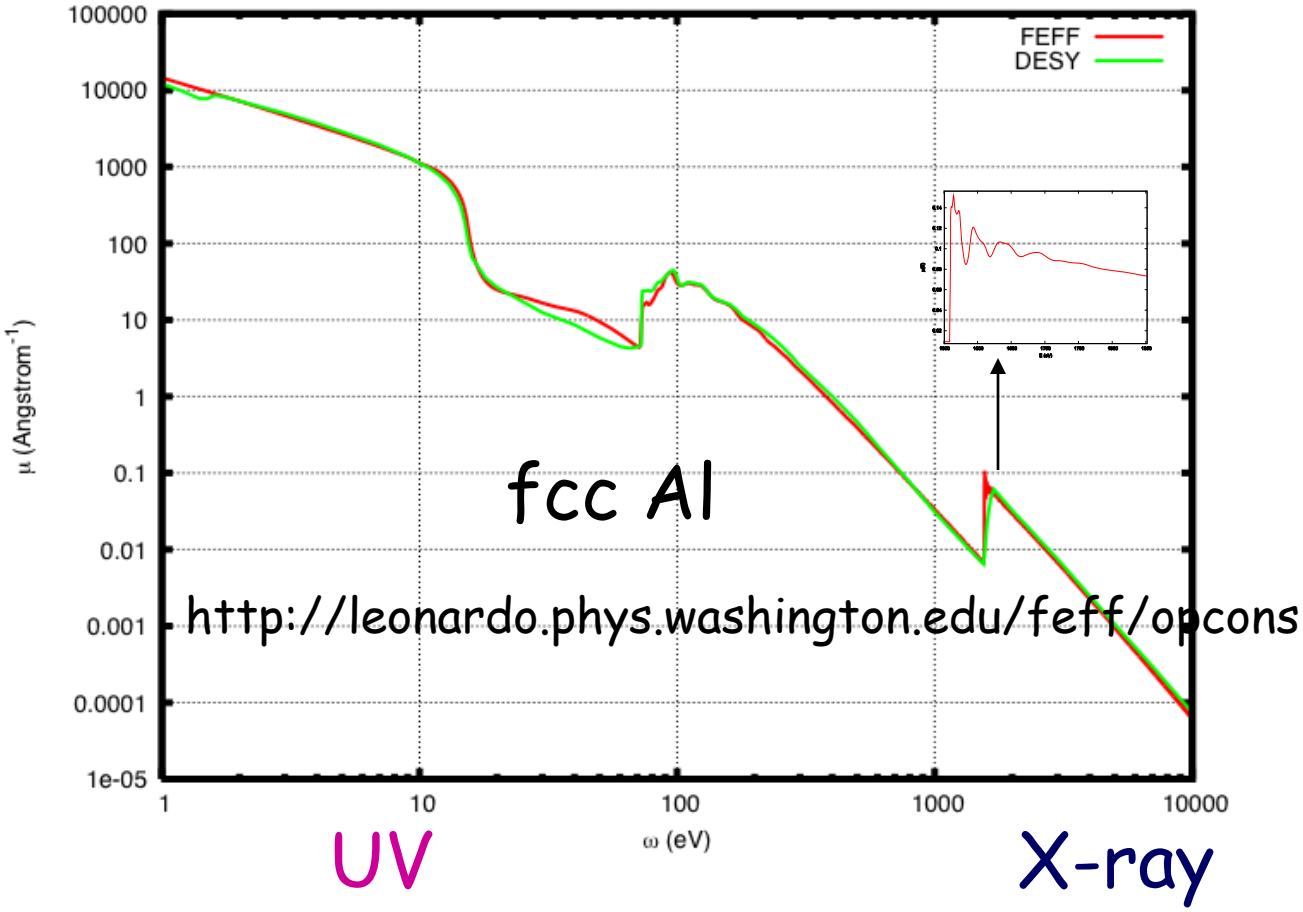
Supported by DOE-BES, DOE-CMCSN, and NSF

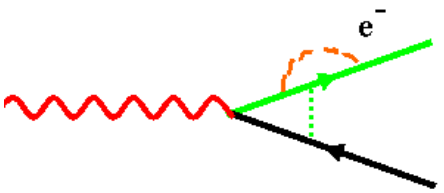
UNIVERSITY OF WASHINGTON

Goal: Full Spectrum Theory



Photon energy (eV)

"Can you write an equation for the theory?"



P.A.M. Dirac

to R. P. Feynman

EXAFS Equation of Stern, Sayers and Lytle*

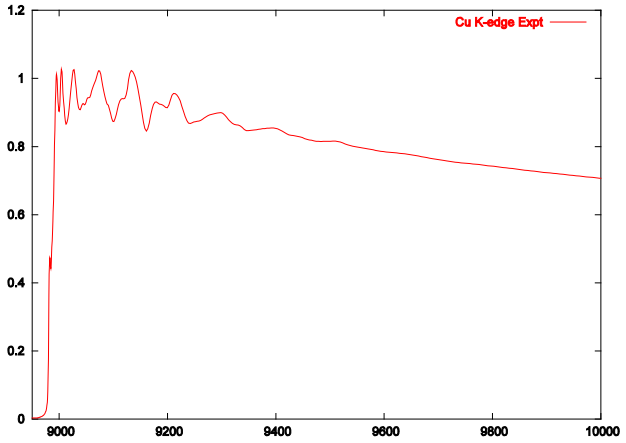
*Phys. Rev. Lett. 27, 1204 (1971)

VOLUME 27, NUMBER 18 PHYSICAL REVIEW LETTERS 1 NOVEMBER 1971

New Technique for Investigating Noncrystalline Structures: Fourier Analysis of the Extended X-Ray–Absorption Fine Structure*

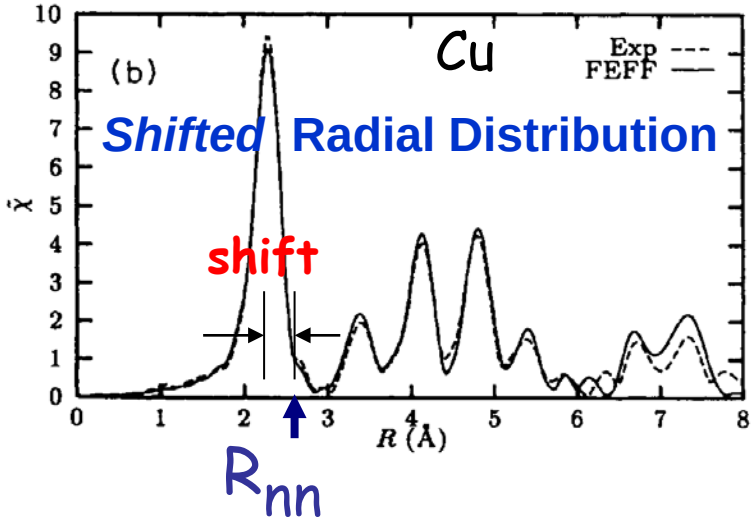
Dale E. Sayers† and Edward A. Stern†‡
Department of Physics, University of Washington, Seattle, Washington 98105
and
Farrel W. Lytle
Boeing Scientific Research Laboratories, Seattle, Washington 98124
(Received 16 July 1971)

We have applied Fourier analysis to our point-scattering theory of x-ray absorption fine structure to invert experimental data formally into a radial structure function with determinable structural parameters of distance from the absorbing atom, number of atoms, and widths of coordination shells. The technique is illustrated with a comparison of evaporated and crystalline Ge. We find that the first and second neighbors in amorphous Ge are at the crystalline distance within the accuracy of measurement (1%).



$$\chi(k) = -kf(k)\sum_j [N_j \exp(-\gamma r_j)/r_j^2] \exp(-\sigma_j^2 k^2/2) \sin[2kr_j + 2\eta(k)]$$

Drawback: need to calibrate with “Standard”



JJR's EXACT Single-scattering EXAFS Eq.*

*Phys Rev B**34**, 4350 (1986) - rejected by PRL

PHYSICAL REVIEW B VOLUME 34, NUMBER 6 15 SEPTEMBER 1986

New high-energy approximation for x-ray-absorption near-edge structure

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and Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

R. C. Albers
Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

C. R. Natoli
Laboratori Nazionali di Frascati dell'Istituto Nazionale di Fisica Nucleare, I-00044 Frascati, Italy

E. A. Stern
Department of Physics, University of Washington, Seattle, Washington 98195
(Received 14 April 1986)

Spherical-wave corrections in x-ray-absorption fine structure (XAFS) are incorporated using a novel high-energy approximation which replaces the plane-wave approximation and is found to be in excellent agreement all the way to the absorption edge. The single-scattering theory of XAFS is recovered in terms of distance-dependent backscattering amplitudes. Application to the *K*-shell XAFS of Cu yields results in close agreement with the corresponding exact treatment. Multiple-scattering contributions in XAFS and spherical-wave corrections in angle-resolved photoemission are treated similarly.

Origin of f_{eff}

An exact single-scattering XAFS equation can now be obtained by using Eqs. (5a) and (5b) in (4) and summing over m. The result now has the same form as Eq. (1), except that the backscattering amplitude and phase Φ are replaced by $\tilde{f}(\pi,R) = |\tilde{f}(\pi,R)|\, e^{i\Phi(R)}$, where

$$\tilde{f}(\pi,R) = \frac{1}{k}\sum_l (-1)^l (2l+1) t_l \times \left[\frac{(l+1)c_{l+1}^2(kR) + l c_{l-1}^2(kR)}{2l+1}\right]. \quad (9)$$

[curved wave corrections]

$$\chi(k) = S_0^2 \sum_R \frac{|f_{\mathrm{eff}}(k)|}{kR^2} \sin(2kR + \Phi_k) e^{-2R/\lambda_k} e^{-2\sigma^2 k^2}$$

Challenge

Can the EXAFS parameters

$$k \quad f_{\mathrm{eff}} \quad \Phi_k \quad \sigma^2 \quad \lambda_k \quad S_0^2$$

-- be calculated theoretically ?

-- up to 1500 eV above threshold ?

Ans 1: *Probably difficult …*

”I always thought it was easier to measure
x-ray absorption spectra than to
calculate it.”

Hans Bethe ~ 1980

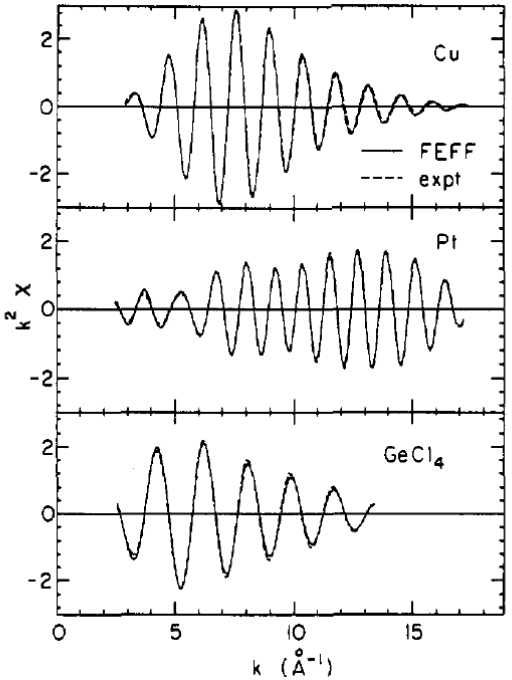
Ans 2 ~ 10 years later

Theoretical X-ray Absorption Fine Structure Standards

J. J. Rehr,*,† J. Mustre de Leon,†,‡ S. I. Zabinsky,† and R. C. Albers§

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.



FEFF3 *JACS **113**, 5136 (1991)

Key ingredients:

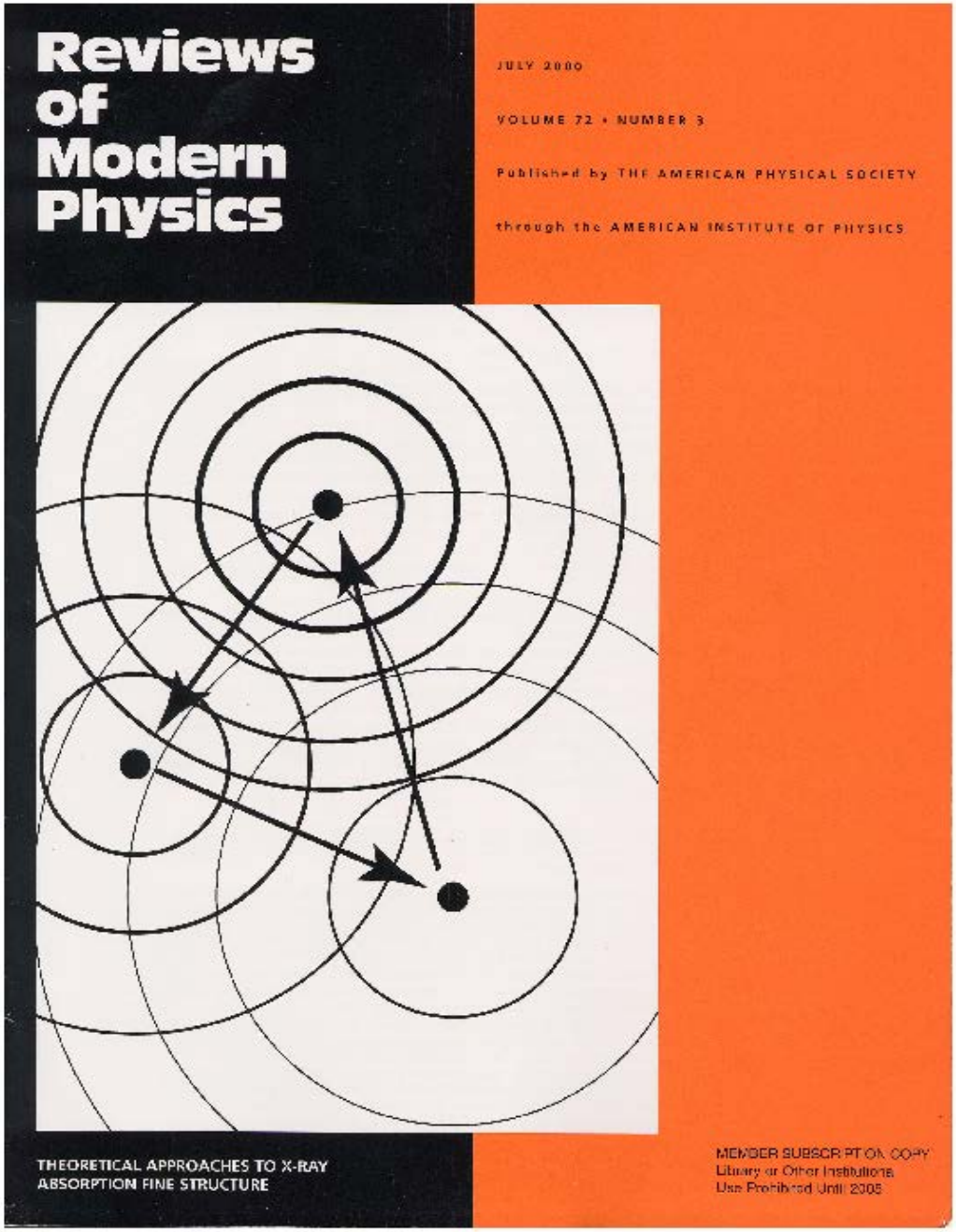
Curved wave theory $f_{\text{eff}}(k)$ to $k = 20$ (1500 eV)

Hedin-Lundqvist self-energy Σ

Dirac-relativistic phase shifts δ_l to $l=20$

Correlated Debye Model σ^2

\+ Integrated, linked, user-friendly code FEFF



Ans 3: ~another10 years with DOE support

Full MS Theory of EXAFS

FEFF6

J. J. Rehr & R.C. Albers

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

http://leonardo.phys.washington.edu/feff/

Developments: SCFQuasi-particle Theory

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

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

Quasi-particle final states ψ_f

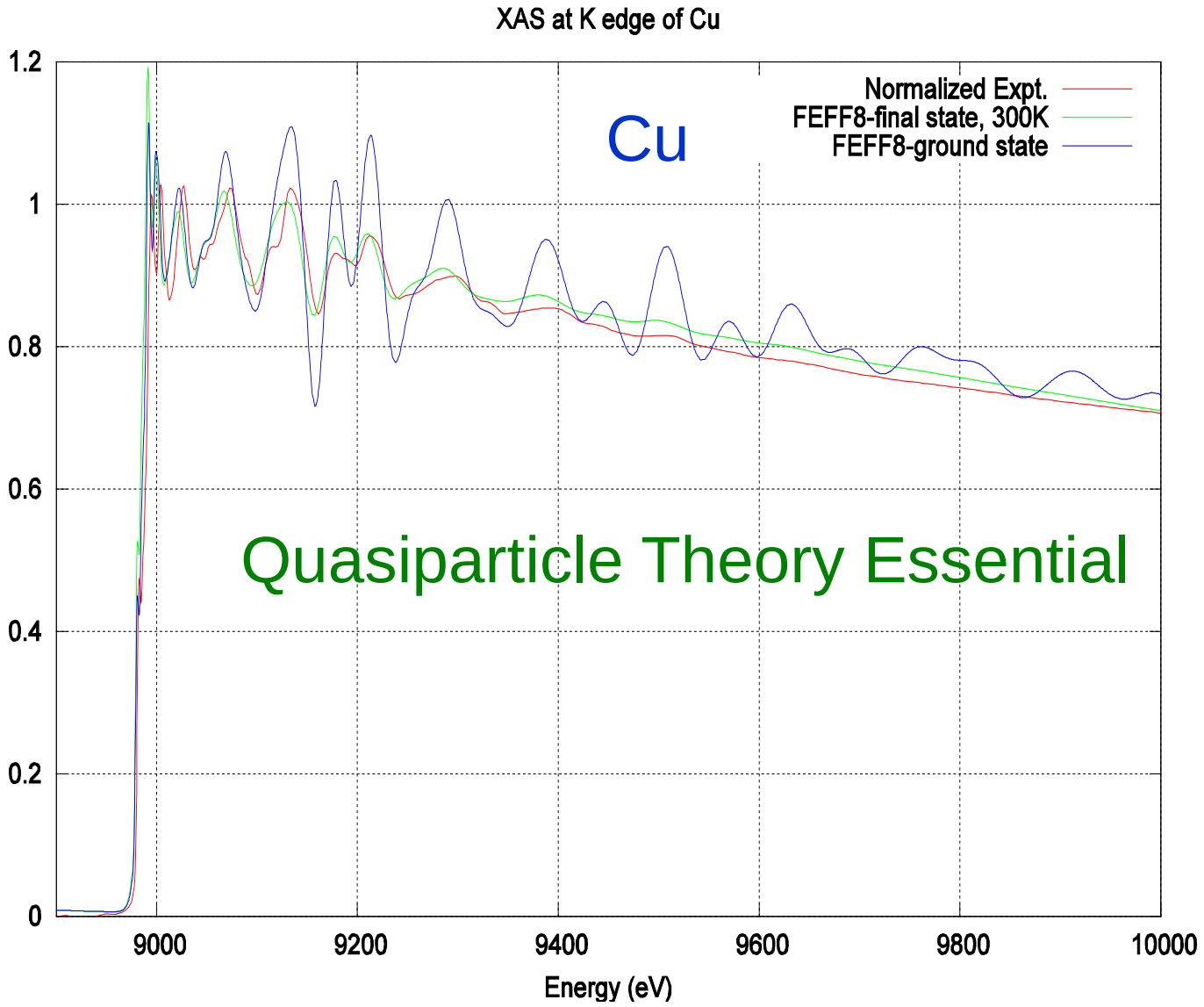
$$\left[\frac{p^2}{2m} + V'_{coul} + \Sigma(E)\right] \psi_f = E_f \psi_f$$

Final state rule

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

Non-hermitian self-energy $\Sigma(E)$ Beyond DFT (replaces Vxc)

Ground-state vs Quasiparticle vs Expt



Real-space Green's Function Theory (RSGF)

Golden rule via Wave Functions

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

Paradigm shift:

Golden rule via *Green's* Functions $\mathbf{G} = 1/(E - h - \Sigma)$

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

No sums over final states !

Real-space Green's Function Formalism

full-multiple scattering vs MS path expansion

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

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

(MS path expansion - geometric series)

$$= [1 - G^0 t]^{-1} G^0$$

"full MS"

"Real-space KKR"

Ingredients:

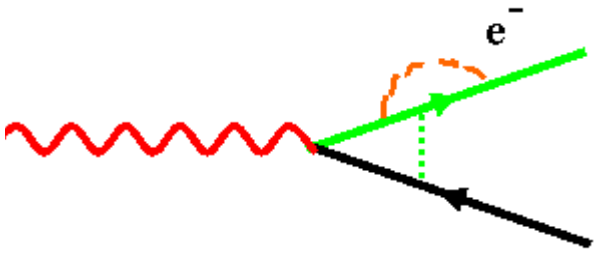
$\boldsymbol{G_0}$ free propagators, $\boldsymbol{t}$-matrix $= e^{i\,\delta_l}\,sin\,\delta_l\,\boldsymbol{\delta}_{RR'}\boldsymbol{\delta}_{ll'}$

Rehr-Albers Scattering Matrix f_{eff}

Relativistic RSGF Theory*

*JJR + A. Ankudinov PRB **56**, R1712 (1997)

2 Steps



1) Production

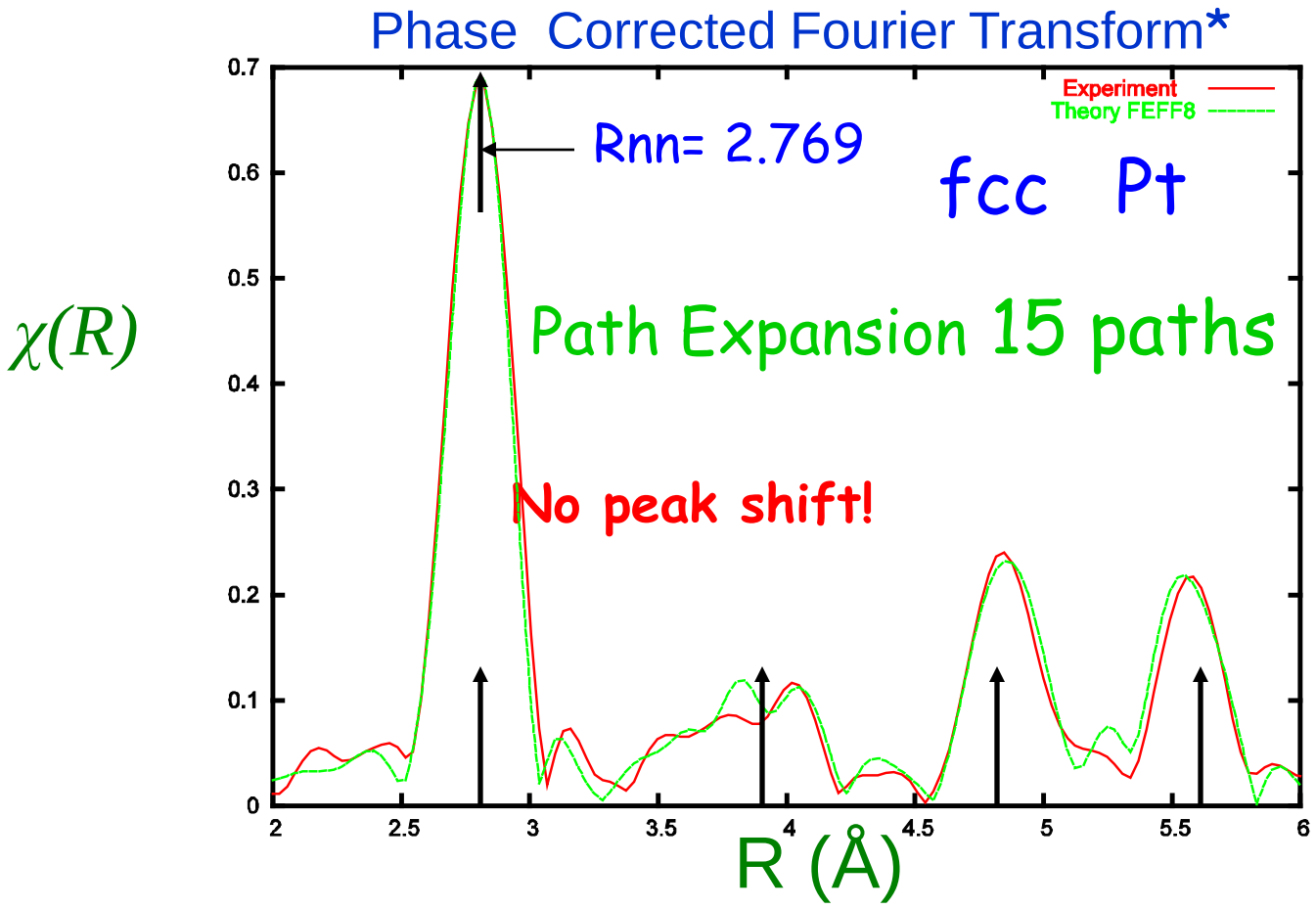
Dirac-Fock atomic theory $|\langle f | d | I \rangle|$

2) Scattering $G = G_0 + G_0 T G$

Non-relativistic, no spin-flips, …

$$\sigma(\omega) = -\frac{4\pi c}{\omega}\mathrm{Im}\sum_{I,Js,J's'}\langle I|d_\epsilon^*|R_{Js}\rangle G_{Js,J's'}\langle R_{J's'}|d_\epsilon|I\rangle.$$

EXAFS - MS Path Expansion

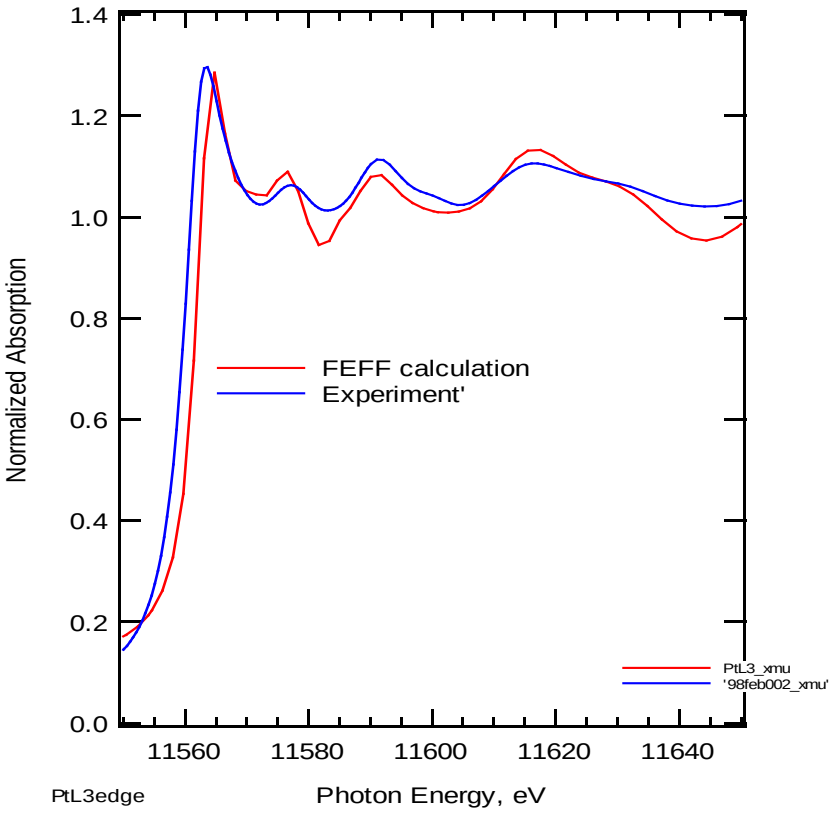


Widely used in expt analysis e.g., with IFEFFIT etc.

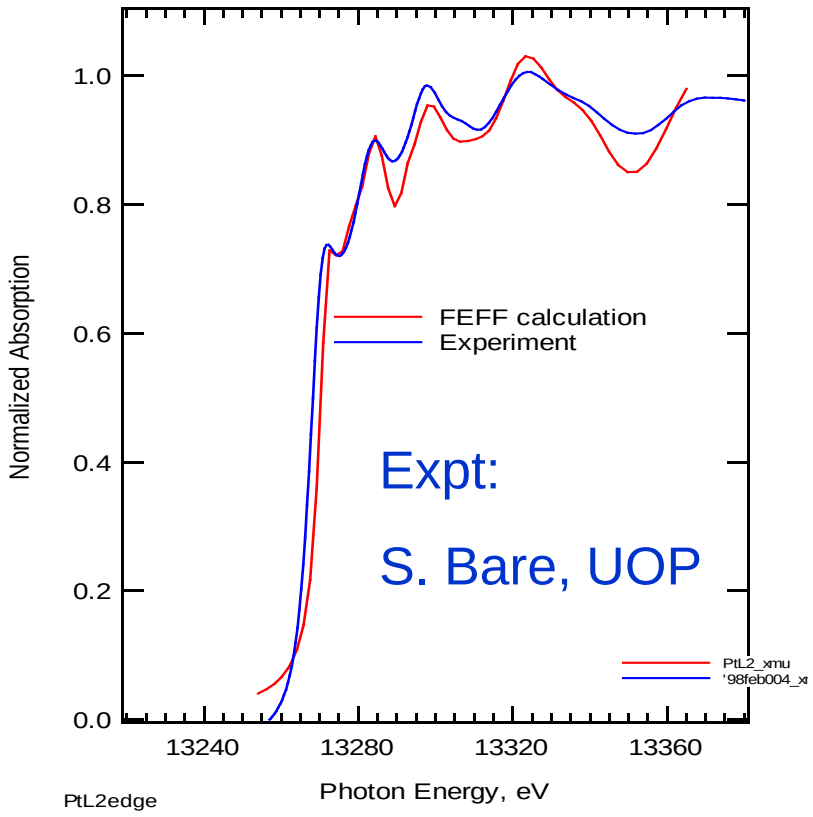
XANES

FEFF8

Pt L_3-edge



Pt L_2-edge



- **Relativistic effects & spin-orbit crucial! -**

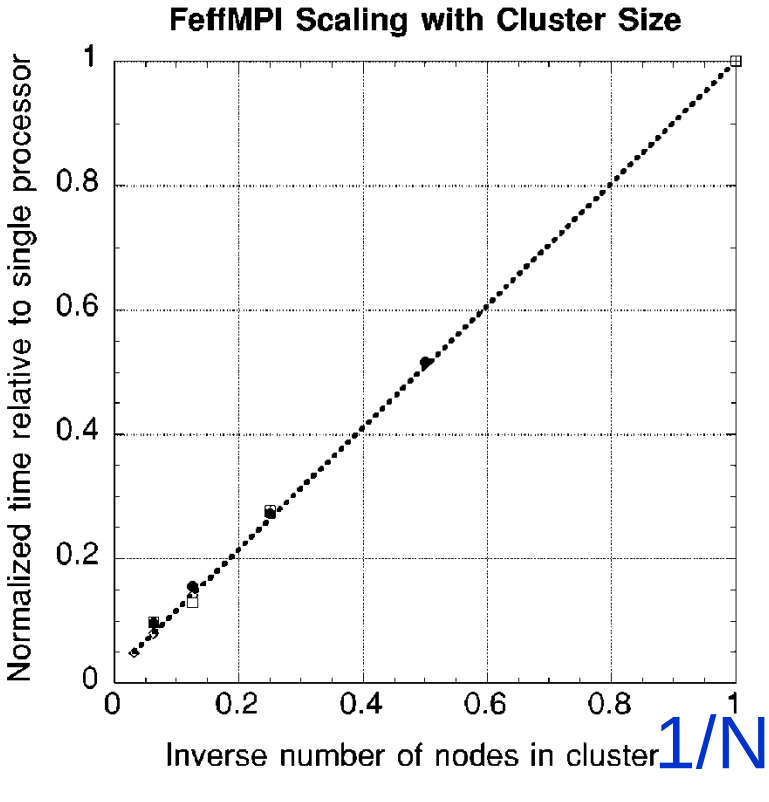
  Reproduces all spectral features e.g. no L_2 white line

Green's Functions and Parallel Computation

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*



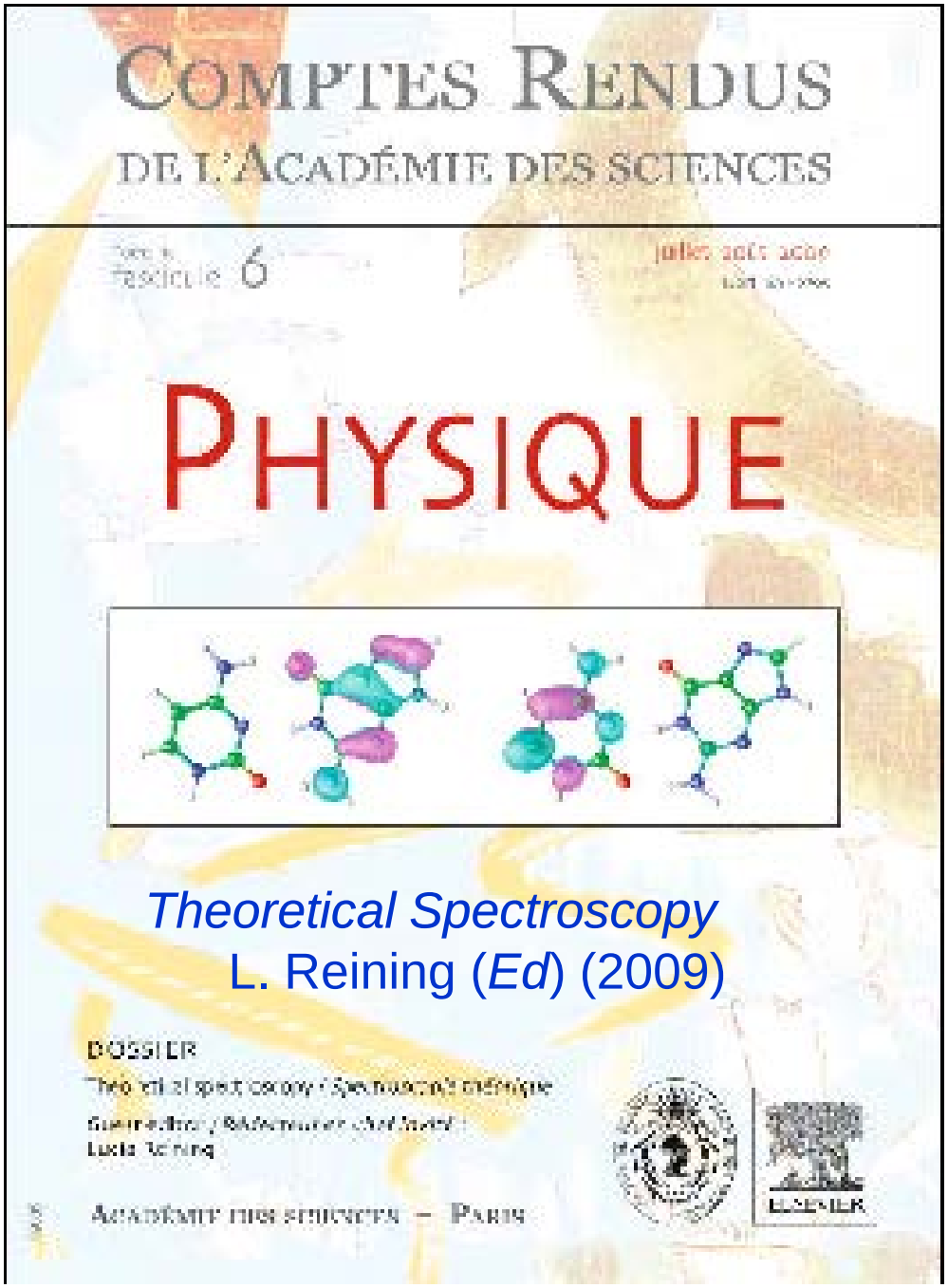
$1/N_{CPU}$

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

Energy E ***is a parameter*** !

"Natural parallelization"

Each CPU does one energy



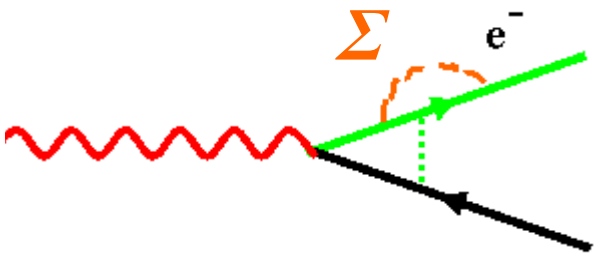
Ans 4 ~10 more years
now with ab initio
many body ingredients

FEFF9

JJR et al., Comptes Rendus
Physique **10**, 548 (2009)

Ab initio Calculations of Many body effects*

Quasi-particles & beyond

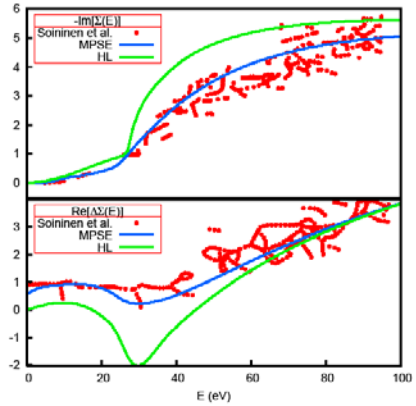


- Self-energy $\Sigma(E)$ Damping
- Core-hole effects Screening
- Debye-Waller factors $e^{-2\sigma^2 k^2}$
- Multi-electron excitations Satellites & Multiplets

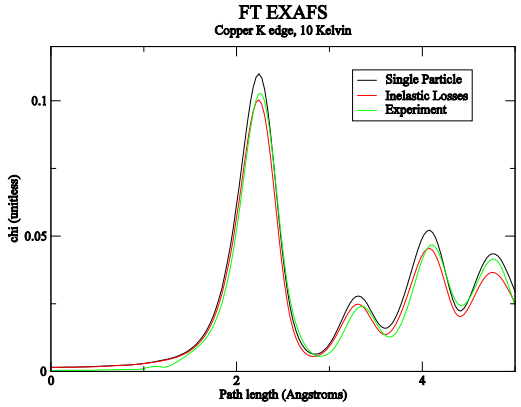
*FEFF9 ~ 10^5 lines of code

Ingredients

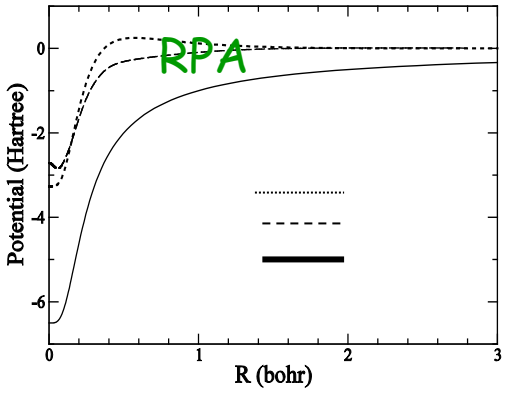
ab initio Self-energies, & mean free paths



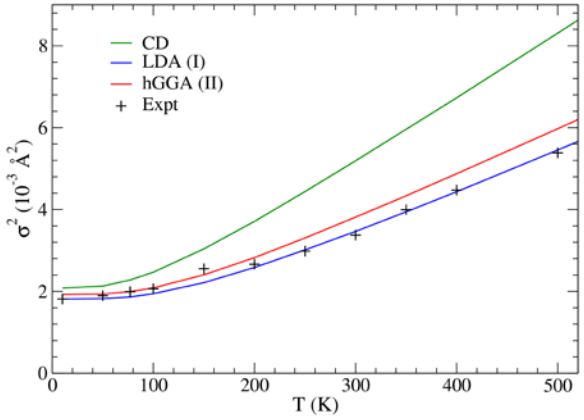
ab initio S_0^2



ab initio RPA Core-hole



ab initio Debye Waller factors



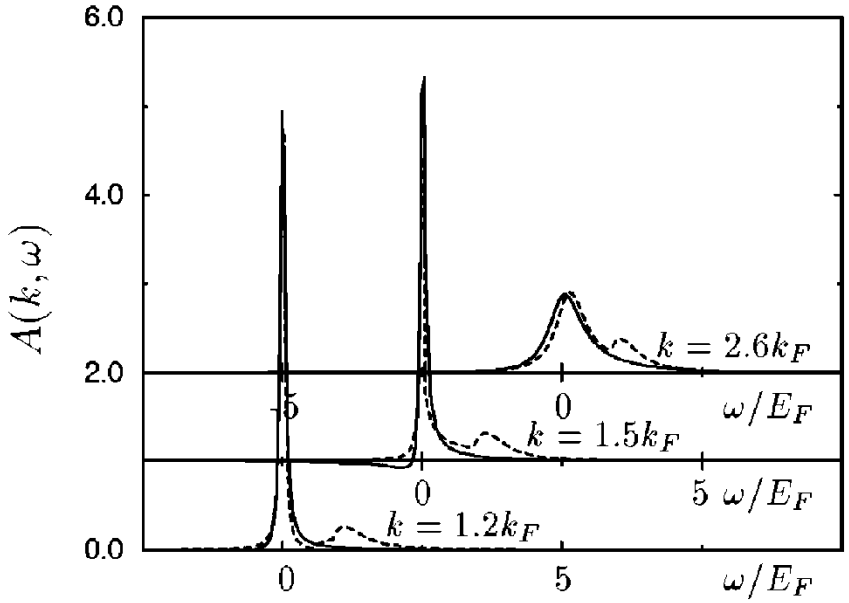
Multielectron Excitations & Satellites

PHYSICAL REVIEW B, VOLUME 65, 064107

Interference between extrinsic and intrinsic losses in x-ray absorption fine structure

L. Campbell,[1] L. Hedin,[2] J. J. Rehr,[1] and W. Bardyszewski[3]
[1]*Department of Physics, University of Washington, Seattle, Washington 98195-1560*
[2]*Department of Physics, Lund University, Lund, S22362 Sweden*
and MPI-FKF, Stuttgart, D70569 Germany
[3]*Department of Physics, Institute of Theoretical Physics, 00-681 Warsaw, Poland*

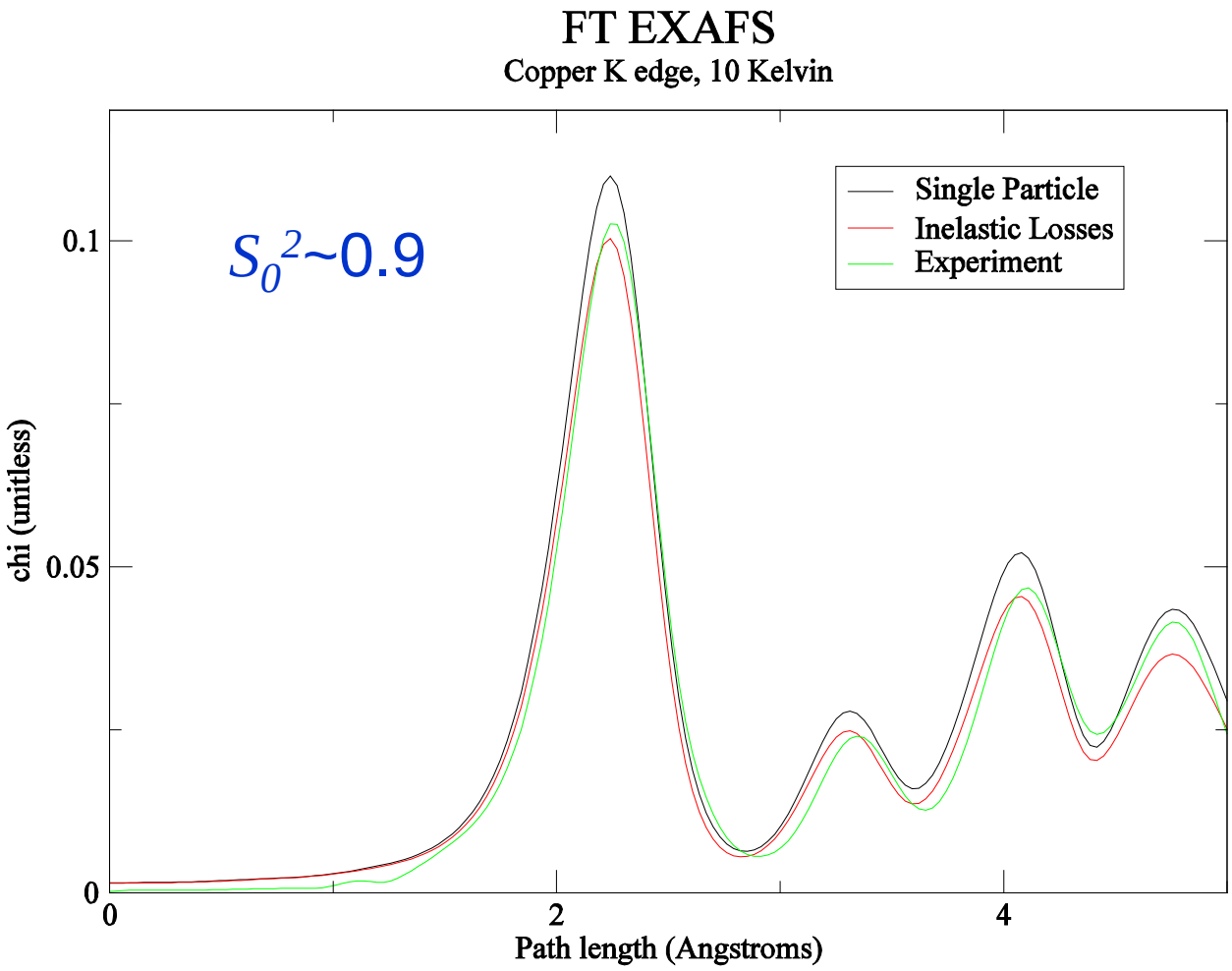
Energy Dependent Spectral Function $A_k(\omega)$



$$A_k(\omega) = (-1/\pi)\ \mathrm{Im}\ G_k(\omega)$$

cf. W. Bardyszewski and L. Hedin, Physica Scripta **32**, 439 (1985)

Example: S_0^2 in EXAFS



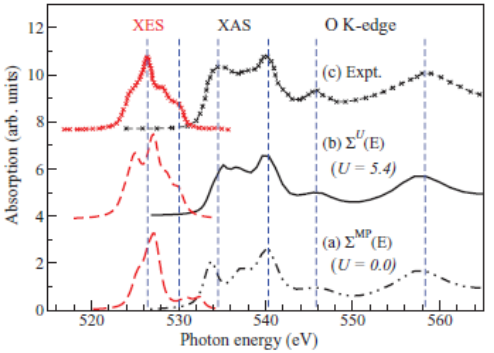
Extensions: Hubbard-model in FEFF9 strong correlation effects

PHYSICAL REVIEW B 85, 165123 (2012)

Hubbard model corrections in real-space x-ray spectroscopy theory

Towfiq Ahmed, J. J. Kas, and J. J. Rehr

O K-edge MnO



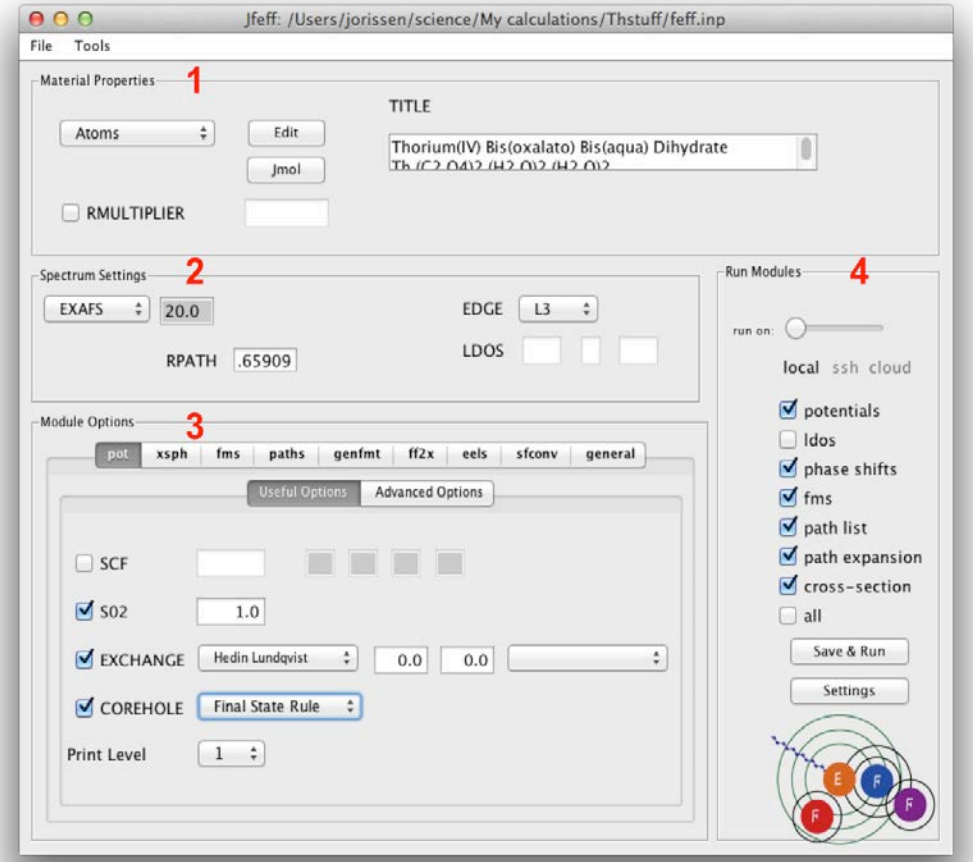
Hubbard U as self-energy correction

$$V^U(\mathbf{r}, E) = V^{SCF}(\mathbf{r}) + \Sigma^{GW}(E) + \Sigma^U_{lm\sigma}(E)$$

cf. H. Jiang, Rinke et al. Phys. Rev. B **82**, 045108 (2010).

JFEFF GUI & Scientific Cloud Platform with improved software practices

- Linux, Windows, Mac
- Automated installers
- Run locally, on cluster, or on **Amazon EC2** cloud
- Reads FEFF9 input files
- 20 example calculations
- Users Guide
- No need to compile
- User-friendly
- Built in help, error checks



*K. Jorissen et al., Comp. Phys. Comm. **183**, 1911 (2012)

Supported by NSF SI2 Grant

Extensions: Scattering spectroscopies

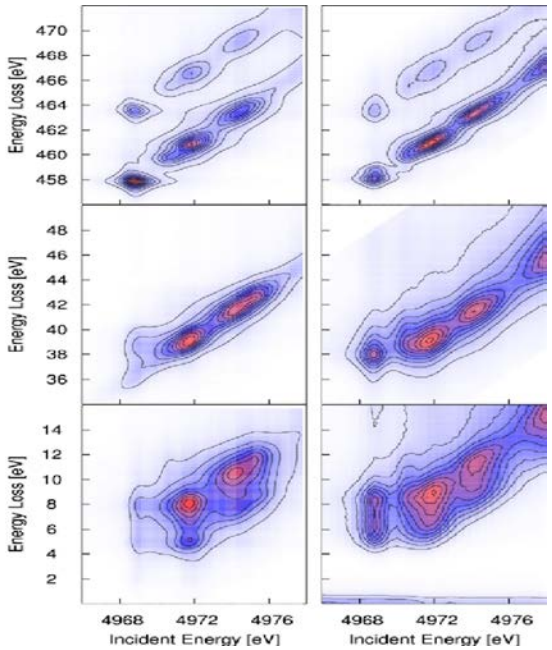
RIXS

PHYSICAL REVIEW B **83**, 235114 (2011)

Real-space Green's function approach to resonant inelastic x-ray scattering

J. J. Kas,[1] J. J. Rehr,[1,*] J. A. Soininen,[2] and P. Glatzel[3]
[1]*Department of Physics, Box 351560, University of Washington, Seattle, Washington 98195-1560, USA*
[2]*Department of Physics, P.O. Box 64, University of Helsinki, FI-00014 Helsinki, Finland*
[3]*European Synchrotron Radiation Facility, B.P. 220, F-38043 Grenoble, France*
(Received 21 January 2011; revised manuscript received 7 April 2011; published 8 June 2011)

We present an *ab initio* theory of core and valence resonant inelastic x-ray scattering (RIXS) based on a real-space multiple-scattering Green's function formalism and a quasiboson model Hamiltonian. Simplifying assumptions are made that lead to an approximation of the RIXS spectrum in terms of a convolution of an effective x-ray absorption signal with the x-ray emission cross section. Additional many-body corrections are incorporated in terms of an effective energy-dependent spectral function. Example calculations of RIXS are found to give qualitative agreement with experimental data. Our approach also yields simulations of lifetime-broadening suppressed x-ray absorption, as observed in high-energy resolution fluorescence detection experiment. Finally, possible improvements to our approach are briefly discussed.



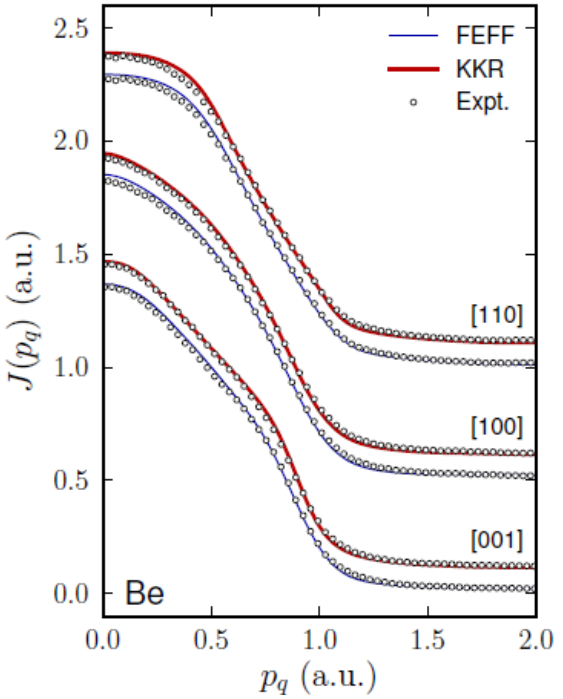
COMPTON

PHYSICAL REVIEW B **85**, 115135 (2012)

Real-space Green's function calculations of Compton profiles

Brian A. Mattern, Gerald T. Seidler,* Joshua J. Kas, Joseph I. Pacold, and John J. Rehr
Department of Physics, University of Washington, Seattle, Washington 98195-1560, USA
(Received 2 February 2012; revised manuscript received 16 March 2012; published 29 March 2012)

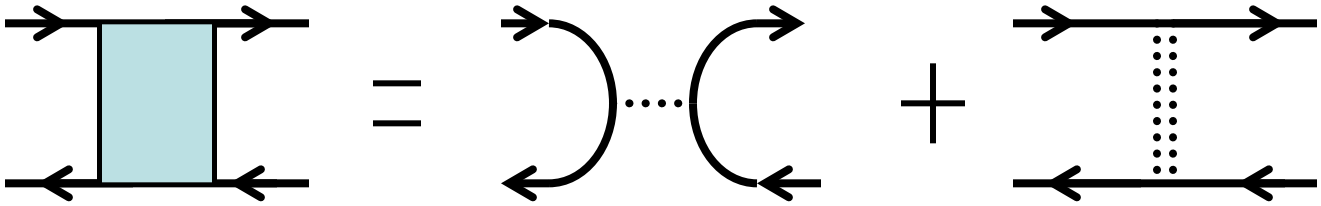
We report the development of a first-principles, real-space Green's function method for calculation of Compton profiles in the impulse approximation. For crystalline Be, we find excellent agreement with prior theoretical treatments requiring periodicity, with prior experimental measurements of the Compton profile, and with present measurements of the dynamical structure factor via nonresonant inelastic x-ray scattering (often also called x-ray Thomson scattering in the plasma physics community). We also find good agreement with prior experimental results for the Compton profile of Cu. This approach can be extended to disordered and very high-temperature systems, such as "warm dense matter," where theories presently used for the interpretation of inelastic x-ray scattering include condensed phase effects only at a perturbative level.



Ans 5: ~2011 Are we there yet ?

FEFF uses MT potentials; also lacks BSE

GW/BSE Theory



$$-\mathrm{Im}\,\epsilon^{-1}(\mathbf{q},\omega) = \frac{4\pi}{q^2}\mathrm{Im}\,\langle\Psi_0|\hat{D}^\dagger \frac{1}{E_0+\omega-\hat{H}+i\gamma}\hat{D}|\Psi_0\rangle$$

Ingredients: Particle-Hole Hamiltonian

$H = h_e - h_h + V_{eh}$ $h_{e/h} = \varepsilon_{nk} + \Sigma_{nk}$

Σ GW self-energy $V_{eh} = V_x + W$ Particle-hole

BSE Core-XAS OCEAN*

Bethe-Salpeter Equation Calculation of Core Excitation Spectra

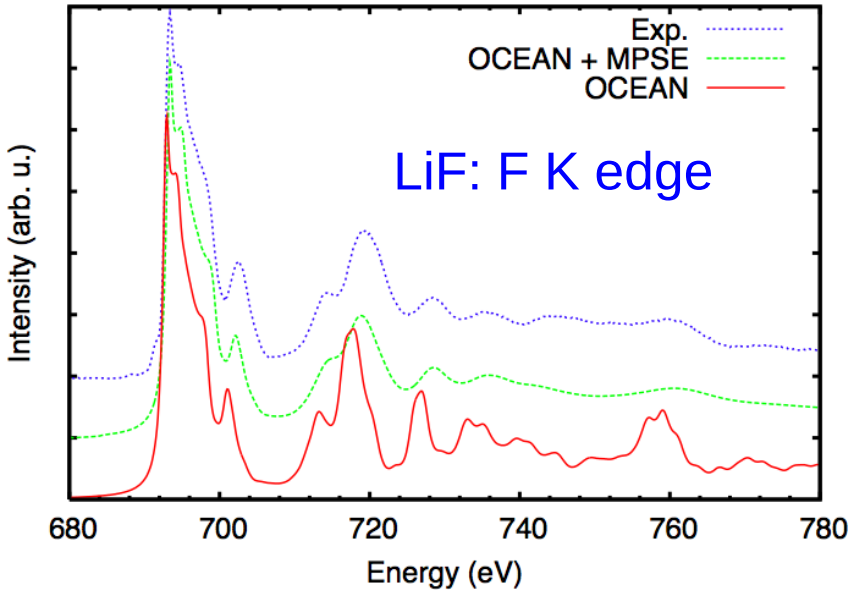
J. Vinson,[1] E. L. Shirley,[2] J. J. Rehr,[1] and J. J. Kas[1]

[1]*Dept. of Physics, Univ. of Washington Seattle, WA 98195*
[2]*National Institute of Standards and Technology, Gaithersburg, MD 20899*

(Dated: June 25, 2010)

We present a hybrid approach for GW/Bethe-Salpeter Equation calculations of core excitation spectra, including x-ray absorption, electron energy loss spectra, and inelastic x-ray scattering. The method is based on *ab initio* wavefunctions from the plane-wave pseudopotential code ABINIT; atomic core-level states and projector augmented wave (PAW) transition matrix elements; the NIST core-level Bethe-Salpeter Equation solver; and a many-pole GW self-energy model to account for final-state broadening and self-energy shifts. Multiplet effects are also included for L-edges. The approach is implemented using an interface dubbed OCEAN (Obtaining Core Excitations using ABINIT and NBSE). Examples are presented for the Li and F K edges in LiF, the Mg $L_{2,3}$ edge in MgO, K and Cl K edges and the K $L_{2,3}$ edge in KCl, and the Ti $L_{2,3}$ edge in $SrTiO_3$, and are compared with experiment and other theoretical approaches.

*Obtaining Core Excitations from ab initio NBSE



Plane-wave, pseudo- potential + supercell + PAW + MPSE

cf. EXC!TING, XSPECTRA

Phys. Rev. B**83**, 115106 (2011)

Unified treatment of multiplets and extended states

Phys. Rev. B **86**, 195135 (2012)

BSE calculations of transition metal L-shell spectra

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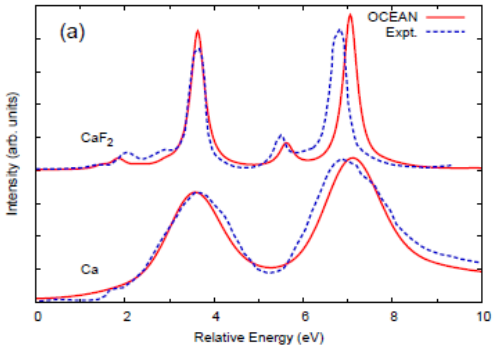
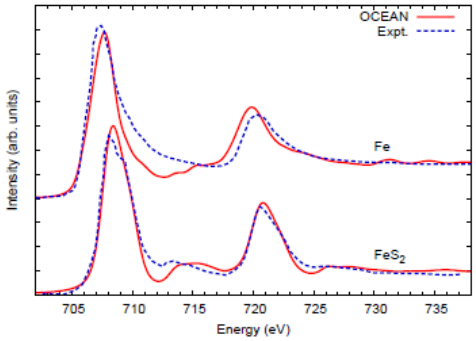
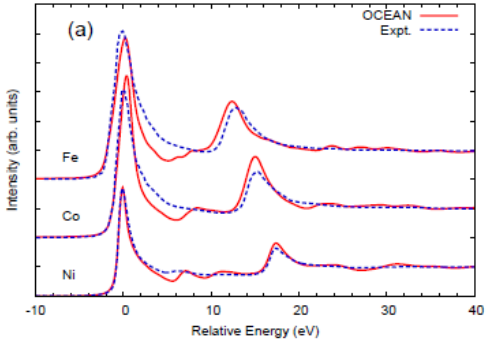
(Dated: July 3, 2012)

We present *ab initio* Bethe-Salpeter equation (BSE) calculations of the $L_{2,3}$ edges of several insulating and metallic compounds containing Ca, V, Fe, Co, Ni, and Cu, spanning a range of *3d*-electron occupations. Our approach includes the key ingredients of a unified treatment of both extended states and atomic multiplet effects, i.e., self-consistent crystal potentials, ground-state magnetism, *GW* self-energy corrections, spin-orbit terms, and Coulomb interactions between the L_2 and L_3 states. The method is implemented in the OCEAN package, which uses plane-wave pseudopotential wave functions from ABINIT as a basis, a PAW construction for transition matrix elements, and a resolvent formalism for the BSE calculation. The results are in near quantitative agreement with experiment, including both fine-structure at the edges and the non-statistical L_3/L_2 ratios observed in these systems.

alá E. Shirley: GW/BSE no crystal field parameters







Summary & Conclusions

- Evolution of FEFF spanned 3 decades !
- Combined advanced codes (FEFF+OCEAN) now yield **quantitative** full spectrum response UV-XAS
- Codes now semi-automated, user-friendly with JFEFF GUI, cloud computing platform
- Synergy between Theory, Computation, and Expt crucial to advance scientific progress

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- **J. Kas (UW)**
- **F. Vila (UW)**
- **K. Jorissen (UW)**
- **J. Vinson (UW)**
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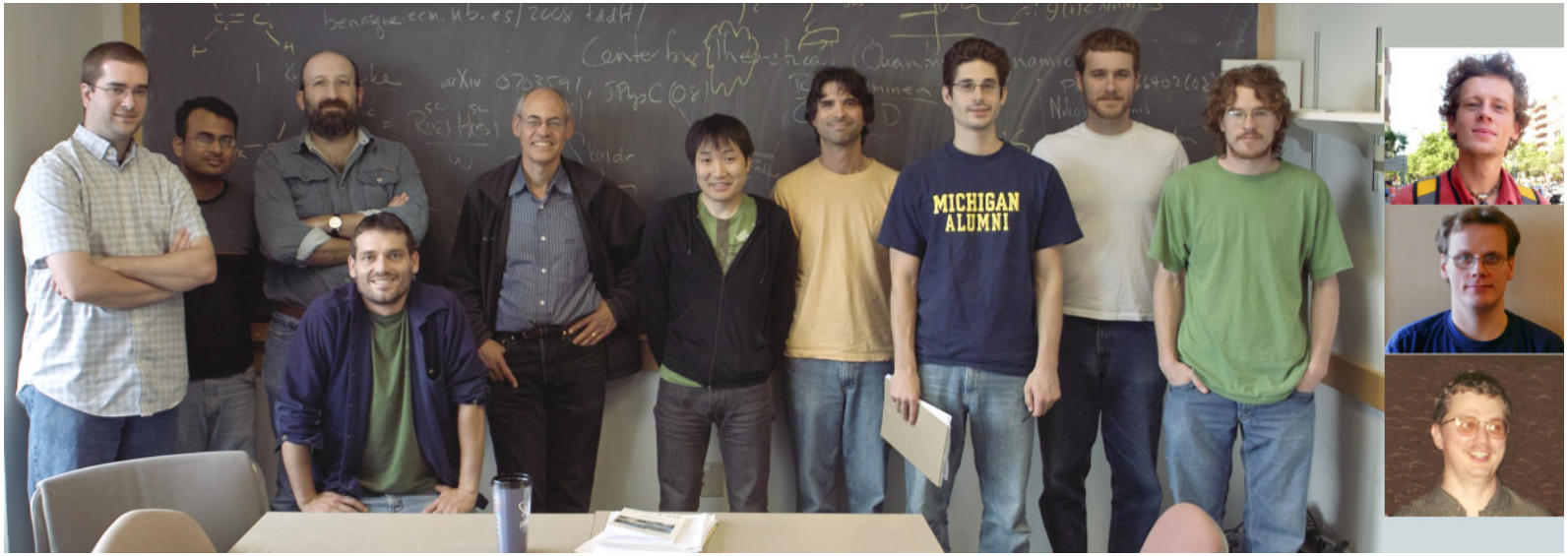

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