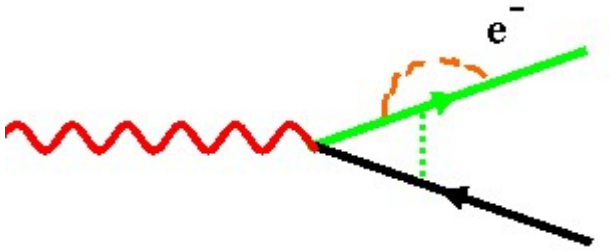
CONEXS 2020: Emerging Trends in X-Ray Spectroscopy
New Castle, UK February 18-20, 2020

Perfecting the Theory and Interpretation of X-ray Spectroscopy

J. J. Rehr

University of Washington and SLAC



UNIVERSITY OF WASHINGTON TIMES Pacific Northwest NATIONAL LABORATORY SPEC U.S. DEPARTMENT OF ENERGY Office of Science

Perfecting the Theory and Interpretation of X-ray Spectroscopy

- **TALK** - Progress toward next generation XAS theory

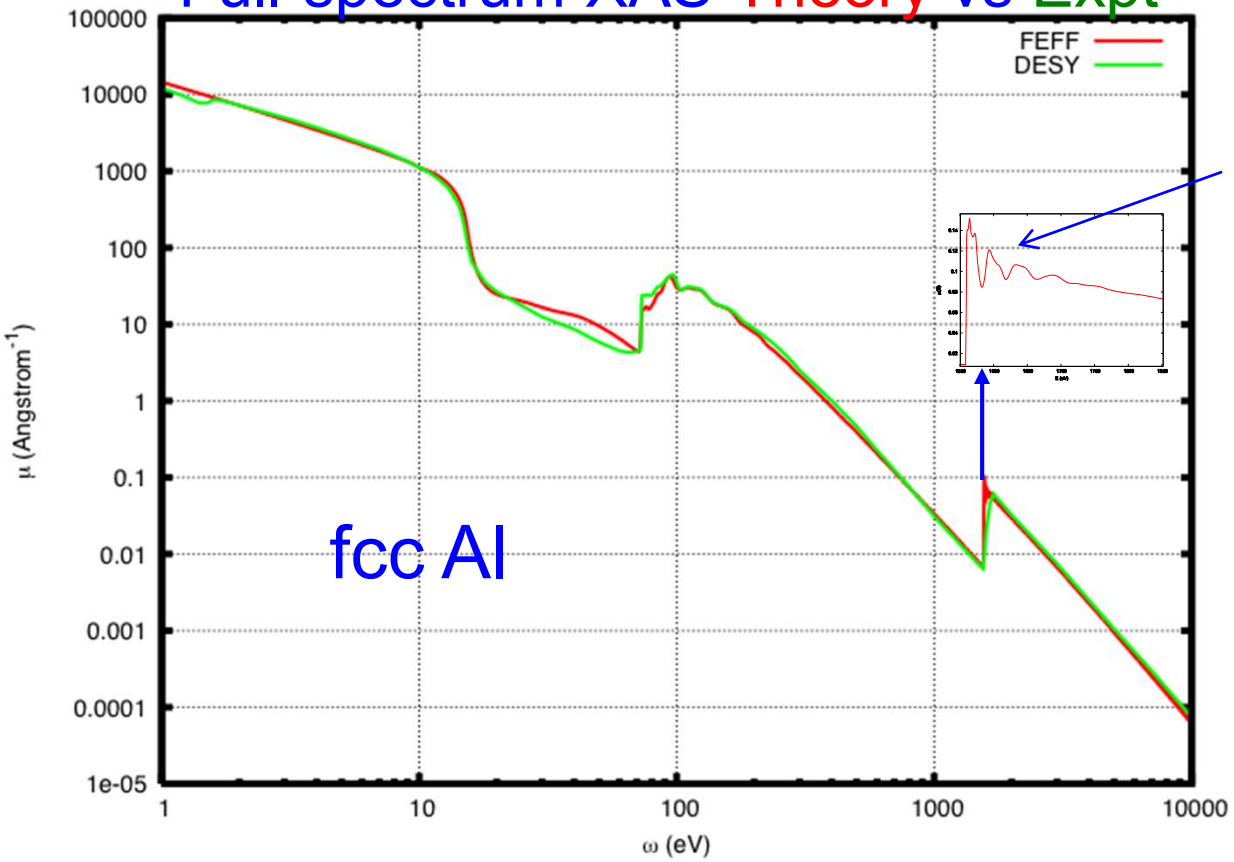
I. Introduction – EXAFS

II. Improved theory – XANES

III. Perfecting the theory …

I. Introduction

Full-spectrum XAS Theory vs Expt



K-edge EXAFS

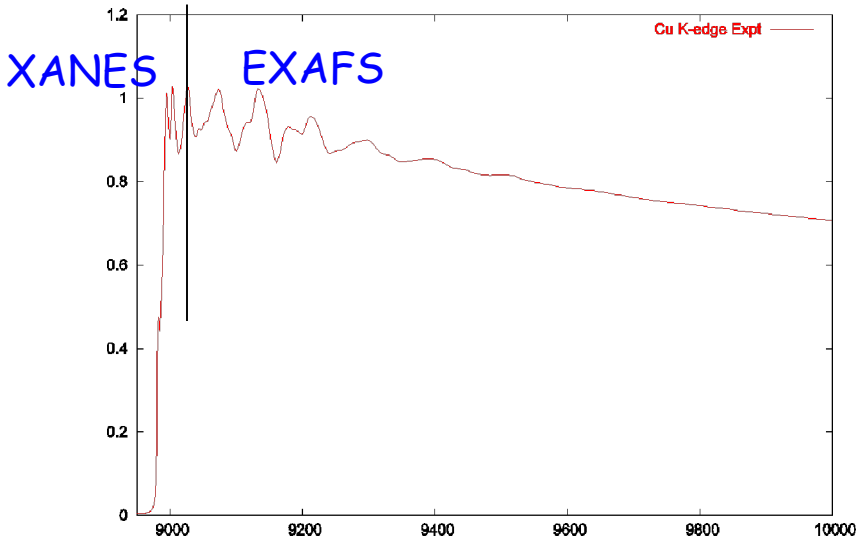
fcc Al

UV X-ray

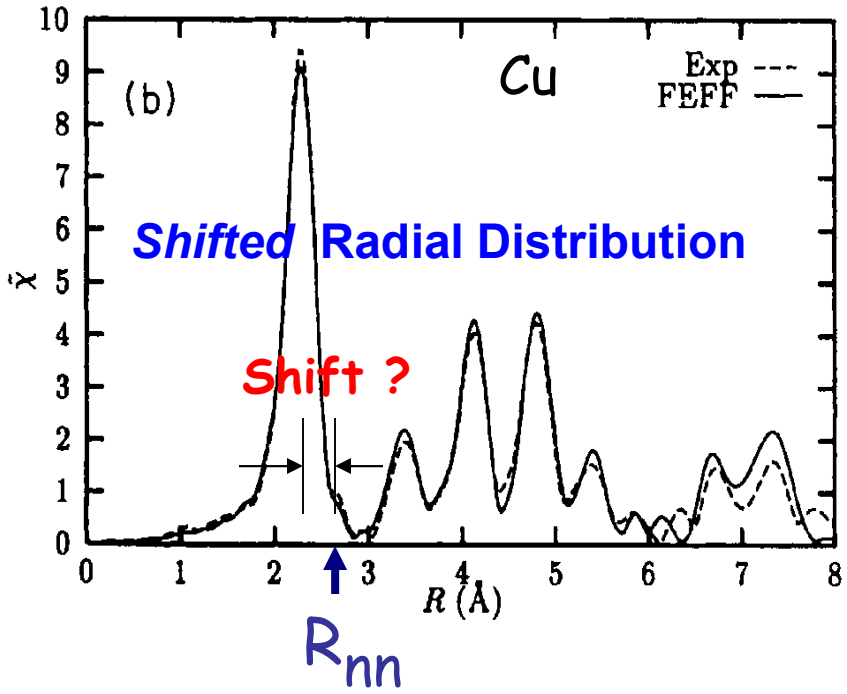
Photon energy (eV)

Historical Interpretation of EXAFS*

EXAFS → Local structure



Fourier Transform



→ X-ray Microscope!

*Stern Sayers Lytle, UW 1971

BUT need to calibrate experiment with "Standard"

Question: Can one calculate EXAFS shifts?

“ If I can’t calculate it

I don’t understand it ”

R. Feynman

Maybe not ?

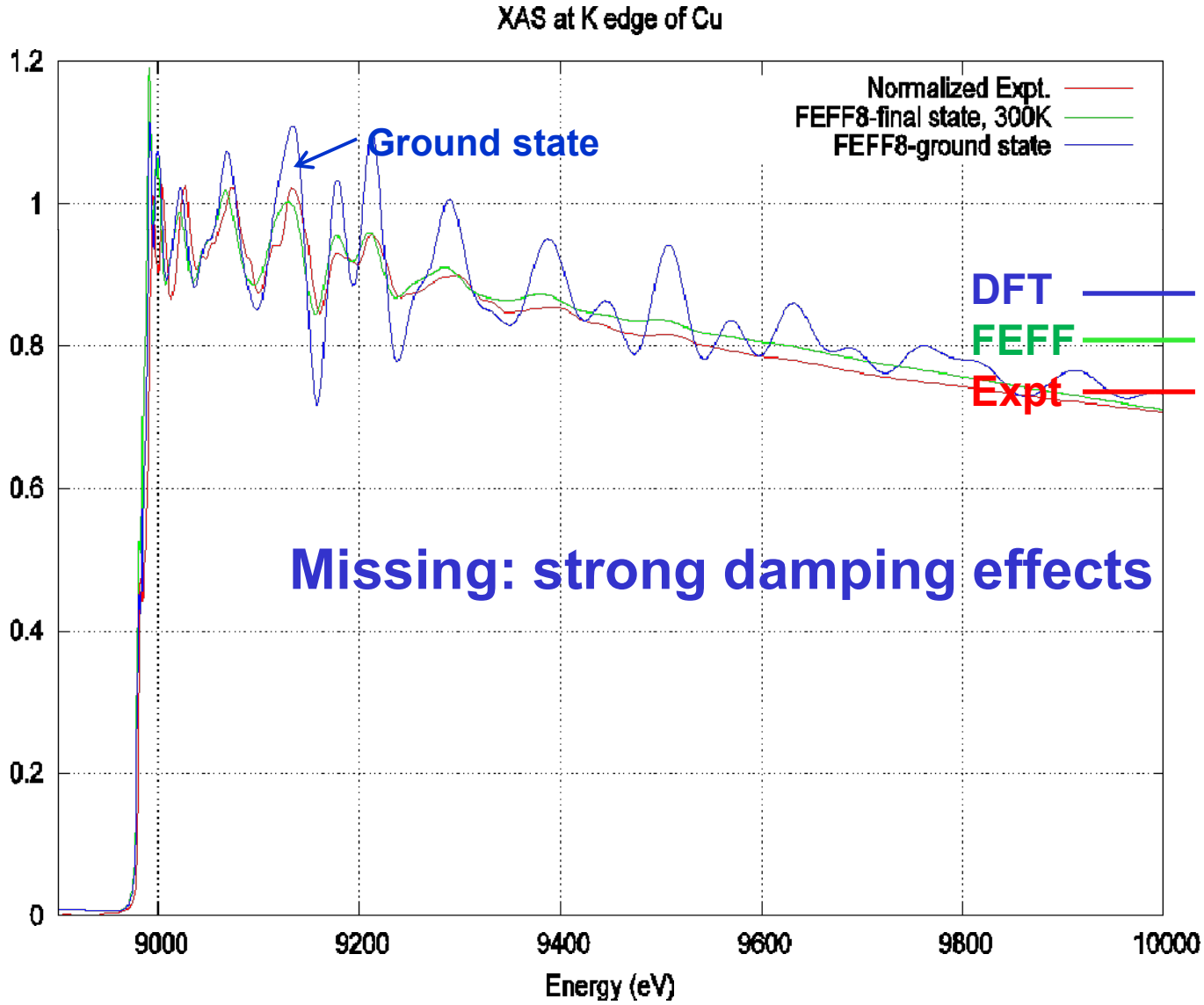
”I always thought it was easier to

measure XAS than to calculate it.”

Hans Bethe

ca 1980

Gotcha: Standard DFT Theory *Fails*



R_x for EXAFS theory

EXAFS Equation : Stern, Sayers, Lytle (1971)

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

All-electron scattering theory, $E \sim 10^4$ eV $l \sim 25$ f_{eff} Φ_k

Short mean free paths $\lambda_k \sim 5 - 20$ Å

Core-hole & lifetime effects Γ

Vibrational damping $e^{-2\sigma^2 k^2}$

No code in 1970's with all those features !

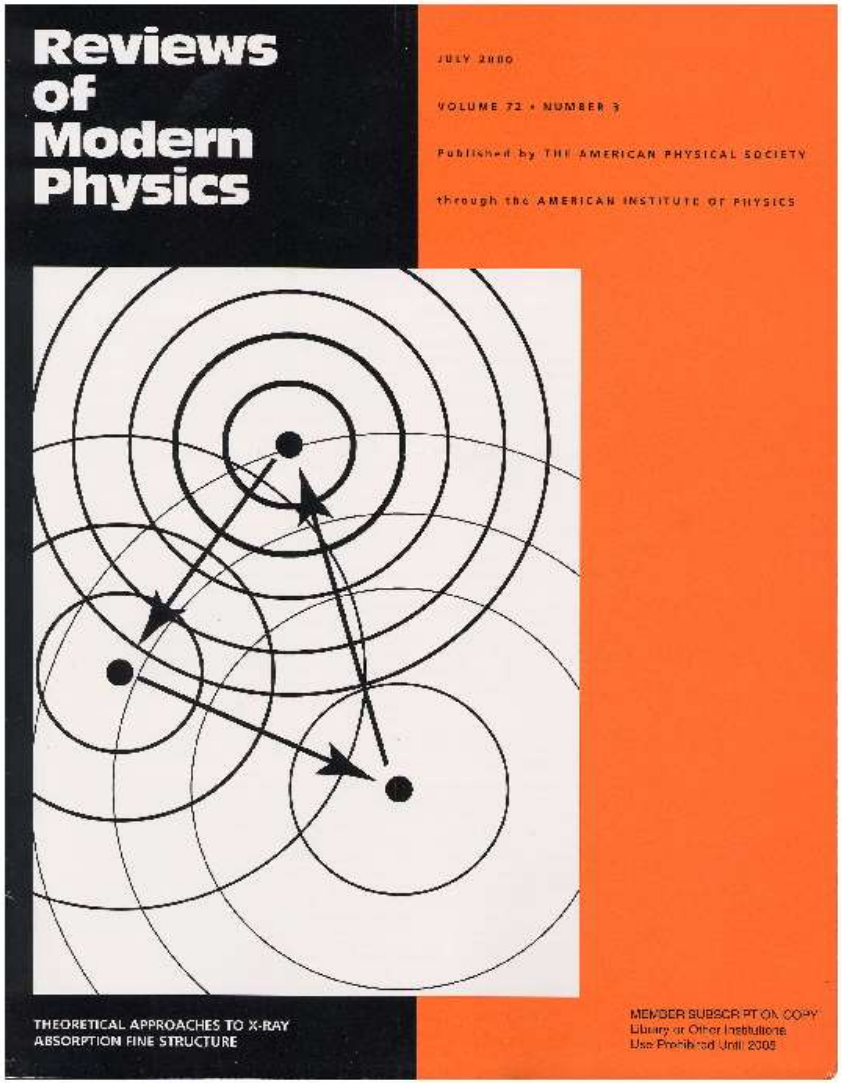
What to do ?

"The chance is high that the truth is in the fashionable direction …

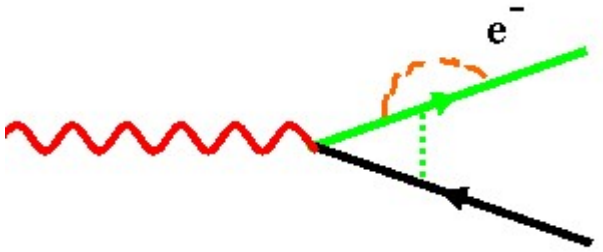
… but if it isn't, who will find it?"

R. Feynman

Breakthrough: Green's function theory*



*Real-space multiple-scattering theory



FEFF

J. J. Rehr & R.C. Albers

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

http://feff.phys.washington.edu

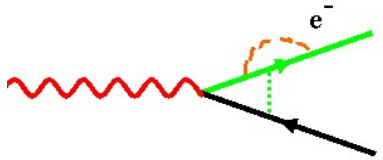
Golden rule via Green's Function

Golden rule for XAS via Wave functions

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

Paradigm shift: XAS via Green's Function

$$\mathbf{G} = 1/(E - h' - \Sigma)$$



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

h' Final-state Hamiltonian with core-hole

What's a Green's function?

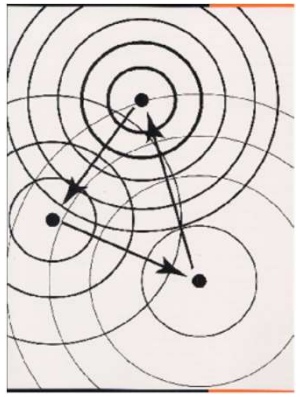
Wave function in QM $H\,\Psi = E\,\Psi$

$\Psi(r)$ = Amplitude to find particle at r

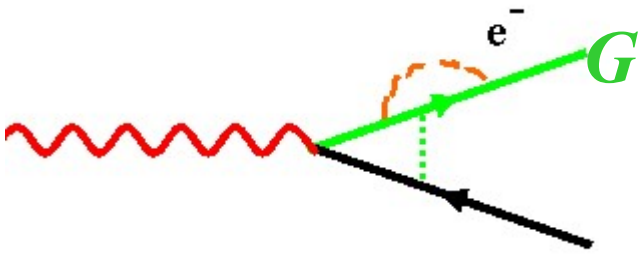
Green's function $(H - E)\,G = -\,\delta(r-r')$

$G(r,r',E)$ *aka Propagator*

= Amplitude to propagate particle from r to r'



Key ingredients in FEFF



- ✓ **Green's fn** $G_{LR,L'R'}$ Propagators
- ✓ **Core-hole** V_c Excitonic effects
- ✓ **Self-energy** $\Sigma(E)$ Mean-free path, energy shifts
- ✓ **Debye-Waller** σ^2 Thermal vibrations
- X Many body factor S_0^2 Multi-electron excitations

Results: Accurate EXAFS Phase shifts* ✓

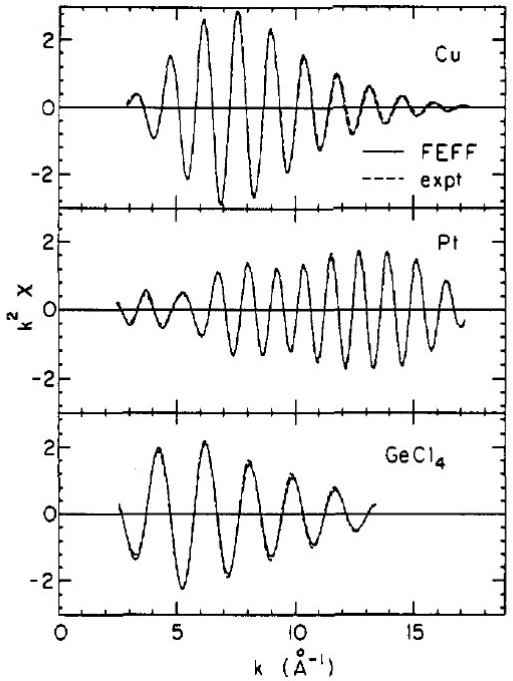
JACS **113**, 5136 **(1991)**

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*

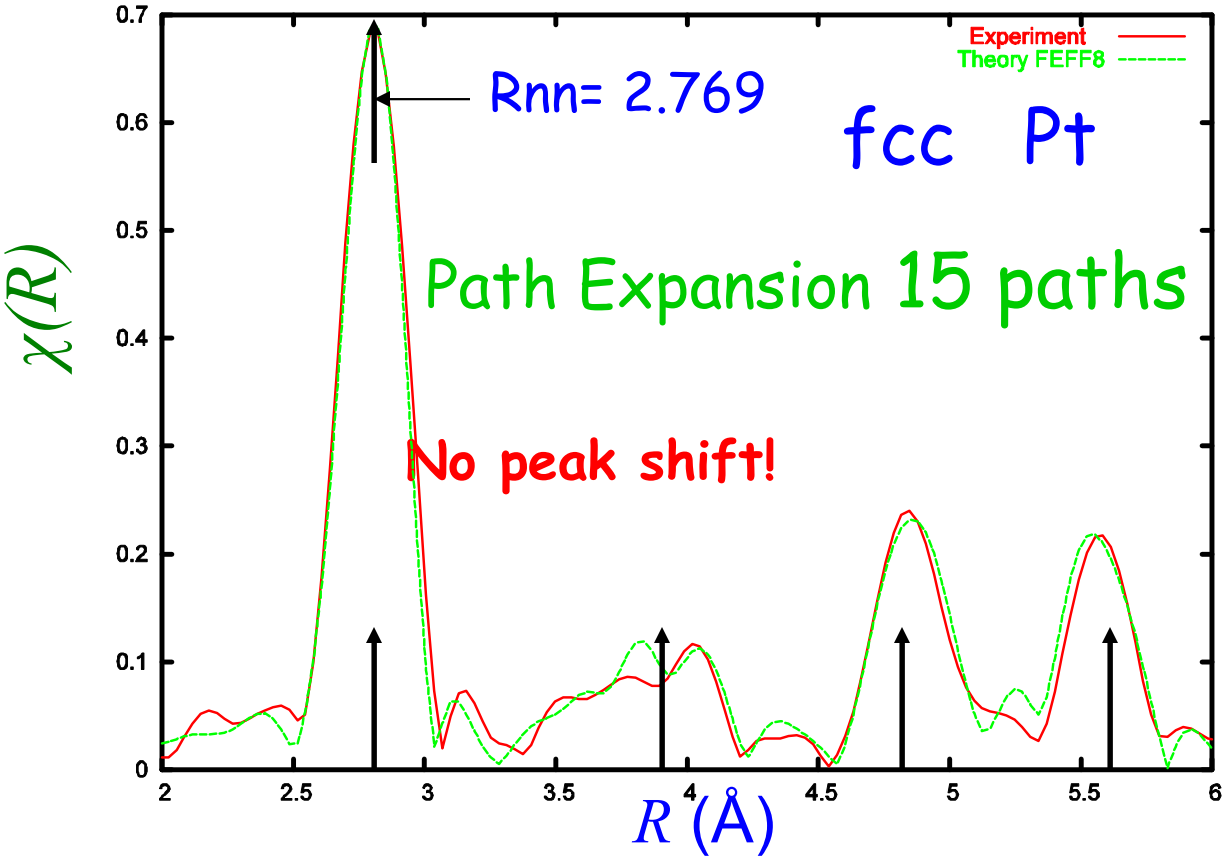
Abstract: Theoretical X-ray absorption fine structure (XAFS) standards are developed for arbitrary pairs of atoms throughout the periodic table ($Z \leq 94$). These standard XAFS spectra are obtained from *ab initio* single-scattering XAFS calculations, using an automated code, FEFF, which takes into 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.



Explains shifts in EXAFS Fourier transform

Results: Accurate EXAFS Calculations

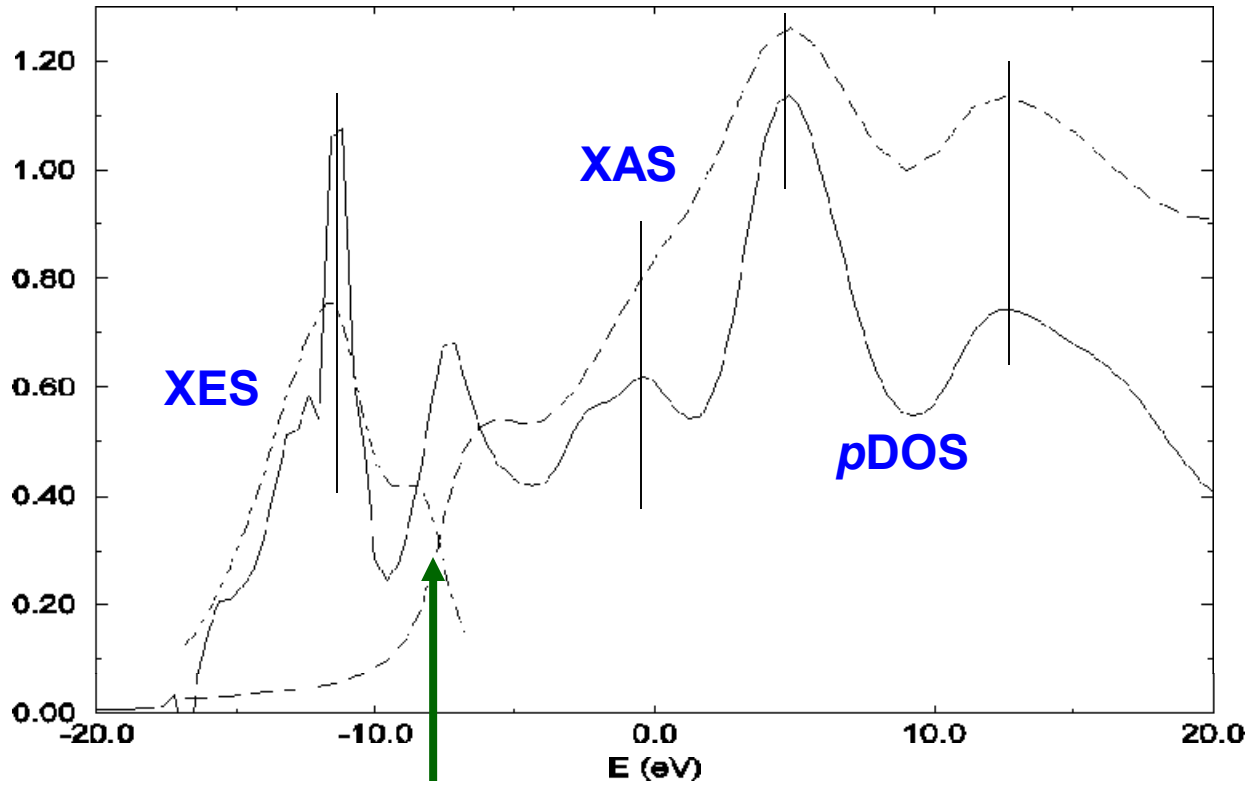
Phase Corrected EXAFS Fourier Transform



Partial answer to Hans Bethe: ”EXAFS may be easier to calculate than to measure - ***IF*** the structure is known. JJR”

Interpretation of XAS ~ Projected density of states

Cu *p*DOS vs XAS and XES



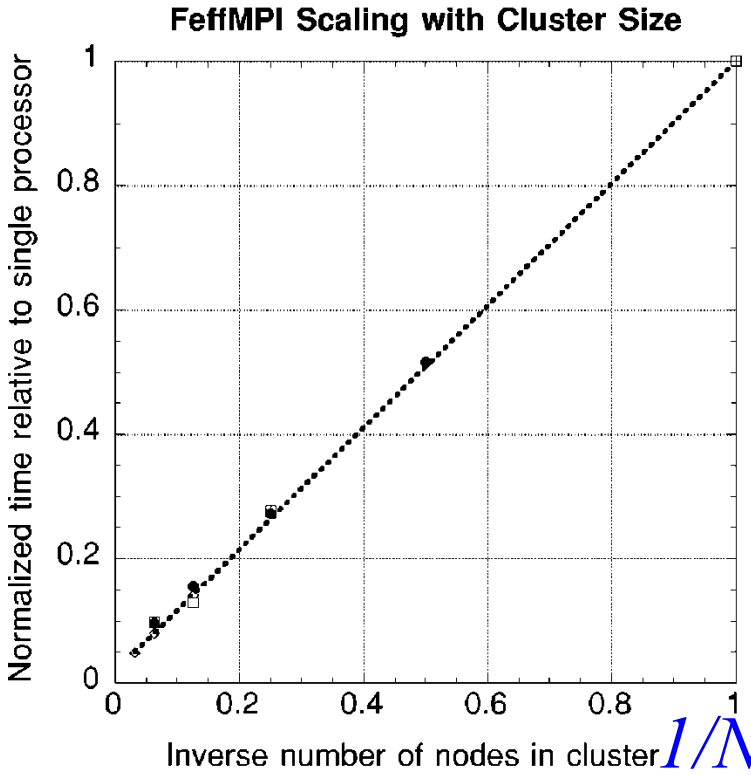
Fermi energy E_F Photoelectron energy E

Green's Functions & Parallel Computations

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*



$1/N_{CPU}$

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

Energy E
is a parameter !

"Natural parallelization"

Each CPU does one energy

High-throughput calculations

All ~10^5 materials & structures in MP Data base

Including feff.inp

SCIENTIFIC DATA | 5:180151 | DOI: 10.1038/sdata.2018.151

Data Descriptor: High-throughput computational X-ray absorption spectroscopy

Kiran Mathew[1,*], Chen Zheng[2,*], Donald Winston[3], Chi Chen[2], Alan Dozier[4], John J. Rehr[5], Shyue Ping Ong[2] & Kristin A. Persson[1]

npj | Computational Materials

www.nature.com/npjcompumats

npj Computational Materials (2018) 4:12 ; doi:10.1038/s41524-018-0067-x Corrected: Author correction

ARTICLE OPEN

Automated generation and ensemble-learned matching of X-ray absorption spectra

Chen Zheng[1], Kiran Mathew[2], Chi Chen[1], Yiming Chen[1], Hanmei Tang[1], Alan Dozier[3], Joshua J. Kas[4], Fernando D. Vila[4], John J. Rehr[4], Louis F. J. Piper[5,6], Kristin A. Persson[2] and Shyue Ping Ong[1]

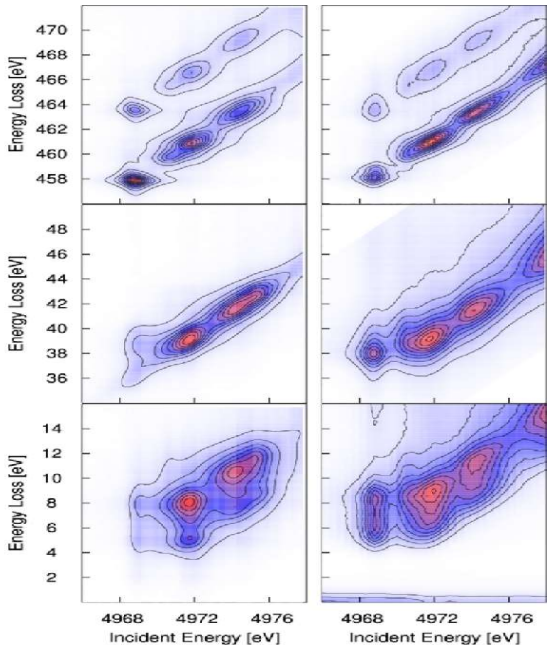
Other spectra: RIXS, NIXS, XMCD, Compton, etc.

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.

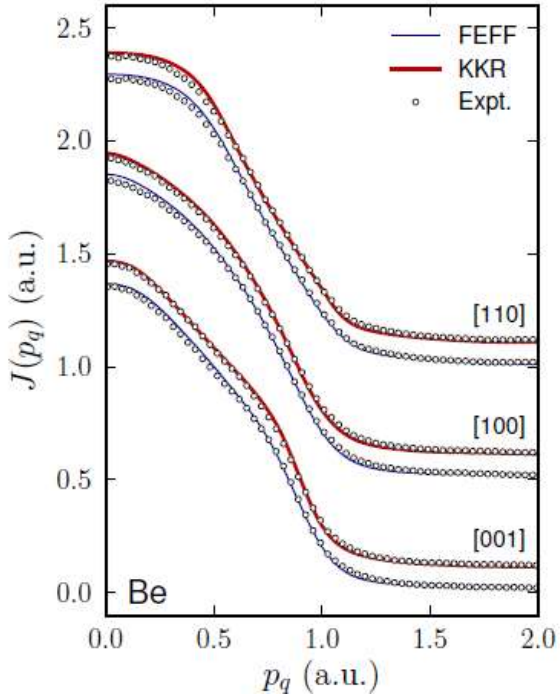


PHYSICAL REVIEW B **85**, 115135 (2012)

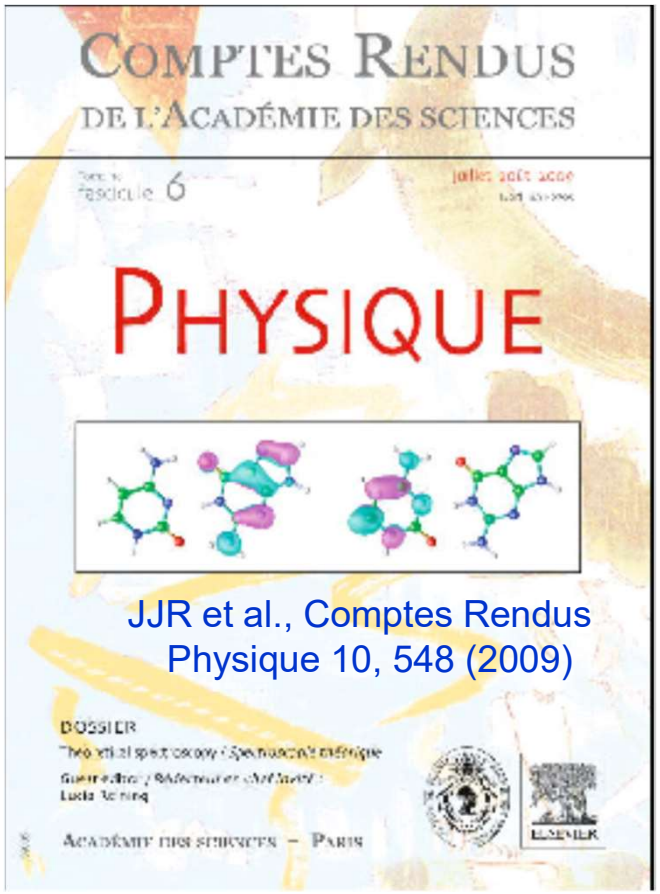
Real-space Green's function calculations of Compton profiles

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.

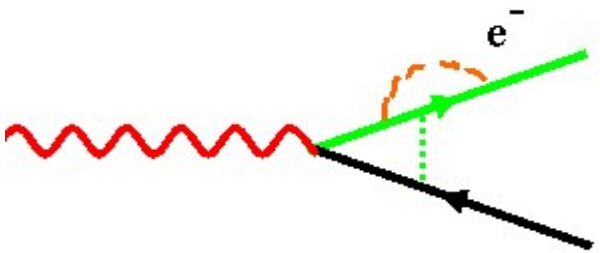


II. Improved theory - Parameter free calculations



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

- Ab initio SCF theory needed for XANES



Phys. Chem. Chem. Phys. 12, 5503–5513 (2010)

PERSPECTIVE www.rsc.org/pccp | Physical Chemistry Chemical Physics

Parameter-free calculations of X-ray spectra with FEFF9

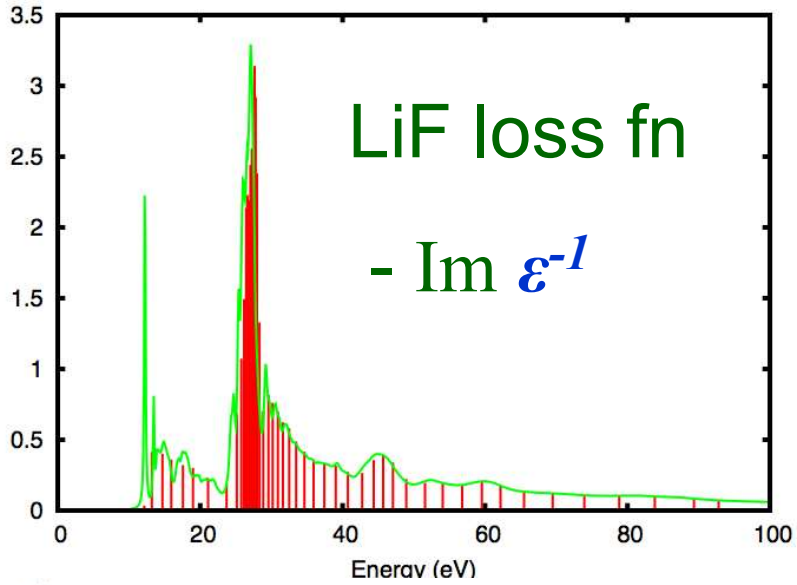
John J. Rehr,*[a] Joshua J. Kas,[a] Fernando D. Vila,[a] Micah P. Prange[bc] and Kevin Jorissen[a]

Many-pole GW Self-energy $\Sigma(E)$* ✓

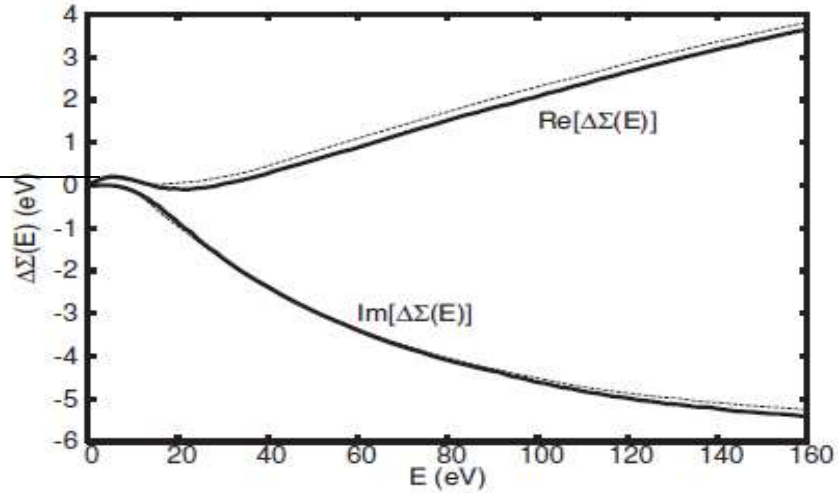
Efficient GW approximation for self-energy Σ & mean free path λ

Sum of plasmon-pole models matched to loss function

$$\Sigma(E) = iGW = \Sigma' - i\,\Gamma$$

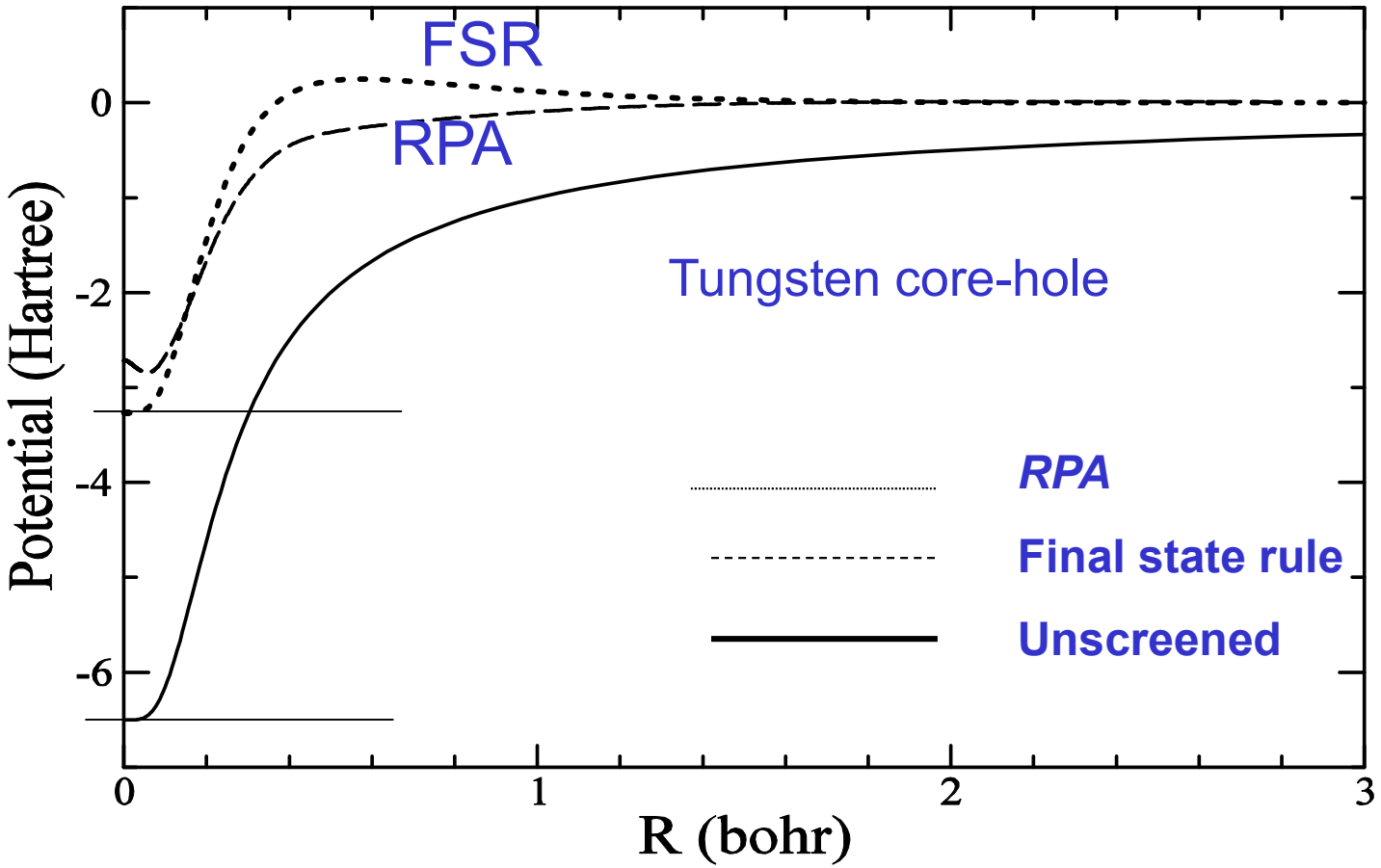


DFT



*J.J. Kas et. al, Phys Rev B **76**, 195116 (2007)

RPA Screened core-hole potential ✓



RPA improves on final state rule, half-core hole, etc

Ab initio Debye Waller factors ✓

An Initio Determination of Extended X-Ray Absorption Fine Structure Debye-Waller Factors*

$e^{-2\sigma^2 k^2}$

Fernando D. Vila, G. Shu, and John J. Rehr
Department of Physics, University of Washington, Seattle, WA 98195

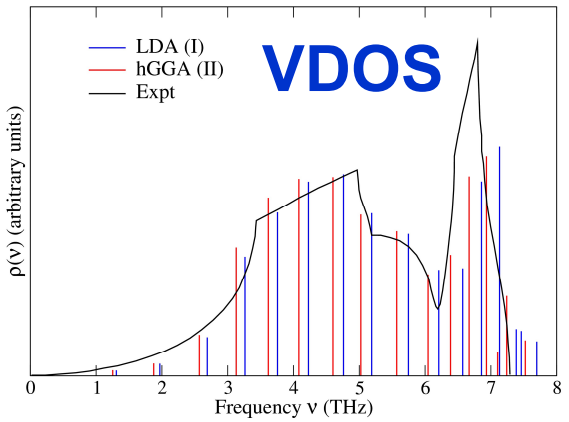
H. H. Rossner and H. J. Krappe
Hahn-Meitner-Institut Berlin, Glienicker Strasse 100, D-14109 Berlin, Germany

(Dated: August 23, 2005)

$$\sigma^2 = \frac{\hbar}{\mu_i}\int_0^\infty \rho(\omega^2)\coth\frac{\beta\hbar\omega}{2}\,d\omega$$

$$\rho(\omega^2) = \langle Q_i \,|\delta(\omega^2 - D)|\, Q_i\rangle$$
$$= \{6-\text{step Lanczos recursion}\}$$

Many pole model for phonons

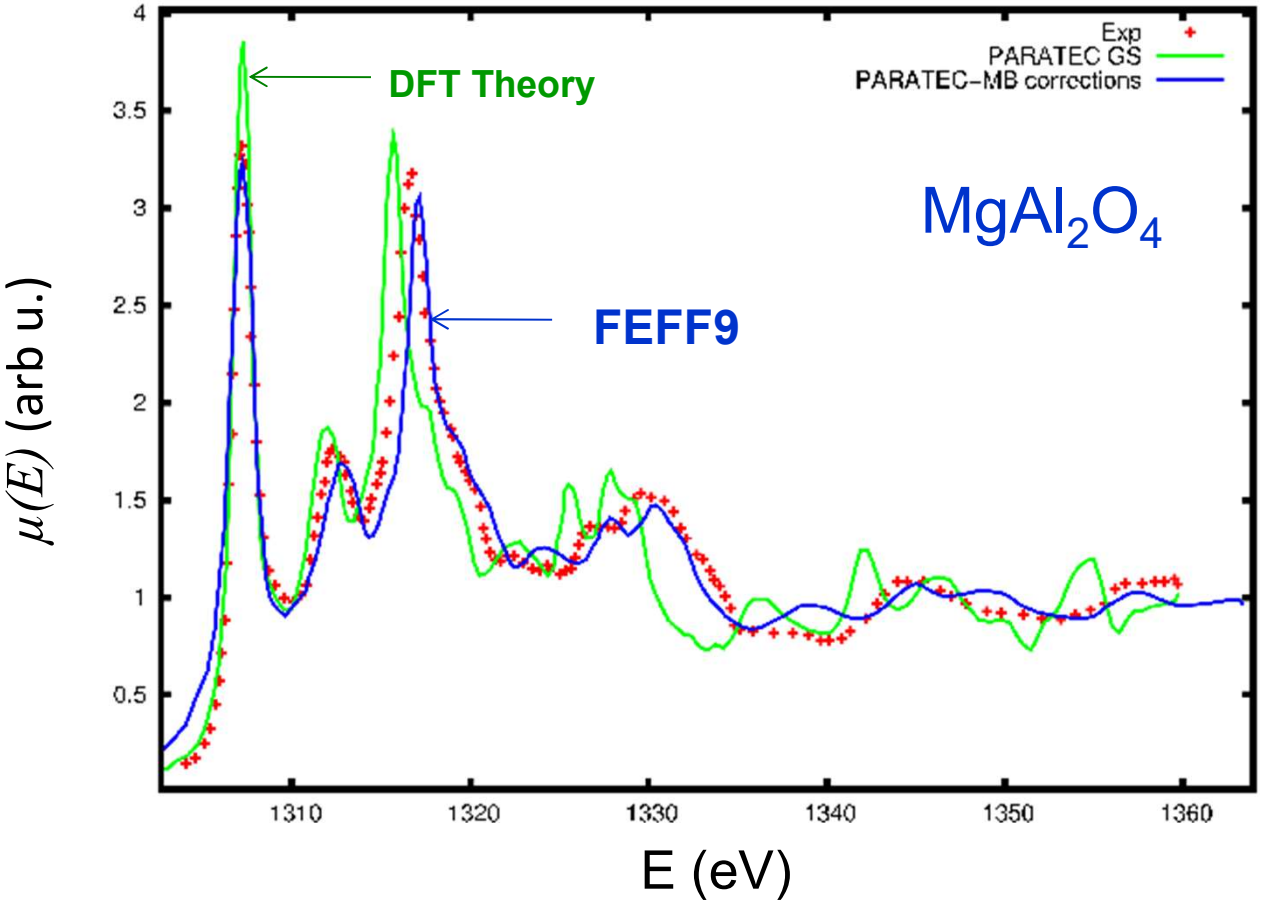


D dynamical matrix < ABINIT

*Phys. Rev. B **76,** 014301 (2007)

Result: Improved XANES

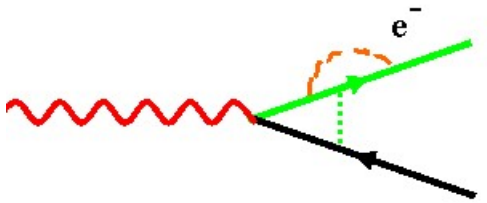
Self-energy & DW factors fix DFT



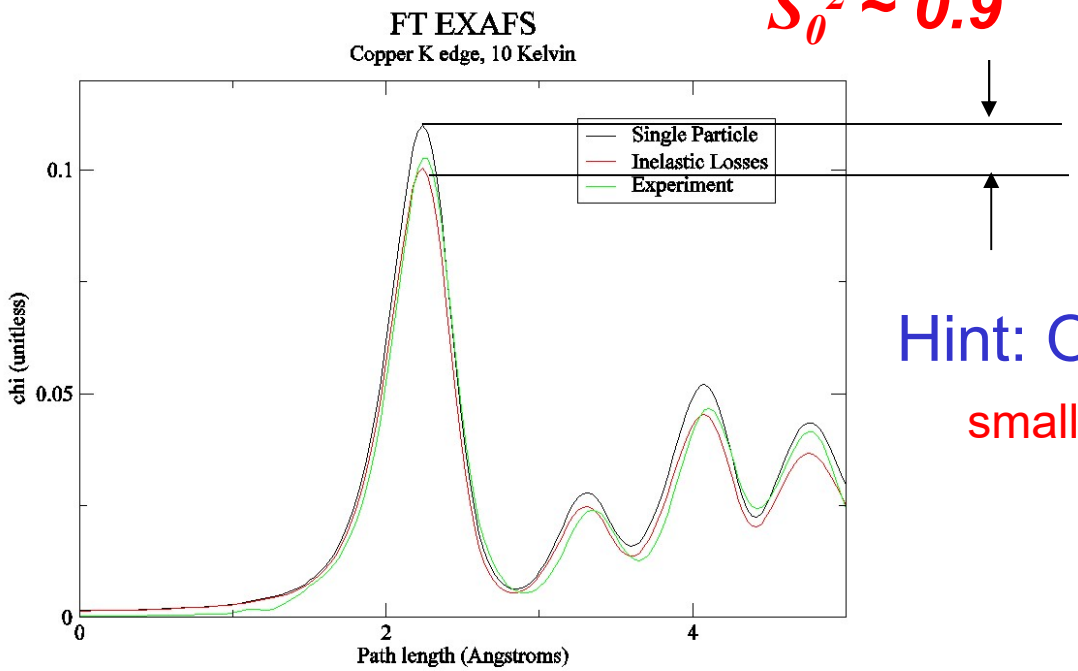
*J. J. Kas et al. J. Phys.: Conference Series **190**, 012009 (2009)

III. Perfecting the theory

Q: What's missing in this picture ?



$S_0^2 \sim 0.9$



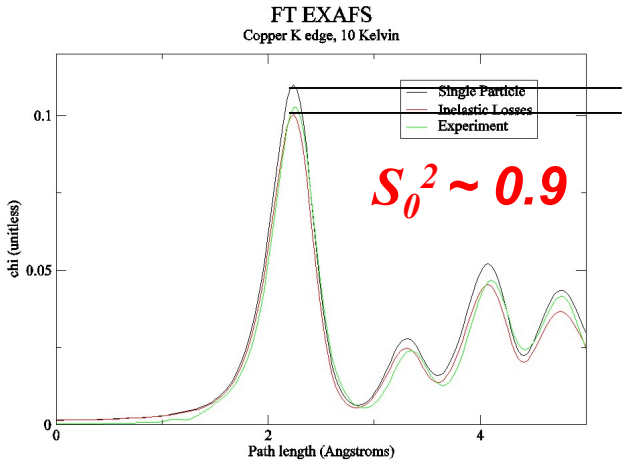
Hint: Observed fine structure smaller than QP theory

Hedin suggestion: Need to include inelastic losses

EXTRINSIC AND INTRINSIC PROCESSES IN EXAFS
Lars Hedin, Dept of Theoretical Physics, University of Lund, Sweden

Physica B 158 (1989) 344–346
North-Holland, Amsterdam

The importance of correlation effects in spectroscopies like EXAFS and photoemission is well recognized. The two main mechanisms are shake-off (in which we include skake-up) when the photoelectron is created, and energy loss of the propagating electron. Shake-off is clearly impossible at threshold, due to lack of energy. For photoemission often the "Spicer three-step model" is used, (1) creation of the photoelectron (including shake-off), (2) propagation to the surface (including losses), and (3) passage through the surface (including losses). Langreth [1] has pointed out that one should add the amplitudes for (2) and (3), and not, as in the Spicer model, convolute their squares, the probabilities. This effect is important primarely at threshold.



Our approach: Cumulant Green's function G_c

GW + Dyson

$$G(\omega) = G_0 + G_0 \Sigma G$$

$$\Sigma^{GW} = iGW$$

$$W = \epsilon^{-1} v$$

No vertex $\Gamma = I$

vs

Cumulant $C(t)$*

$$G_c(t) = G_0(t)\, e^{C(t)}$$

$$C(t) = \int d\omega' \beta(\omega') \frac{e^{i\omega' t} - i\omega' t - 1}{\omega'^2}$$

All excitations in $C(t)$

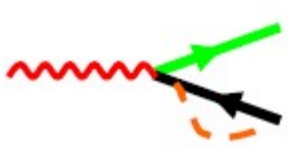
$C(t) \sim |\mathrm{Im}\, \Sigma^{GW}|$

vertex Γ implicit

*Recent review and new derivation, see J. Zhou et al. J. Chem. Phys. 143, 184109 (2015).

Example: Intrinsic losses

Multi-electron excitations, shake-up, etc.
due to suddenly turned-on core-hole:



Implicit in core hole Green's function $G_c(\omega)$ ←

Result: Convolution formula

Quasiparticle XAS

$$\mu(\omega) = \int_0^\infty d\omega' \, \tilde{A}(\omega, \omega') \mu_{qp}(\omega - \omega') \equiv \langle \mu_{qp}(\omega) \rangle$$

Core-hole spectral function – broadens & shifts the spectrum

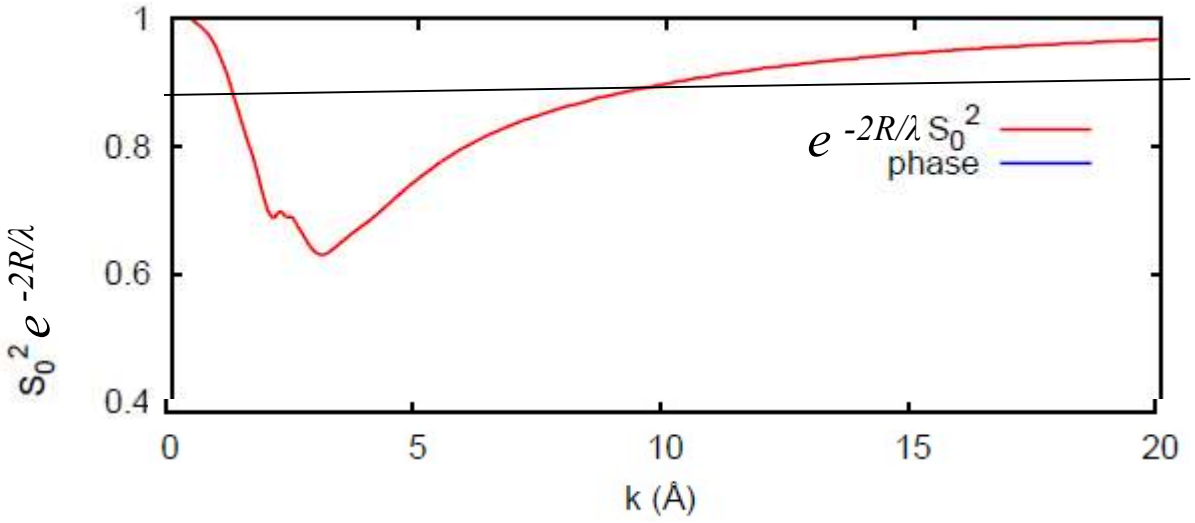
$$A(\omega) = (1/\pi) \, |\mathrm{Im} \, G_c(\omega)|$$

Result: many-body amplitude factor S_0^2 ✓

Cumulant approach for inelastic losses in x-ray spectra

John J. Rehr and Joshua J. Kas

$$S_0^2(R) = \int_0^{\omega} \mathrm{d}\omega' \tilde{A}(\omega, \omega') \mathrm{e}^{\mathrm{i}2[k(\omega-\omega')-k(\omega)]R}$$



$S_0^2 = 0.9$

NEW: Intrinsic losses in Molecular Systems ✓

Equation of motion coupled-cluster approach for intrinsic losses in x-ray spectra

arXiv:2002.05841 (2020)

J. J. Rehr,[1] F. D. Vila,[1] J. J. Kas,[1] N. Y. Hirshberg,[1] K. Kowalski,[2] and B. Peng[3]

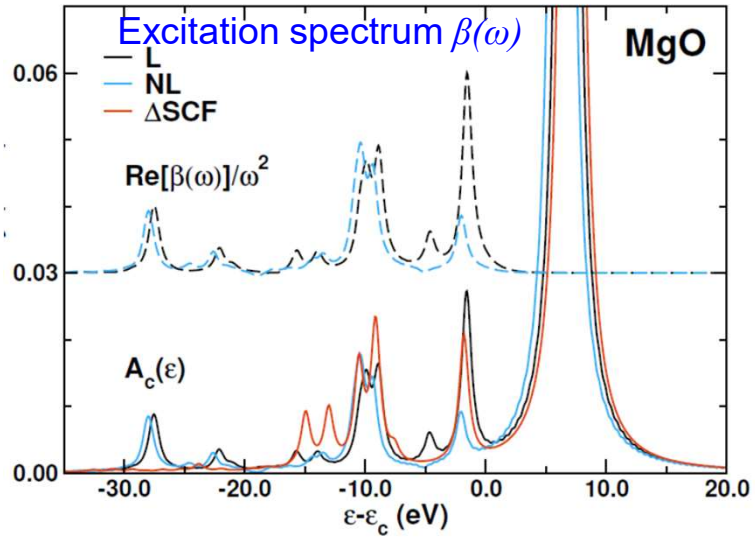
[1)] *Dept. of Physics, Univ. of Washington Seattle, WA 98195, USA*

[2)] *William R. Wiley Molecular Sciences Laboratory, Battelle, Pacific Northwest National Laboratory, K8-91, PO Box 999, Richland, WA, 99352, USA*

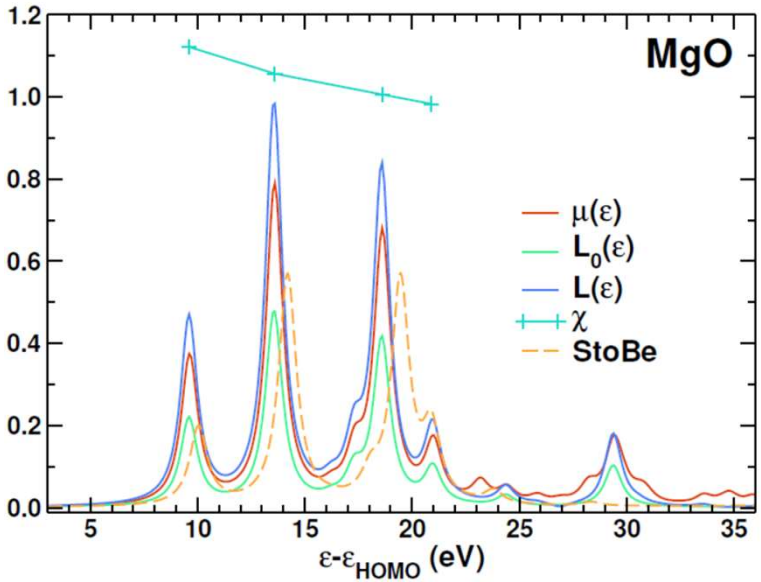
[3)] *Advanced Computing, Mathematics, and Data Division, Battelle, Pacific Northwest National Laboratory, K8-91, PO Box 999, Richland, WA 99352, USA*

$$\mu(t) = \langle \Psi | D(0) D(t) | \Psi \rangle = L(t) G_c(t) \rightarrow \mu(\omega) = \int d\omega' \mu_1(\omega - \omega') A_c(\omega')$$

Spectral function $A_c(\omega)$



XAS $\mu(\omega)$



Full theory: All inelastic losses

Extrinsic ✓ Intrinsic ✓ − 2 x Interference

Full theory is given EXACTLY by convolution :

Particle-hole spectral function ⊗ QP XAS

$$\mu(\omega) = \int d\omega' \, \tilde{A}_K(\omega') \mu_K(\omega - \omega')$$

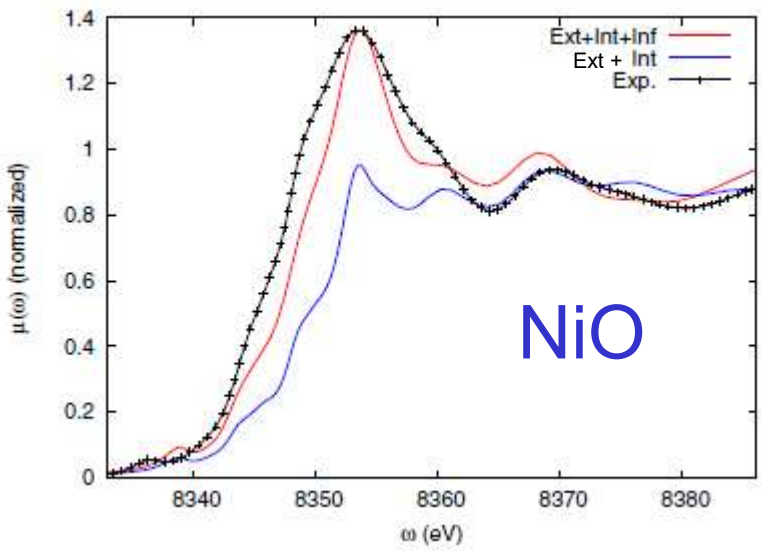
Particle-hole Green's function theory*

PHYSICAL REVIEW B **94**, 035156 (2016)

Particle-hole cumulant approach for inelastic losses in x-ray spectra

J. J. Kas,[1] J. J. Rehr,[1] and J. B. Curtis[2]
[1]*Department of Physics, University of Washington, Seattle, Washington 98195-1560, USA*
[2]*Department of Physics, University of Rochester, Rochester, New York 14927, USA*

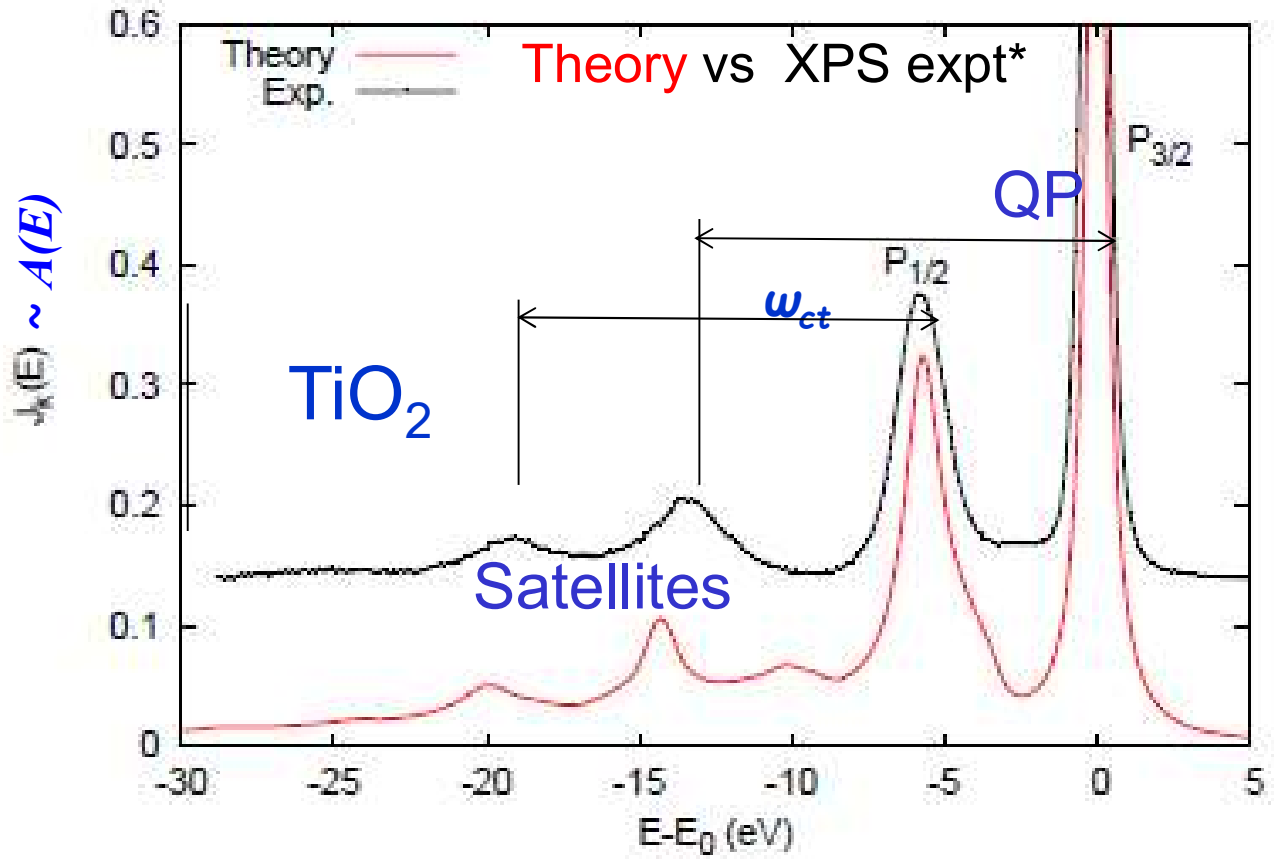
$$\tilde{C}_K(t) = \int d\omega\, \gamma_K(\omega)(e^{i\omega t} - i\omega t - 1) = C_{ext} + C_{int} + C_{inf}$$



* *cf.* L. Campbell, L. Hedin, J. J. Rehr, and W. Bardyszewski, Phys. Rev. B **65**, 064107 (2002)

Result: accurate satellites in XPS ✓

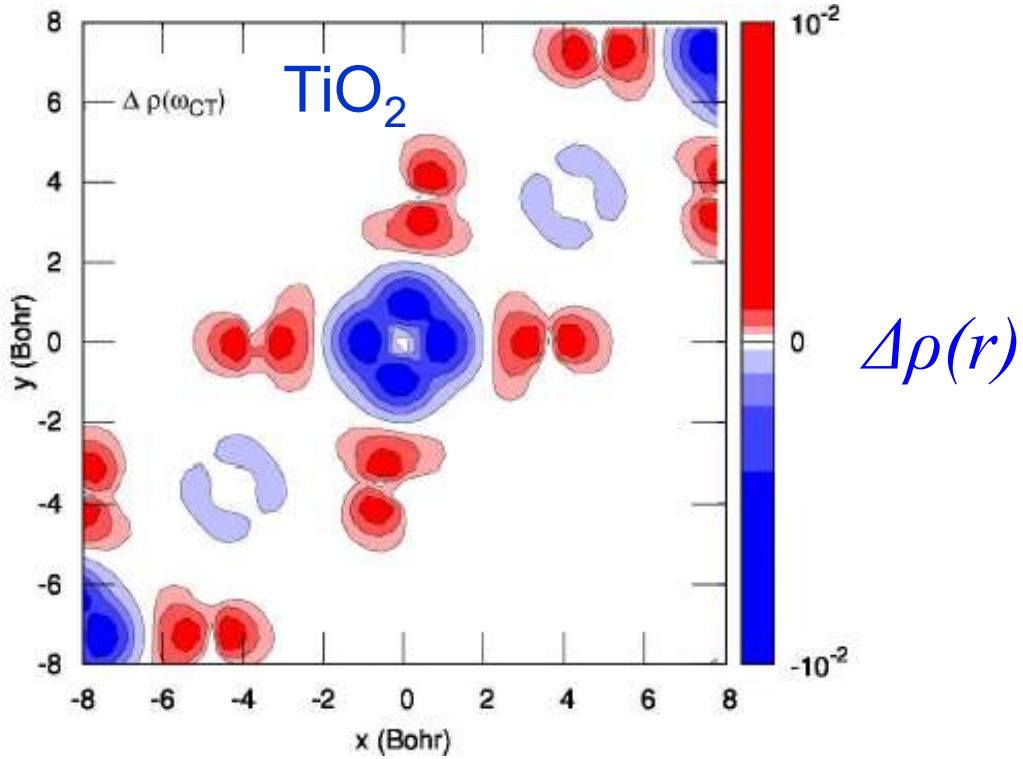
Spectral function $A_c(\omega) = (1/\pi)\,|\mathrm{Im}\,G_c(\omega)|$ ~ XPS $J_k(E)$



J. J. Kas, F. D. Vila, J. J. Rehr, and S. A. Chambers, PRB **91**, 121112(R) (2015)

Real-space interpretation of satellites

Charge-transfer density fluctuations $\Delta\rho(r)$



$\Delta\rho(r)$

Interpretation: CT satellites arise from charge transfer between ligand O-p and Ti -d at frequency $\sim \omega_{CT}$ due to core-hole

Result: Theory explains satellites in XAS ✓

PHYSICAL REVIEW B 86, 165102 (2012)

K-edge x-ray absorption spectra in transition-metal oxides beyond the single-particle approximation: Shake-up many-body effects

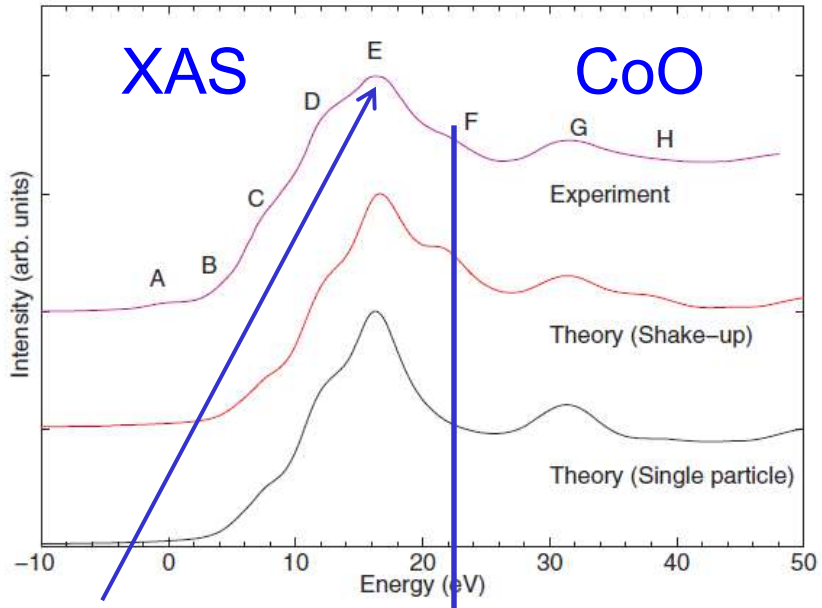
M. Calandra,[1] J. P. Rueff,[2,3] C. Gougoussis,[1] D. Céolin,[2] M. Gorgoi,[4] S. Benedetti,[5] P. Torelli,[6] A. Shukla,[1] D. Chandesris,[7] and Ch. Brouder[1]

Convolution formula

$$\sigma_{\mathrm{XAS}}(\omega) = \int d\epsilon\, \sigma^{\mathrm{exp.}}_{\mathrm{XPS}}(\epsilon)\sigma^{\mathrm{sp}}_{\mathrm{XAS}}(\omega - \epsilon$$

$\wr$

$A_c(\varepsilon)$



Reduction in peak height

Satellite peaks

Better codes: Bethe-Salpeter Equation (BSE)

aka *Particle-Hole Green's function*

Contents lists available at ScienceDirect

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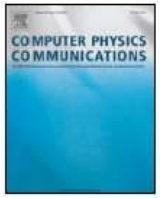
journal homepage: www.elsevier.com/locate/cpc



Ocean

Efficient implementation of core-excitation Bethe–Salpeter equation calculations

K. Gilmore [a,b,*], John Vinson [c], E.L. Shirley [c], D. Prendergast [d], C.D. Pemmaraju [d], J.J. Kas [e], F.D. Vila [e], J.J. Rehr [e]

IOP Publishing

Journal of Physics: Condensed Matter

J. Phys.: Condens. Matter **26** (2014) 363202 (24pp)

doi:10.1088/0953-8984/26/36/363202

Exciting

exciting: a full-potential all-electron package implementing density-functional theory and many-body perturbation theory

Andris Gulans[1], Stefan Kontur[1], Christian Meisenbichler[1], Dmitrii Nabok[1], Pasquale Pavone[1], Santiago Rigamonti[1], Stephan Sagmeister[2], Ute Werner[1] and Claudia Draxl[1,3]

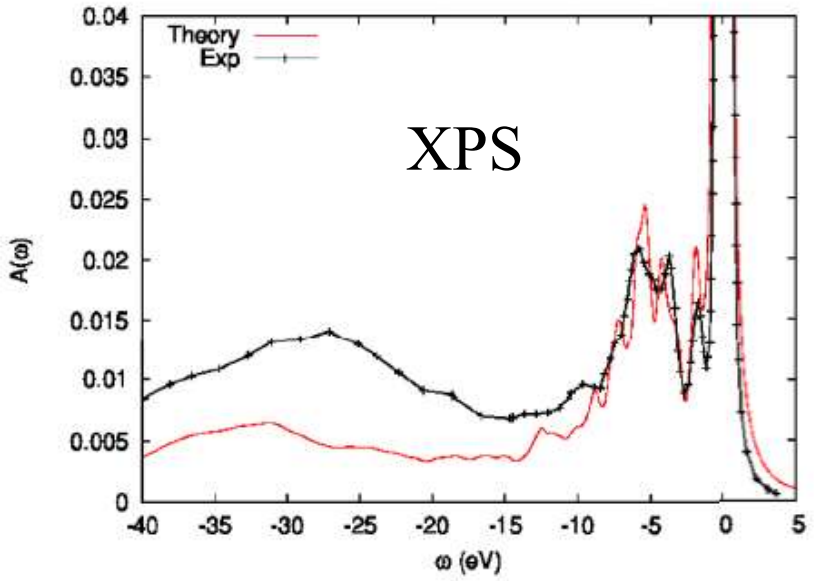
Examples: High accuracy XPS and XAS

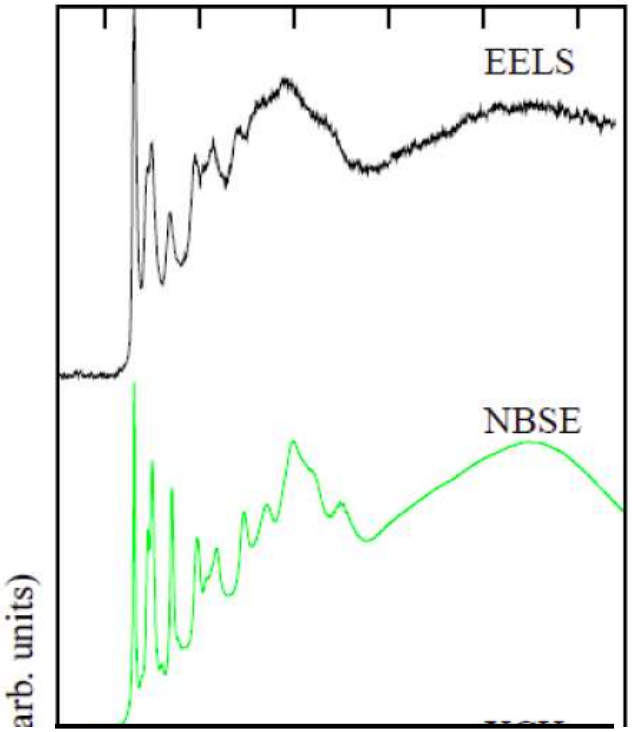
Phys. Rev. B **95**, 115112 (2017)

High-resolution valence and core excitation spectra of solid C_{60} via first-principles calculations and experiment

F. Fossard, K. Gilmore, G. Hug, J J. Kas, J J Rehr, E L Shirley and F D Vila

BSE⊗Particle-hole spectral function





? Correlated systems ?

Question: Does the particle-hole cumulant GF apply to correlated d- and f-electron systems ?

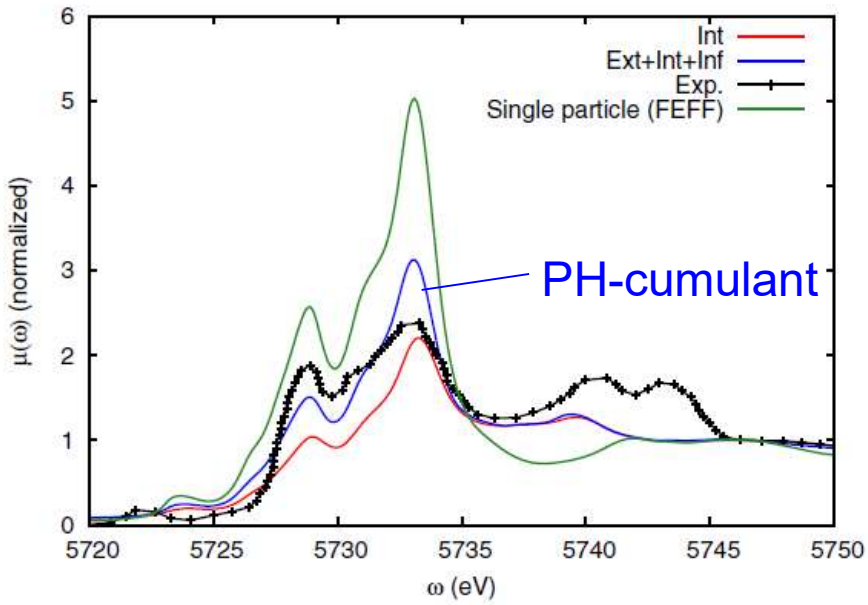
Hedin's answer* **MAYBE**

"Calculation similar … not a question of principle, but of computational work..."

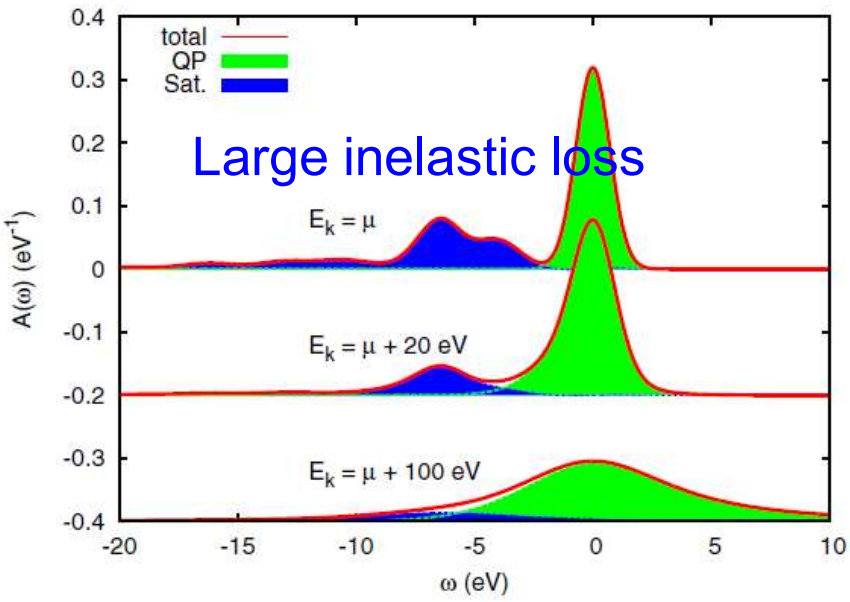
* L. Hedin, J. Phys.: Condens. Matter **11,** R489 (1999)

Particle-hole theory for CeO_2*

Ce L_3 XAS of CeO_2



Spectral function



Summary: fair agreement even in correlated systems

*J.J. Kas et al. Phys Rev B **94**, 035156 (2016)

Conclusions

EXAFS – Theory & interpretation well understood ✓

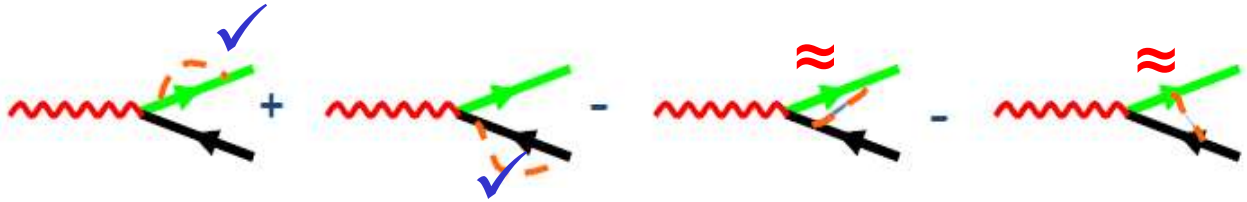
XANES – Parameter free theory fairly accurate ✓

Full theory – Convolution now accounts for S_0^2 & satellites ✓

$$\mu(\omega) = \int d\omega' \, \tilde{A}_K(\omega') \mu_K(\omega - \omega')$$

Closer to perfection BUT still room for improvement

Challenge – improved treatment of interference



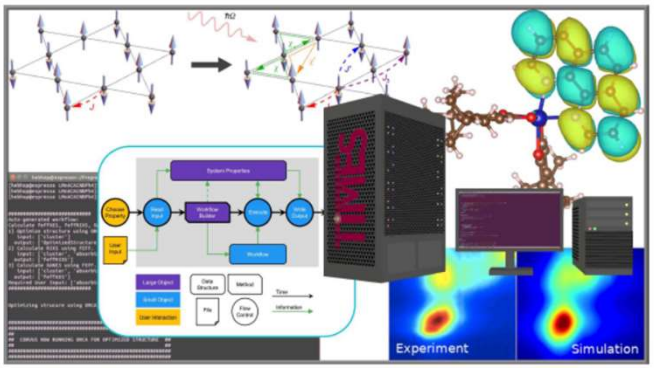
Next Generation Software initiatives

TIMES@SLAC

FEFF10, Corvus, etc

U.S. Department of Energy: Office of Basic Energy Sciences
Materials Sciences & Engineering Division

Theory Institute for Materials and Energy Spectroscopies (TIMES)



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EOM-CC, Real-time, etc

July 2017

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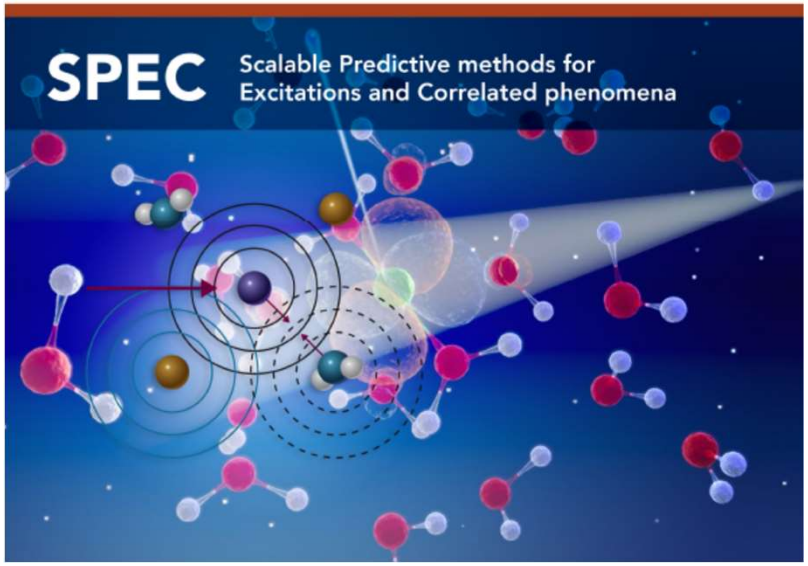

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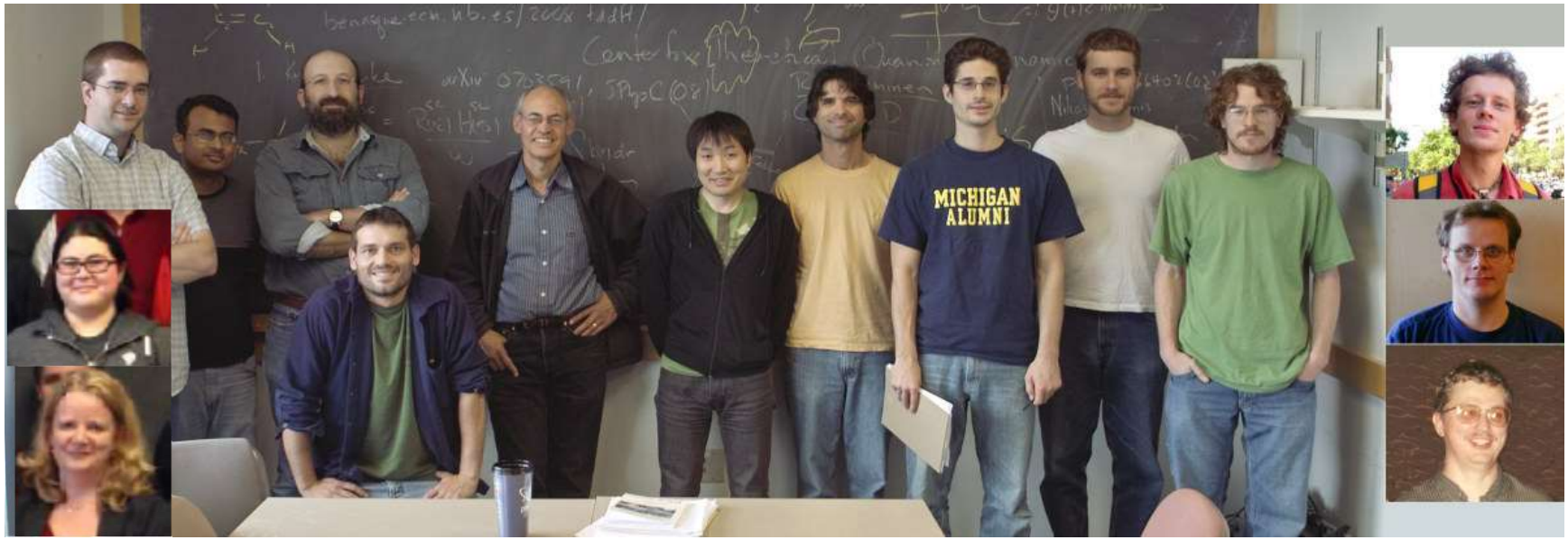
S. Story
C. Draxl



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