Summer School: Electronic Structure Theory for Materials and Molecules
IPAM Summer School, UCLA Los Angeles, CA 29 July, 2014

Theory and Interpretation of Core-level Spectroscopies*

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Supported by DOE BES and NSF

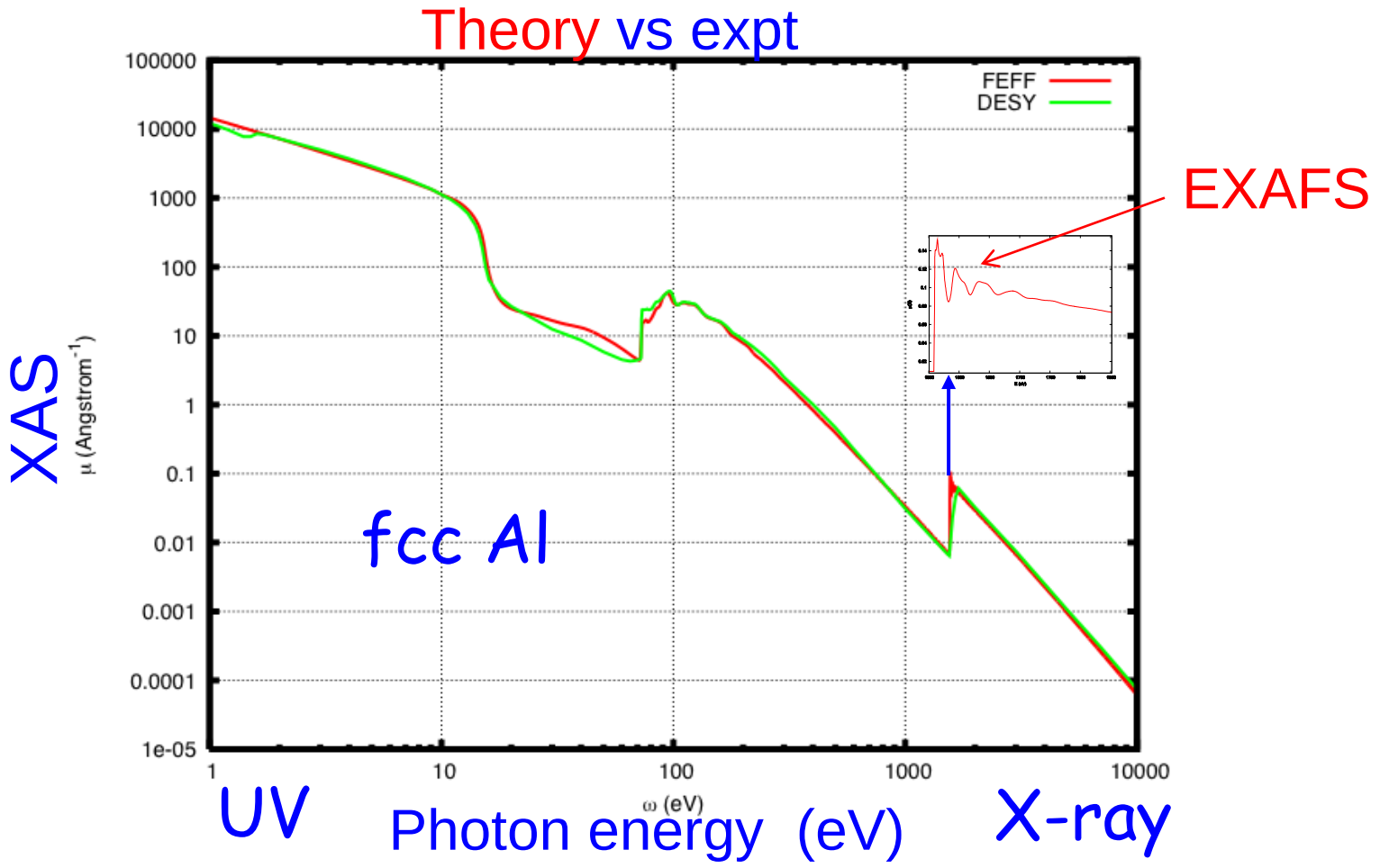
Theory and Interpretation of Core-level Spectroscopies

- **GOALS**: *ab initio* theory of XAS, XPS, etc.
  Accuracy ~ experiment

- **TALK**: Excited state electronic structure

I. Introduction	History & motivation
II. Real-space Green's Fn	FEFF9 code
III. GW/BSE	OCEAN code
IV. Extensions	Correlated systems

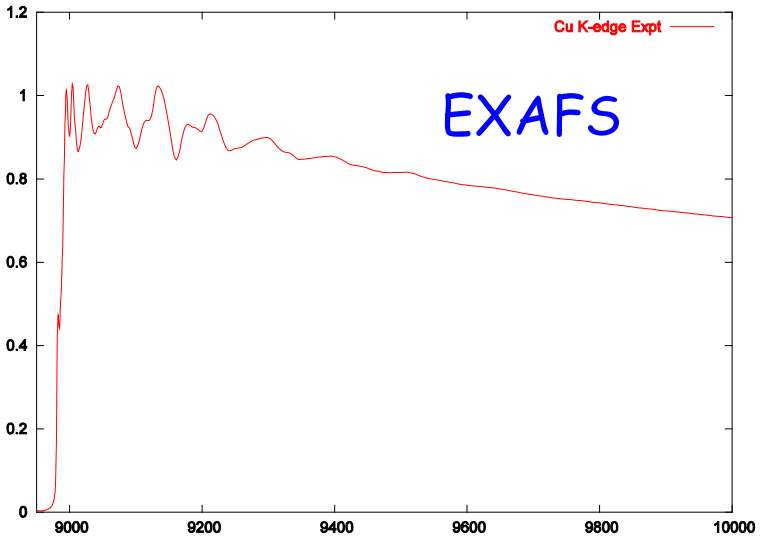
I. Introduction: X-ray Absorption Spectra



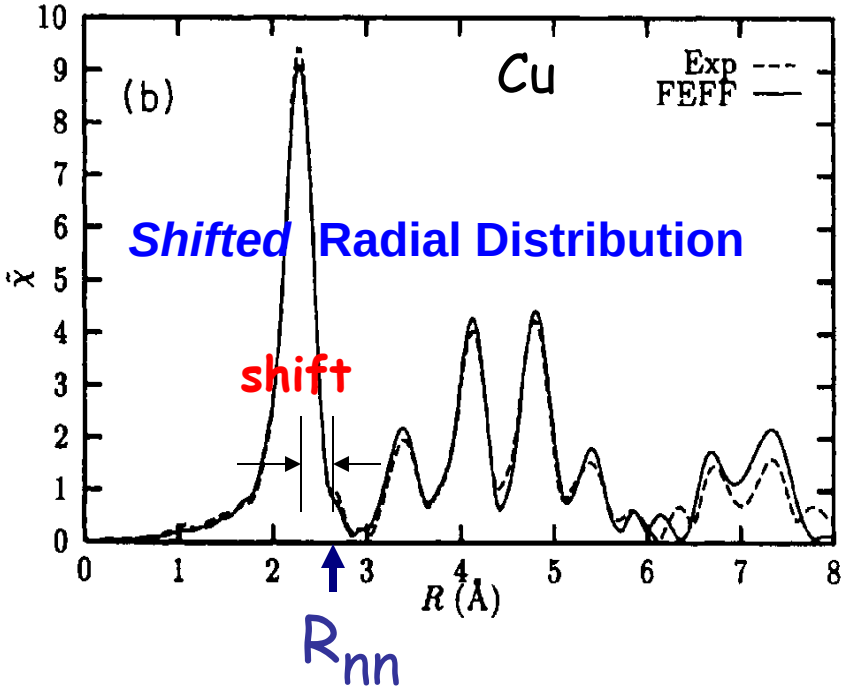
Q: How to calculate & interpret ?

Heuristic Interpretation of EXAFS*

EXAFS → Local structure



Fourier Transform



R_{nn}

→ X-ray Microscope!

*Stern Sayers Lytle, UW **1971**

BUT need to calibrate experiment with “Standard”

Answer 1

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

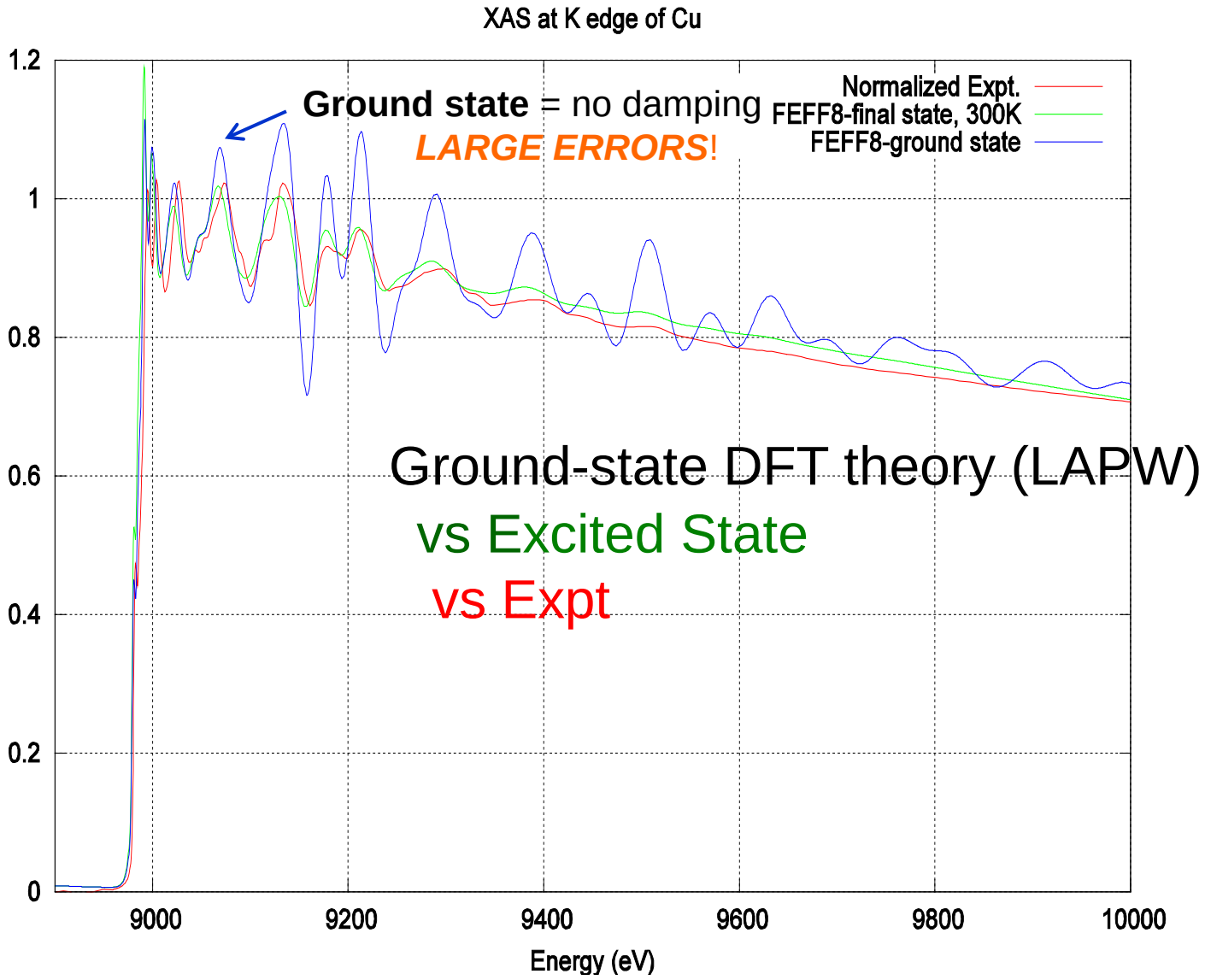
Hans Bethe

~ 1980

”The chance is high that the truth lies in the fashionable direction. But on the off chance that it isn’t, who will find it?”

R. P. Feynman

Gotcha: Standard DFT theory fails!



Why the difficulty ?

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

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

Too many quasi-particle final states ψ_f

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

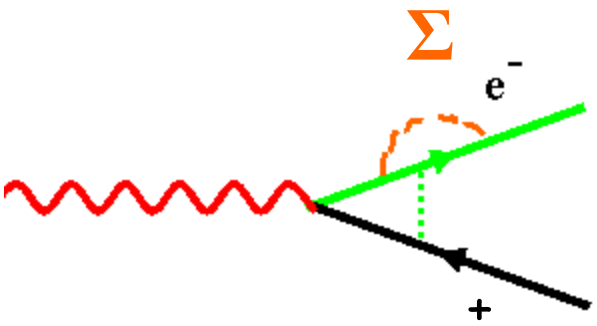
Final state rule

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

Non-hermitian **self-energy** $\Sigma(E)$

(replaces DFT Vxc)

Theoretical Breakthroughs



4 developments beyond DFT

- Scattering theory of excited states

  HIGH energy ~ 10^3 **eV**

  LARGE angular momentum ***l* = 20**
- Inelastic mean free paths λ
- Screened core-hole
- Debye-waller damping factors

Answer 2 (JJR)* "Now (1990) it is easier to calculate EXAFS than to measure it"

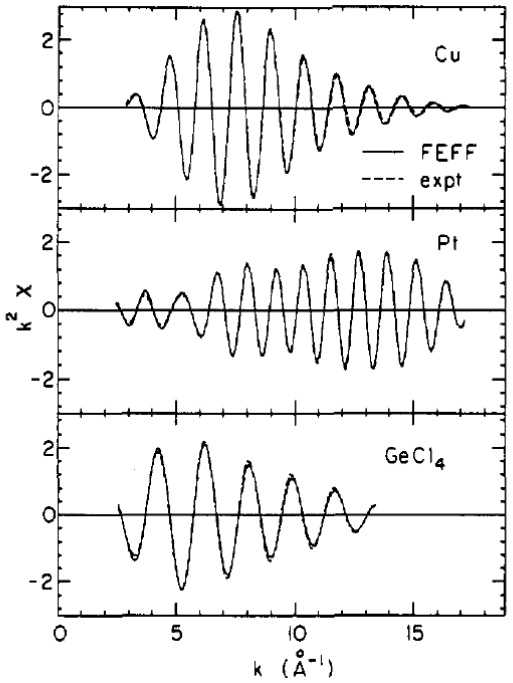
(**if structure is known)

Theoretical X-ray Absorption Fine Structure Standards

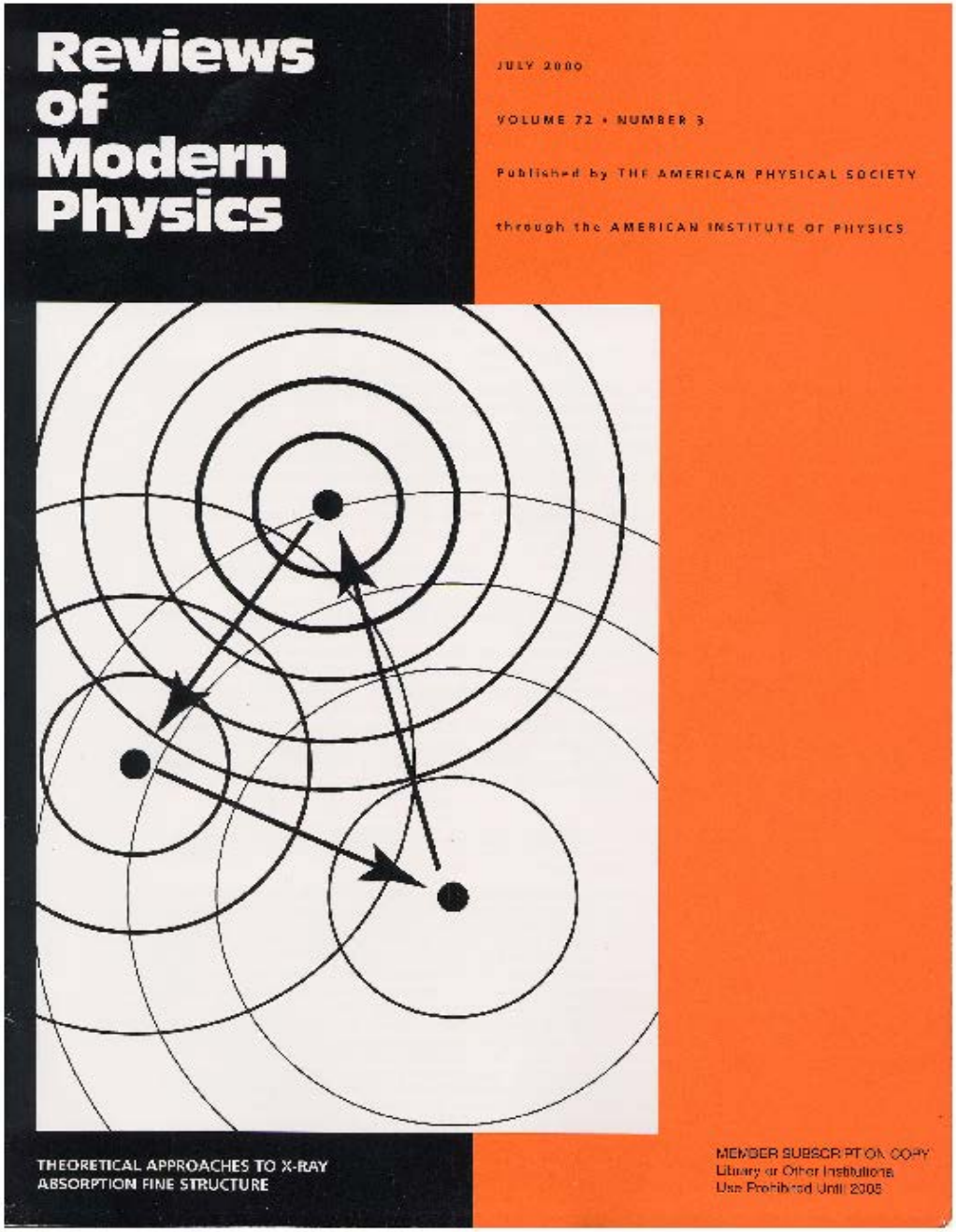
J. J. Rehr,*,† J. Mustre de Leon,†,‡ S. I. Zabinsky,† and R. C. Albers§

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.



**** 10 years later** - JACS **113**, 5136 **(1991)**



How?

Quantitative

XAS theory

FEFF

J. J. Rehr & R.C. Albers

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

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

II. Real-space Green's Function Theory

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

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

No sums over final states !

What's a real space Green's function?

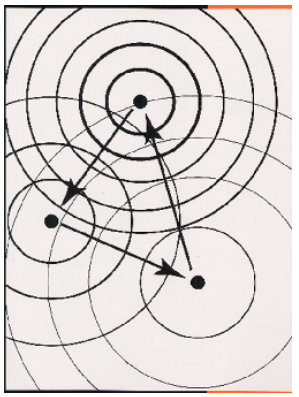
Wave function in QM $H\,\Psi = E\,\Psi$

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

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

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

= Amplitude to go from r to r'



Exact in various limits !

Multiple-scattering calculations of G

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

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

(MS path expansion - geometric series) **MS Path**

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

Full MS

Ingredients:

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

Implementation: RSGF Code FEFF

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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B. Ravel
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J. J. Rehr
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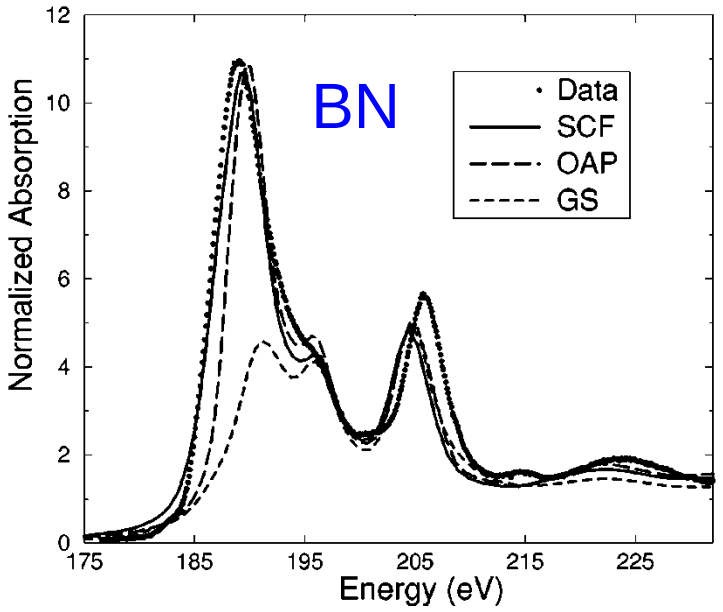
S. D. Conradson
MST-11, Los Alamos National Laboratory, Los Alamos, New Mexic

89 atom cluster

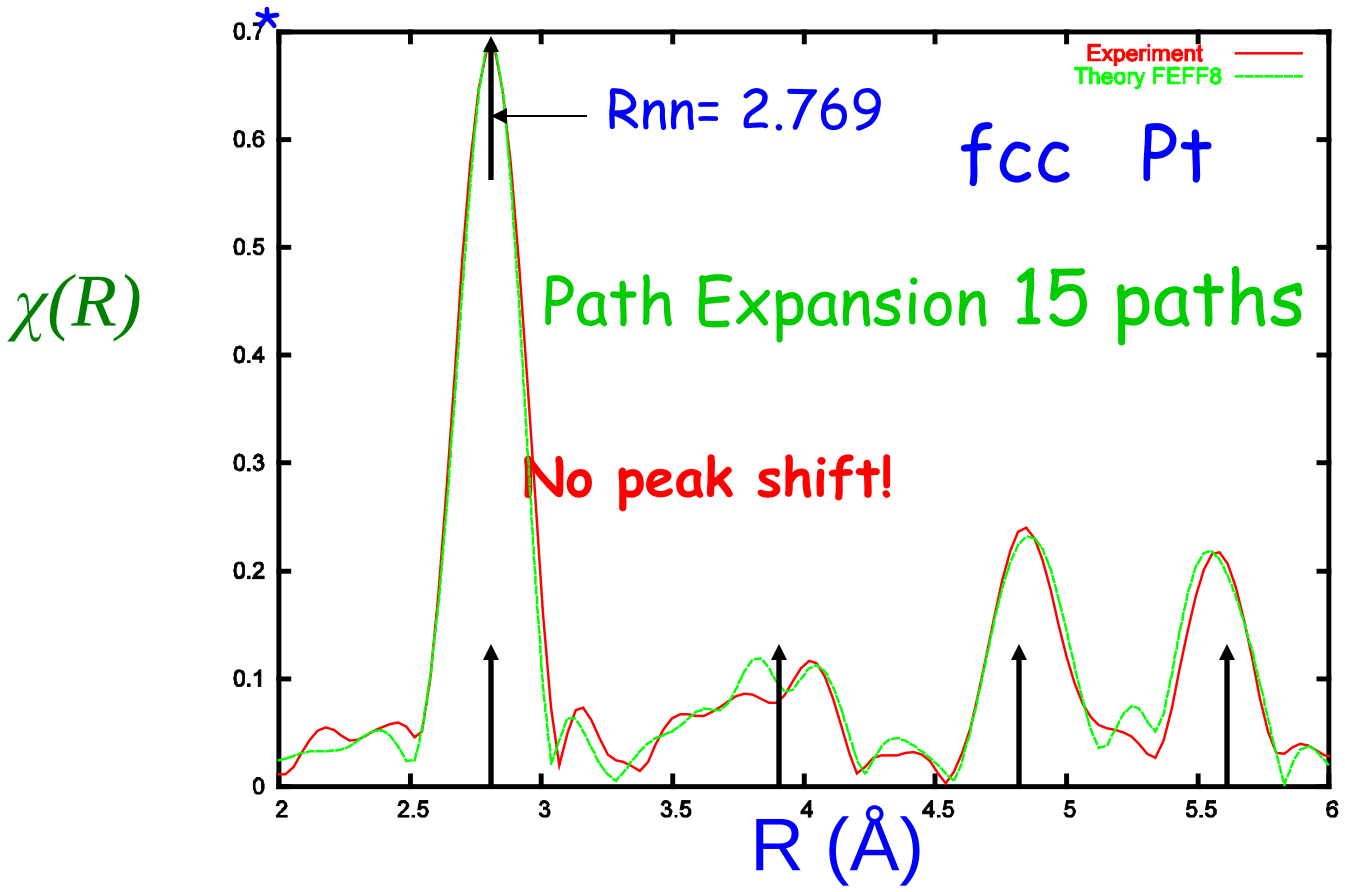
Core-hole, SCF potentials

Essential!



Example: Pt EXAFS – MS path expansion

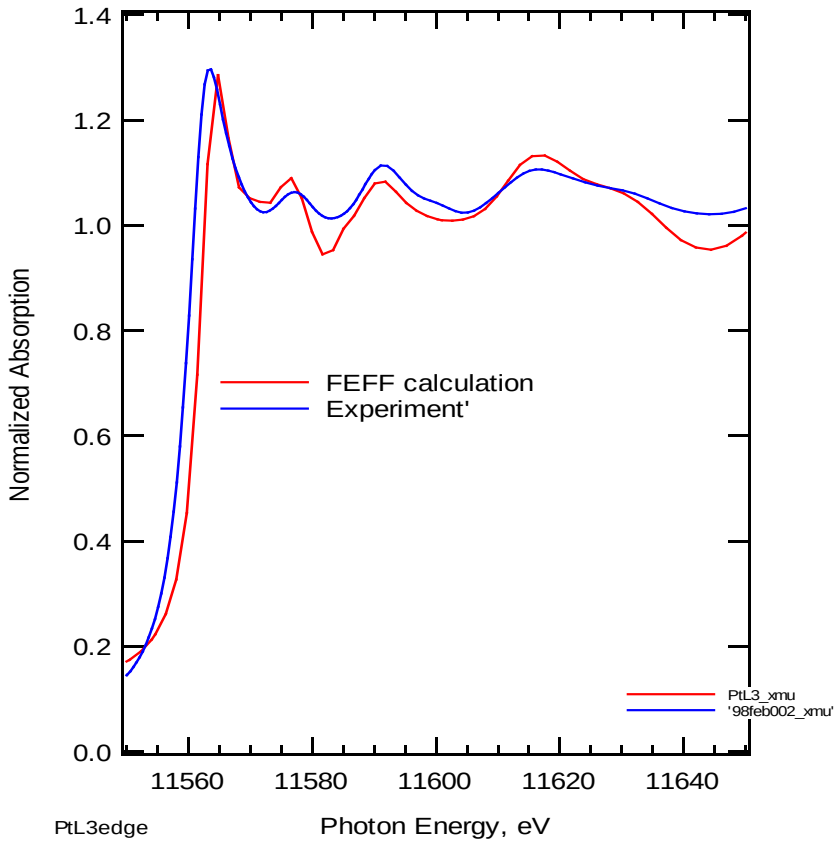
Phase Corrected EXAFS Fourier Transform*



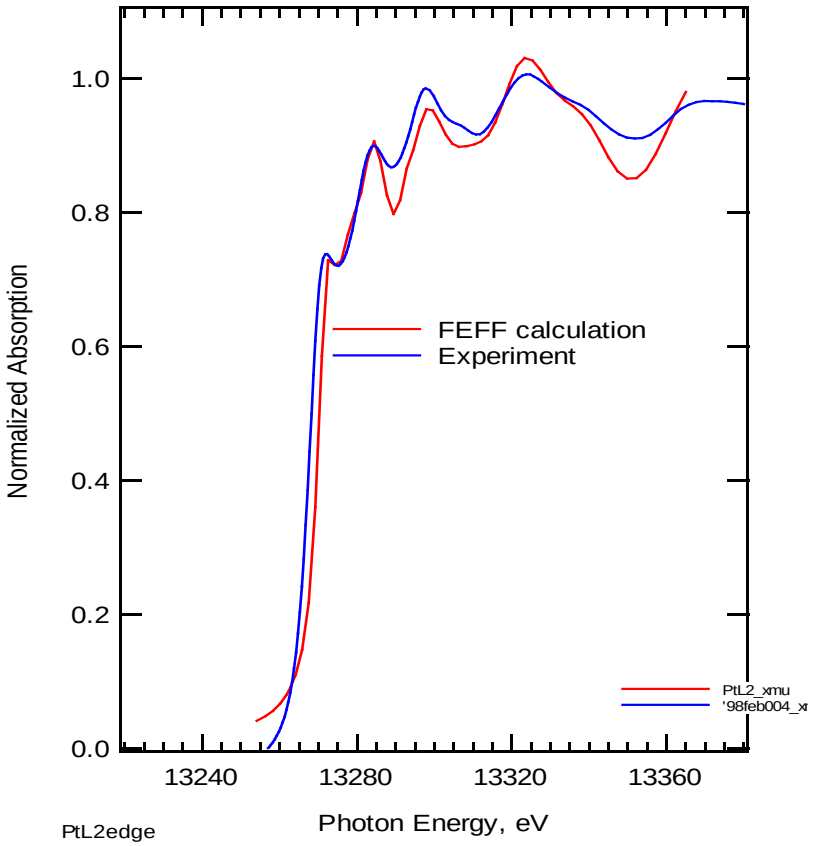
Theoretical phases → accurate distances to < 0.01 Å

Example: Pt XANES full multiple-scattering

Pt L_3-edge



Pt L_2-edge (S. Bare, UOP)



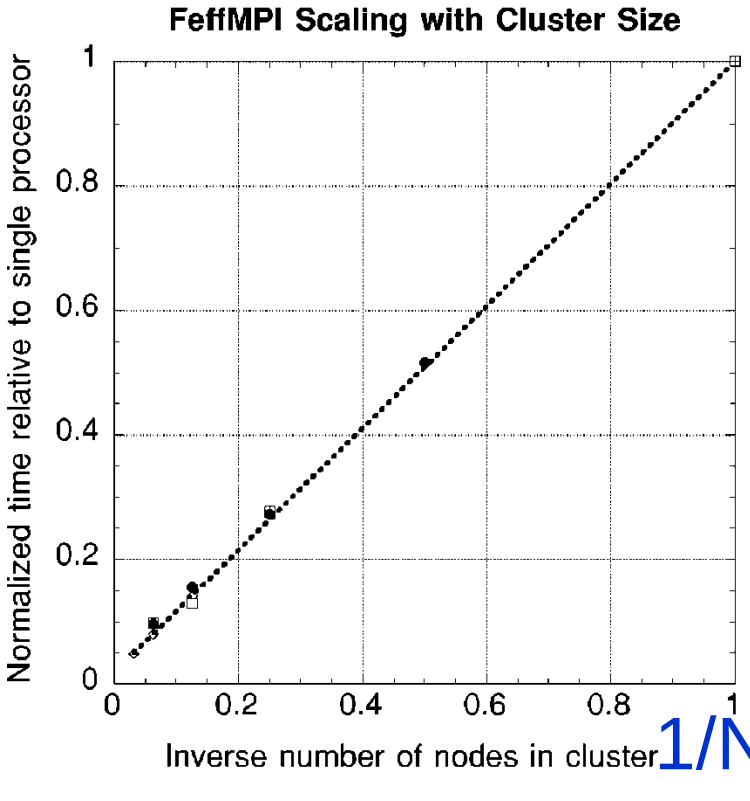
- Good agreement: *Relativistic* FEFF explains all spectral features, *including absence of white line at L_2-edge*.
- Self-consistency essential

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*



$1/N_{CPU}$

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

Energy E is a **parameter !**

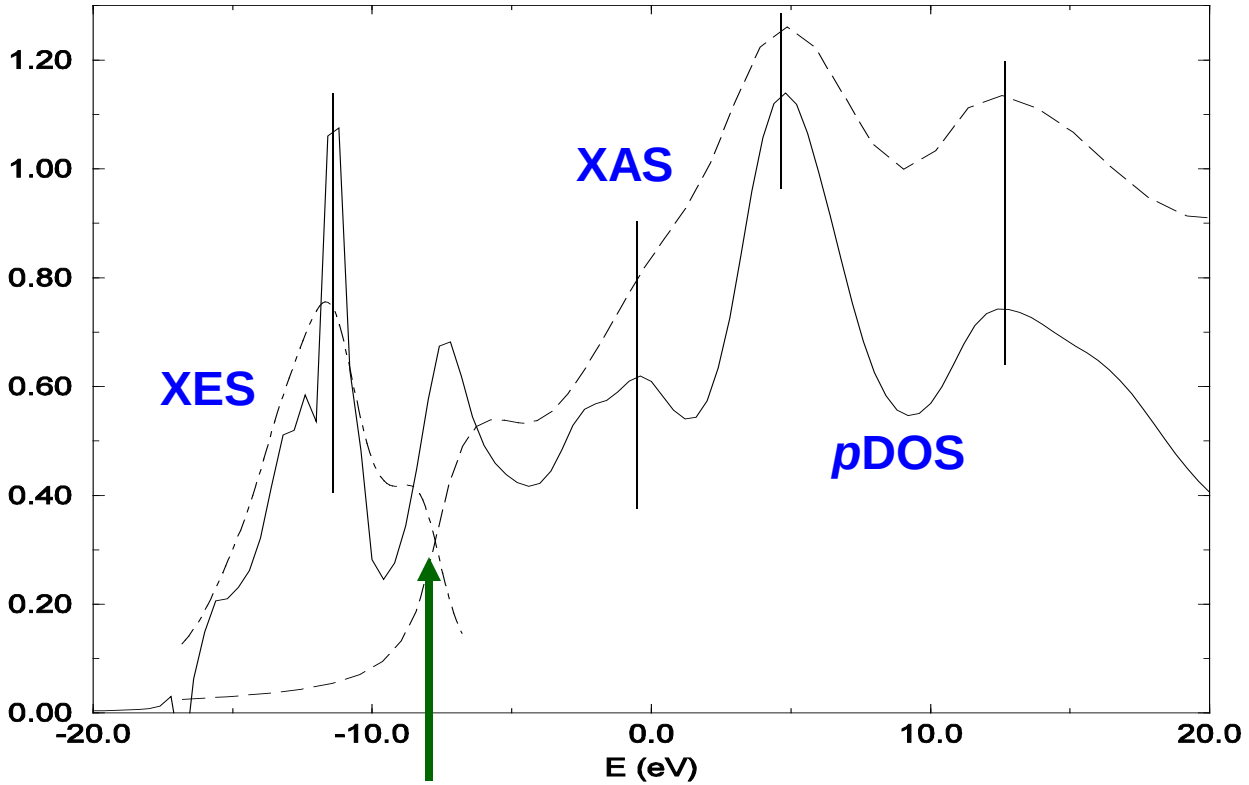
"Natural parallelization"

Each CPU does one energy

Denstity of States interpretation of XANES :

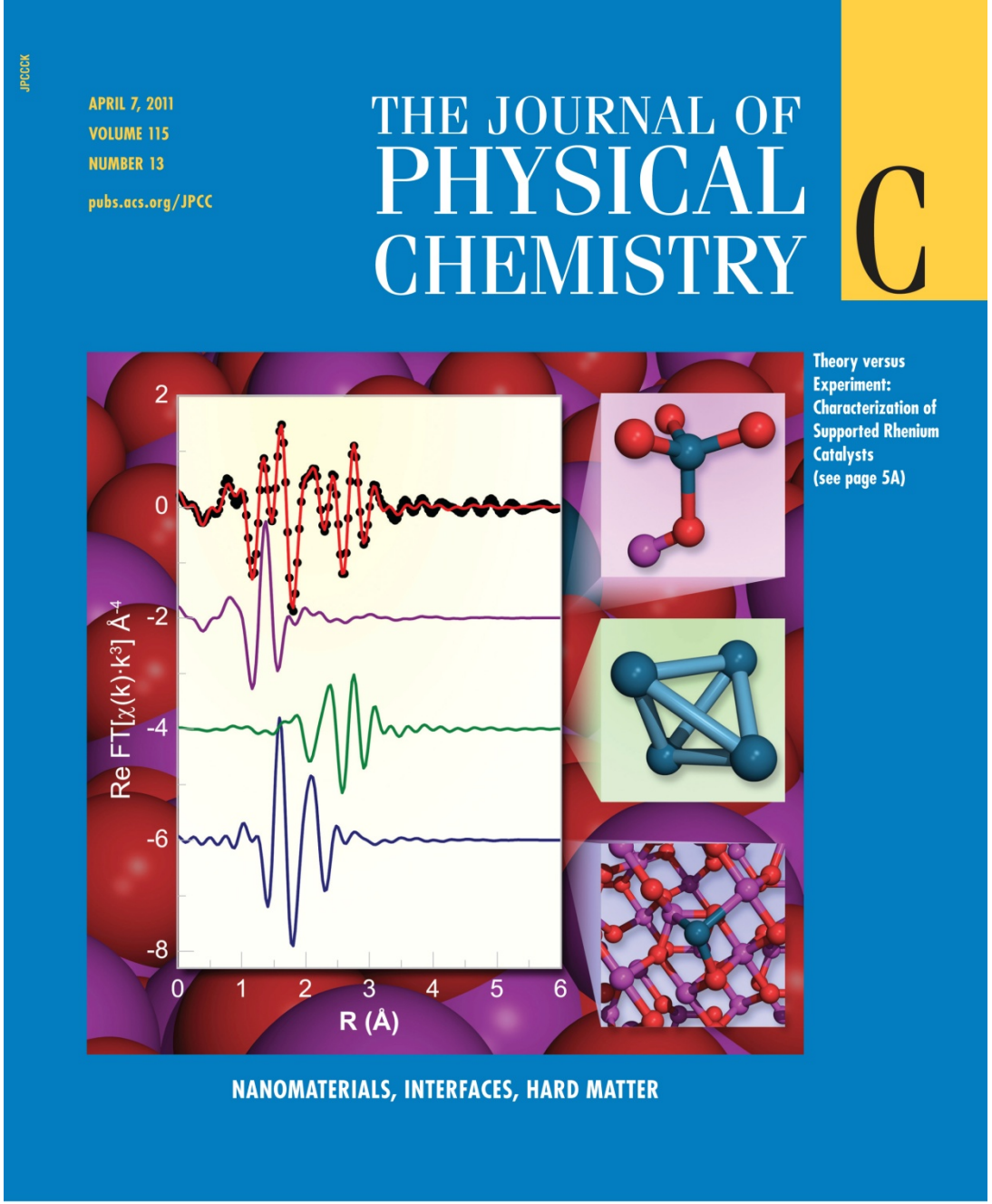
Excited State Electronic Structure

Cu *p*DOS vs XAS and XES



Fermi energy E_F

Final state energy E



Application

EXAFS analysis of Re-catalysts

Simon R. Bare, et al., J. Phys. Chem. 115, 5740 (2011)

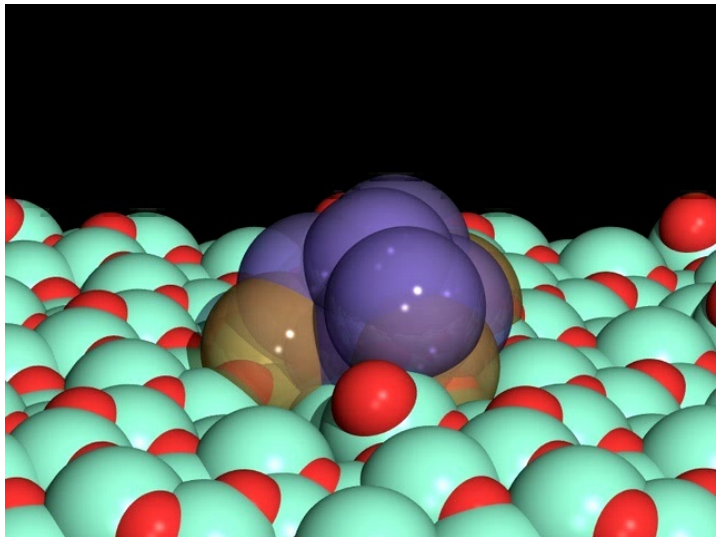
Application: Pt catalysts

$Pt_{10}/\gamma\text{-}Al_2O_3$

Finite Temp, Real-time DFT/MD

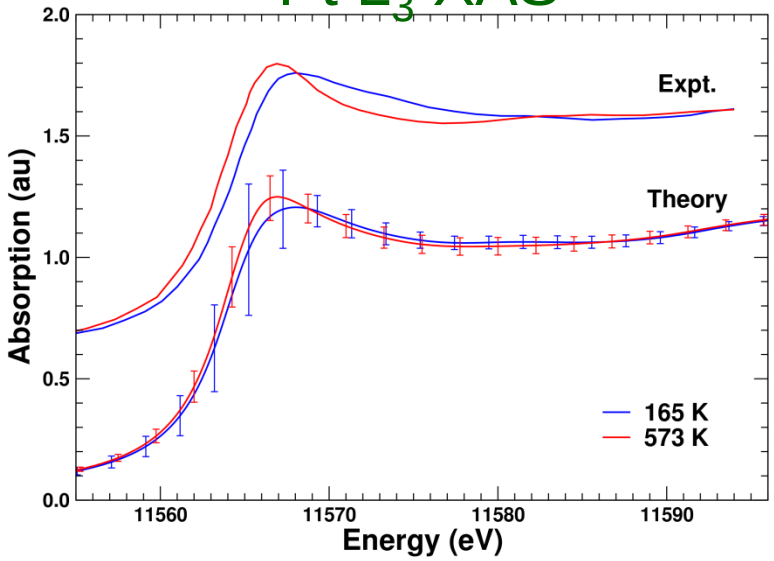
+ XAS of supported

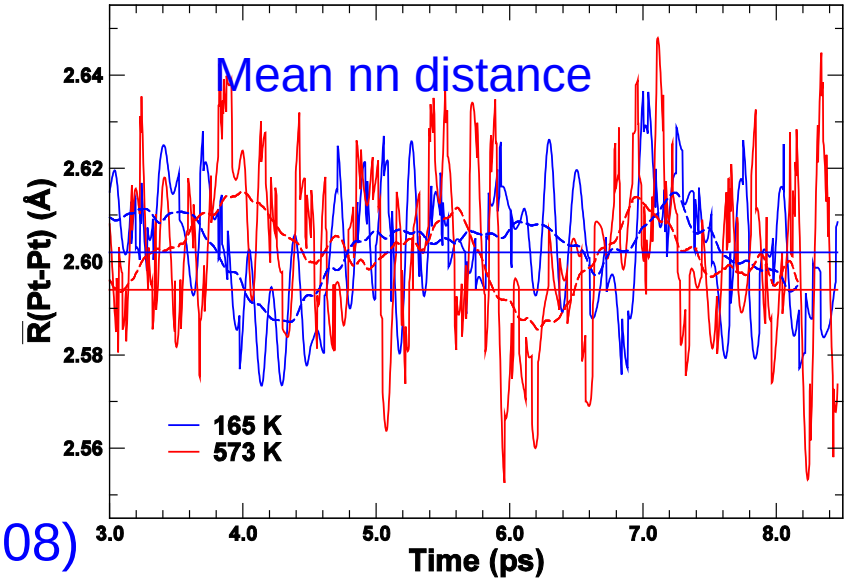
Pt nano-catalysts*



2500 3 fs time-steps

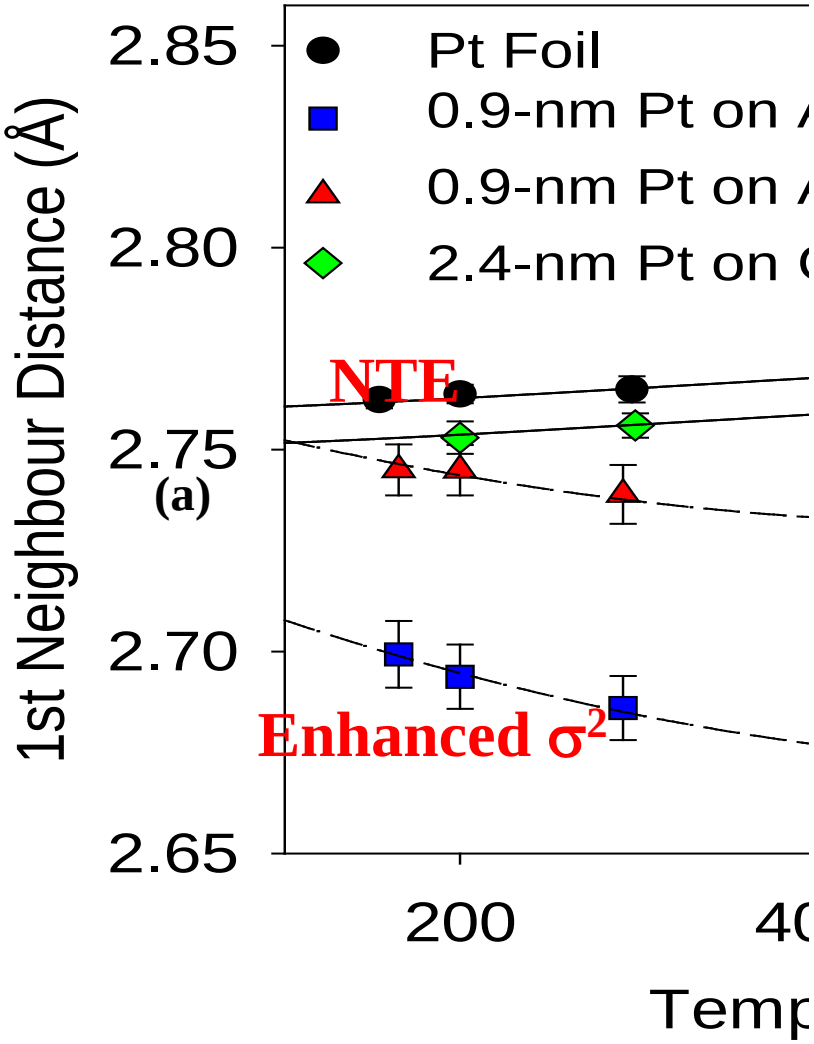
Pt L_3 XAS

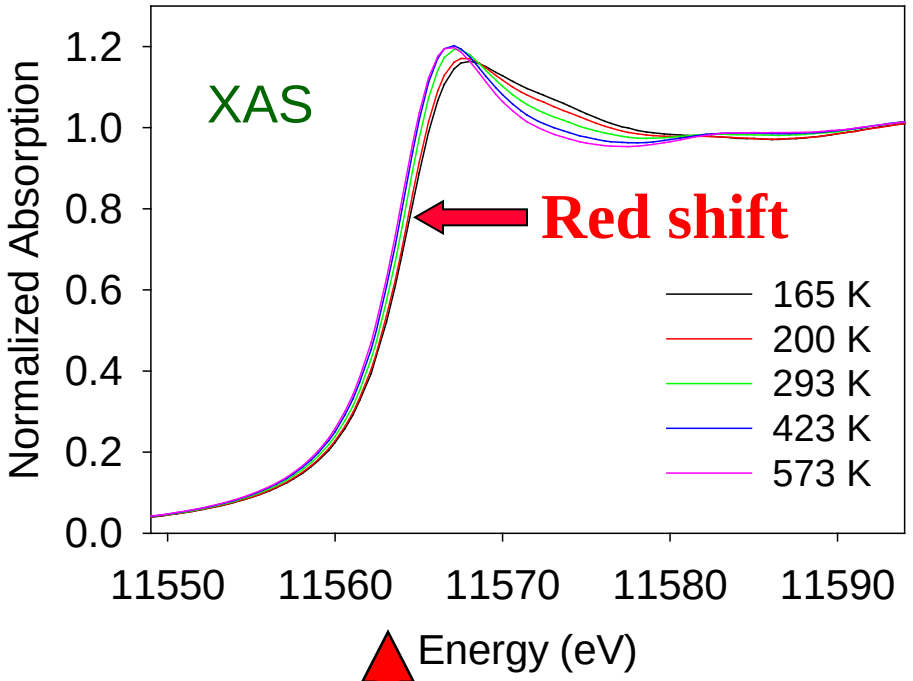




*F. Vila et al. Phys Rev B**78**, 121404(R) (2008)

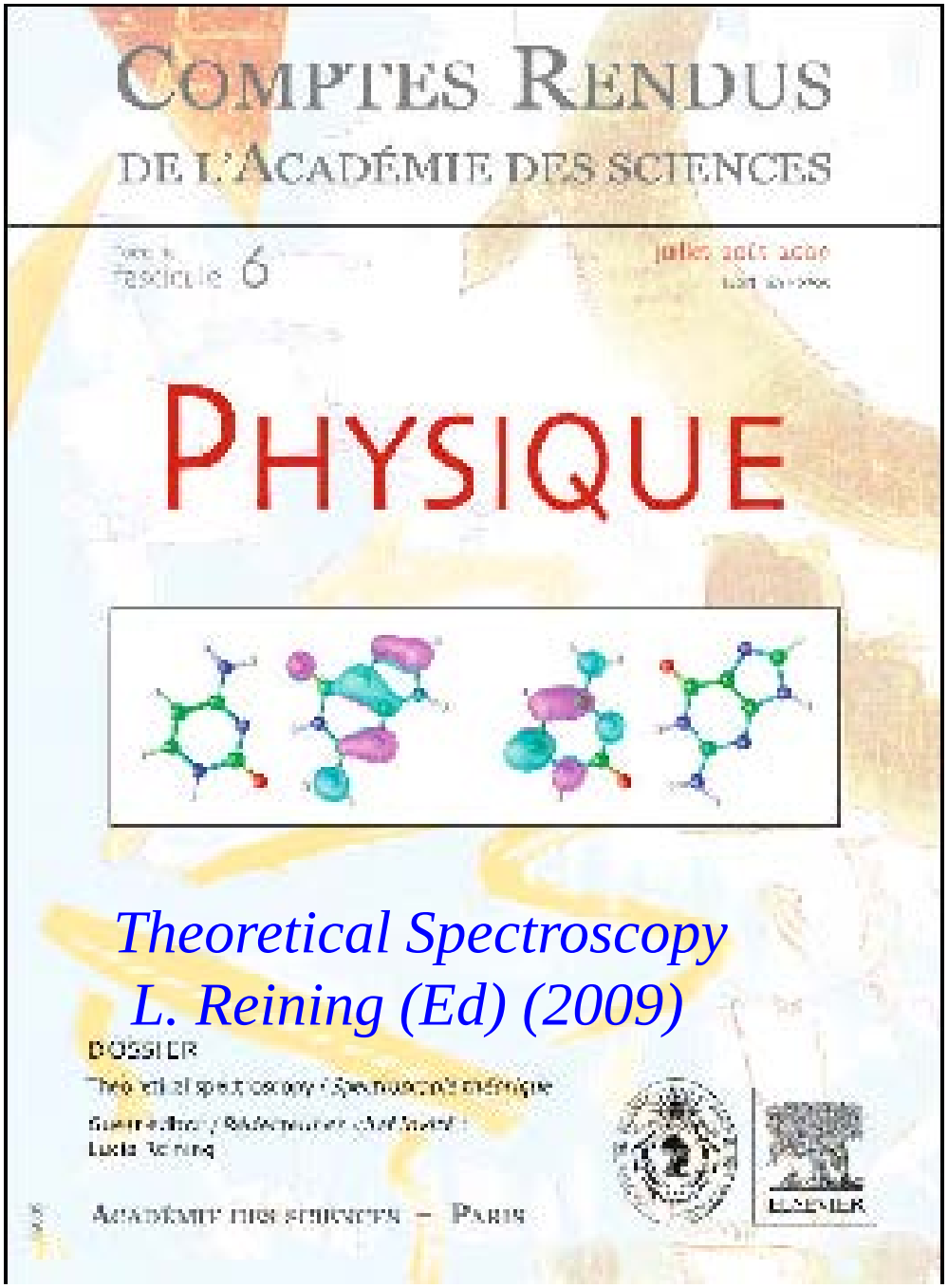
Experimental Observations (X-ray Absorption Expt)*





FEFF explains all surprising anomalies

*Kang, Menard, Frenkel, Nuzzo., JACS Commun. 128, 12068 (2006)



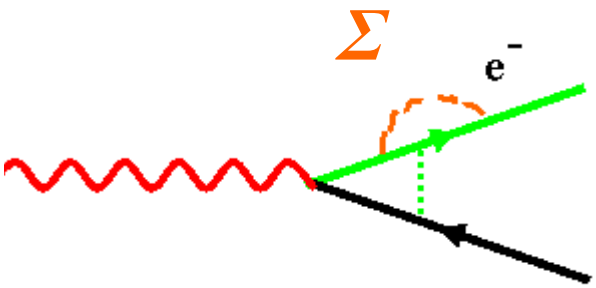
(10 more years)

Improved many-body Corrections

FEFF9

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

Key many-body effects in XAS



- **Self-energy $\Sigma(E)$** — **Energy shifts, losses**
- **Core-hole effects** — **Excitons, Screening**
- **Multi-electron excitations** — **Satellites**
- **Debye-Waller factors** — **Phonons, disorder**

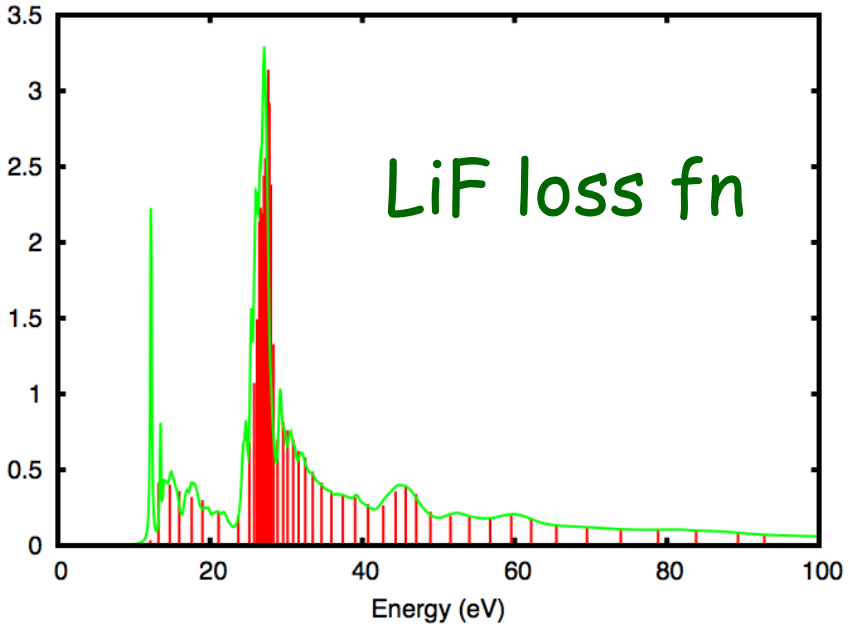
Many-pole GW Self-energy*

MPSE: $\Sigma(E)$ Energy dependent

Extension of Hedin-Lundqvist plasmon-pole

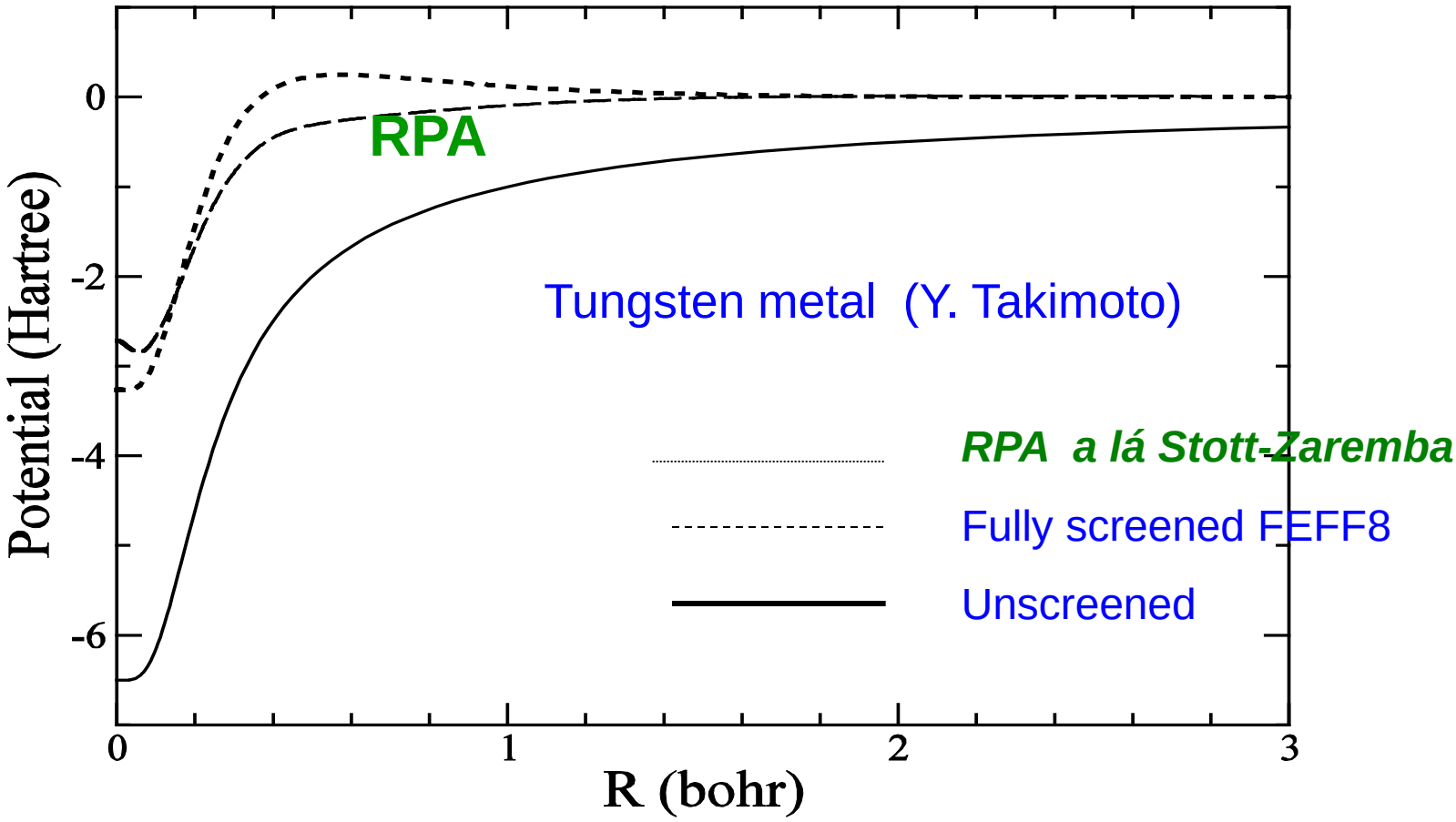
Sum of plasmon pole models matched to loss function

Efficient



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

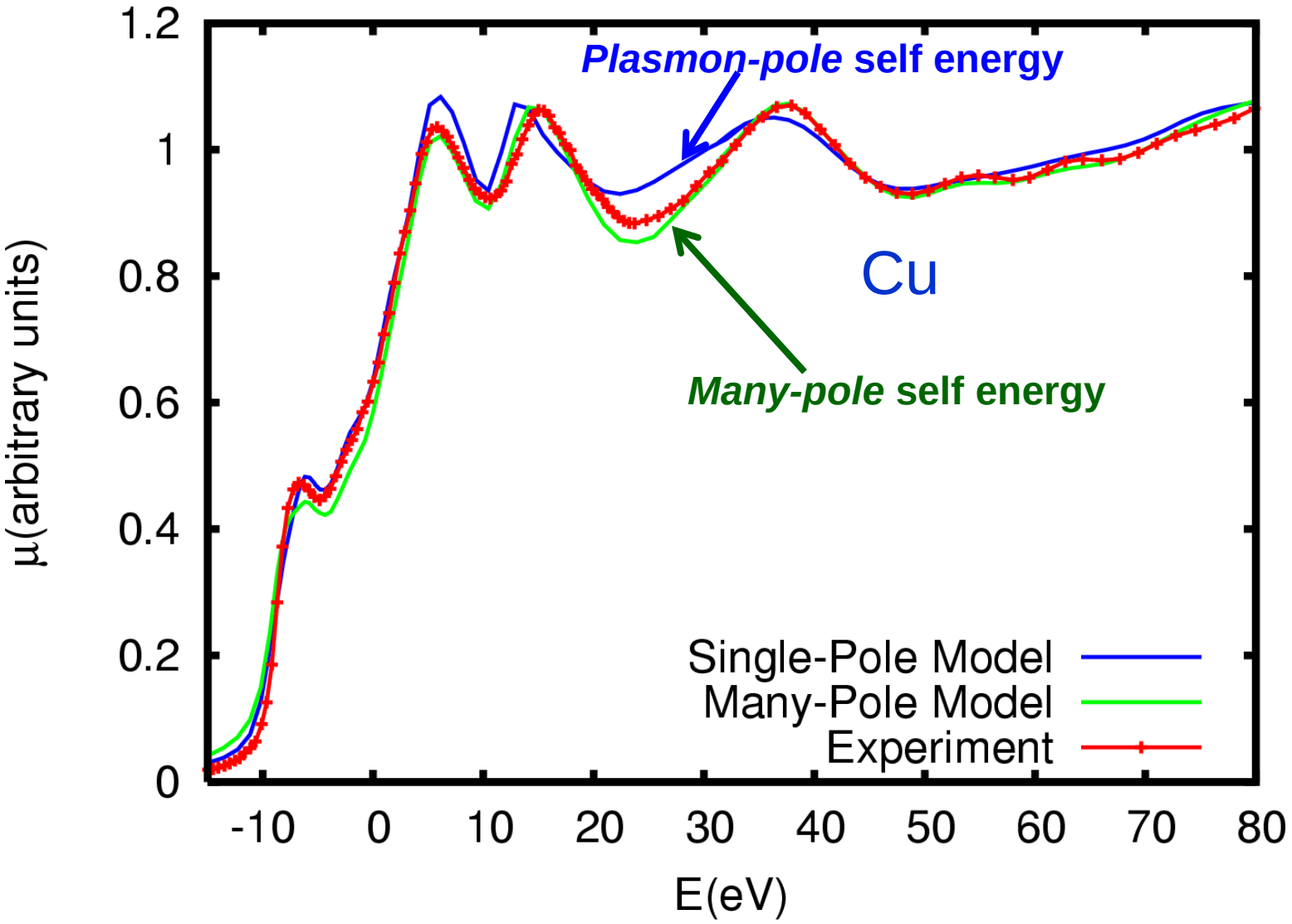
RPA Core-hole potential



Similar to Bethe-Salpeter Eq for W

Improves on final state rule, $Z+1$, half-core hole

Results: Accurate K-edge XANES



Ab initio XAS Debye Waller Factors $e^{-2\sigma^2 k^2}$

*

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

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

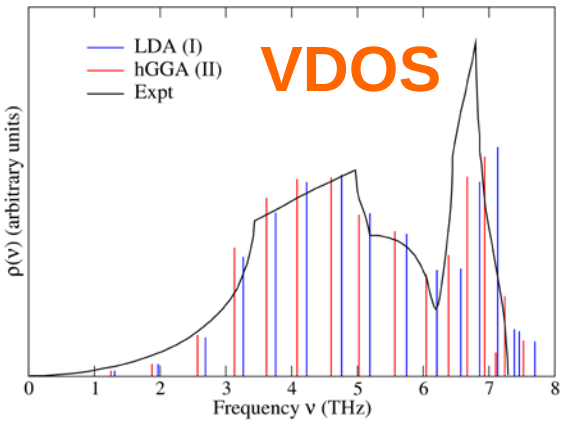
H. H. Rossner and H. J. Krappe
Hahn-Meitner-Institut Berlin, Glienicker Strasse 100, D-14109 Berlin, Germany
(Dated: August 23, 2005)

Many Pole model

for phonons

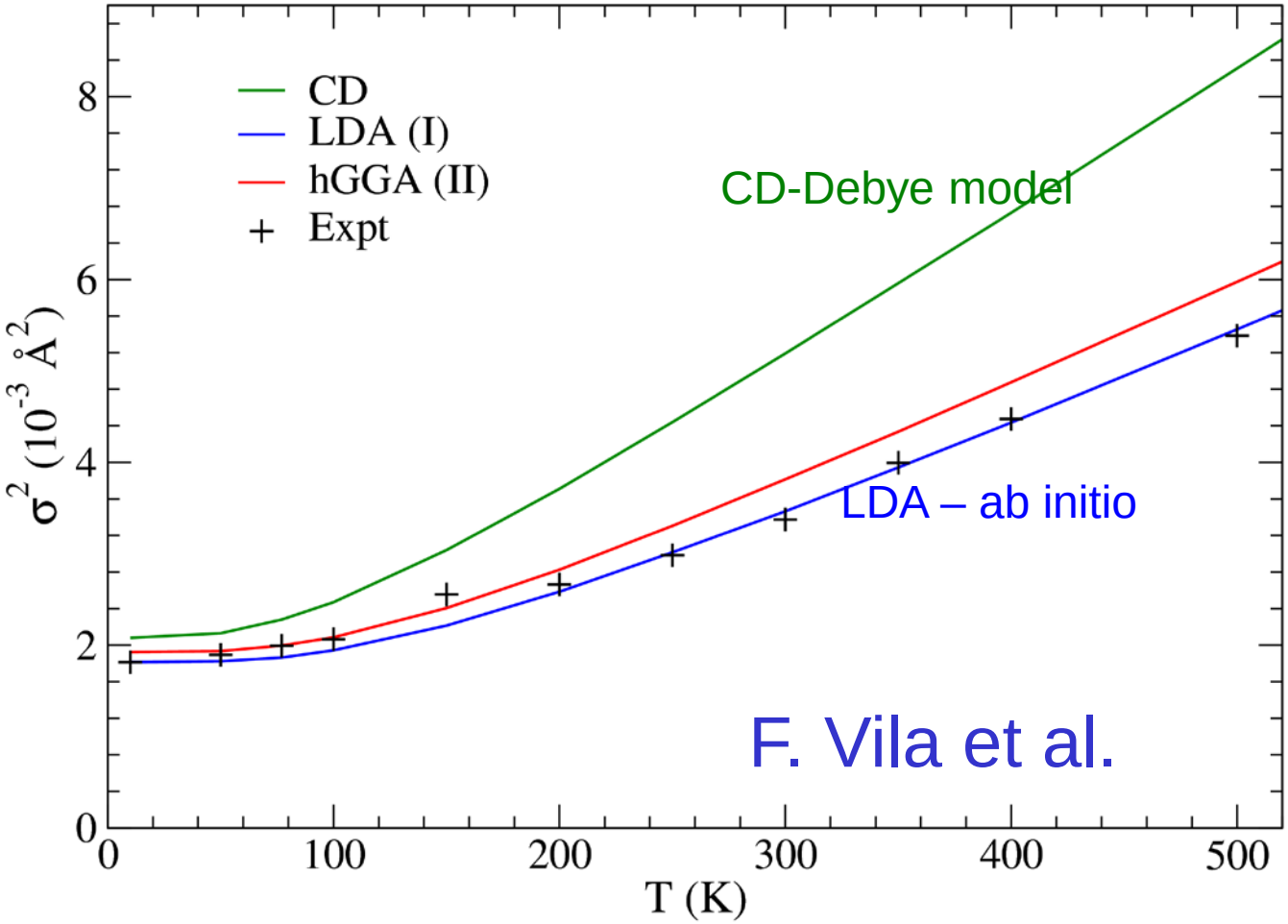
$$\sigma^2 = \frac{\hbar}{\mu_i}\int_0^\infty \rho(\omega^2)\coth\frac{\beta\hbar\omega}{2}\,d\omega$$

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



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

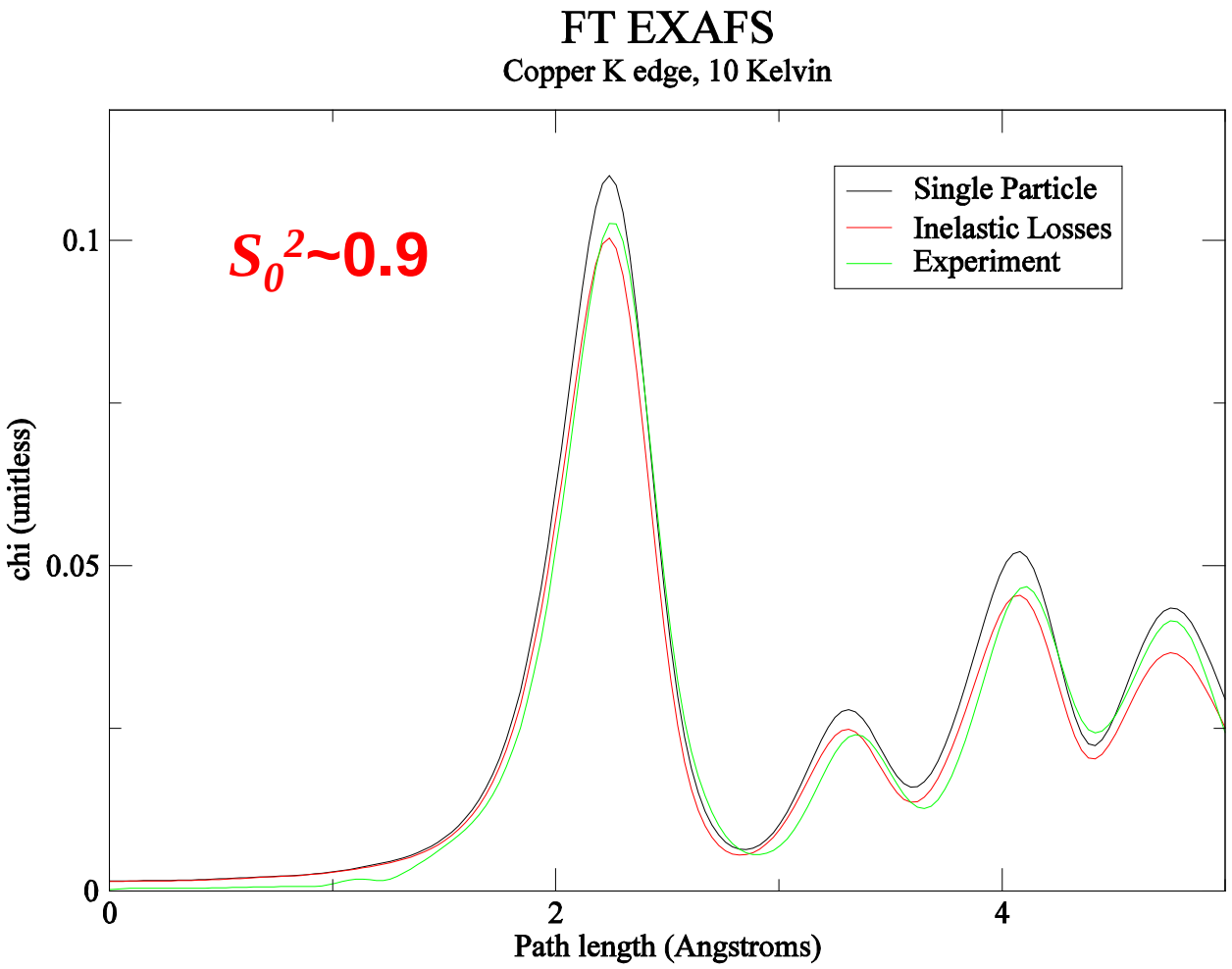
Example: XAFS Debye-Waller Factor of Ge



Expt: Dalba *et al.* (1999)

Many-body amplitude factors S_0^2

Q: What is S_0^2



Inelastic losses in XAS beyond QP

- **Many-body XAS** = Convolution of QP XAS with energy dependent spectral function $A(\omega, \omega')$

$$\mu(\omega) = \int_0^\infty d\omega' \tilde{A}(\omega, \omega') \mu_{qp}(\omega - \omega')$$
$$\equiv \langle \mu_{qp}(\omega) \rangle \approx \mu_{qp}(\omega)\, S_0^2$$

- Explains crossover: **adiabatic** to sudden approximation

Theory: Quasi-Boson Model*

IDEA: Neutral Excitations - plasmons, electron-hole pairs, phonons, are **bosons**

Many-body Model: $|N\rangle = |e^-, h, \text{bosons}\rangle$

- Excitations: $H_v = \Sigma_n \omega_n a_n^\dagger a_n$
- Electrons: $h' = \Sigma_k \epsilon_k c_k^\dagger c_k$
- e-boson coupling $V_{pv} = \Sigma_{nkk'} \left[V_{kk'}^n a_n^\dagger + (V_{kk'}^n)^* a_n \right] c_k^\dagger c_{k'}$
- Core-hole-boson coupling: $V_{vc} = -\Sigma_n V_{bb}^n \left(a_n^\dagger + a_n \right)$

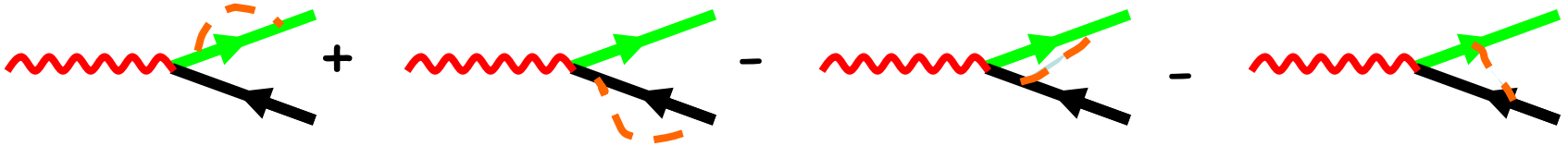
$V^n \rightarrow -\mathrm{Im}\, \varepsilon^{-1}(\omega_n, q_n)$ "fluctuation potentials"

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

Effective GW++ Green's Function*

Spectral function: $A(\omega) = -(1/\pi)\ \mathrm{Im}\ g_{eff}(\omega)$

$$g_{eff}(\omega) = e^{-a}\left[g'(\omega) + \Sigma_n \left(\frac{V^n_{bb}}{\omega_n}\right)^2 g'(\omega-\omega_n) - 2\Sigma_n \frac{V^n_{bb}}{\omega_n} g'(\omega-\omega_n) V^n g'(\omega)\right]$$



Extrinsic + Intrinsic - 2 x Interference

Leading term: Damped Green's function in presence of core-hole (~ final state rule!)

$$g'(\omega) \equiv [\omega - h' - \Sigma(\omega) + i\gamma]^{-1}$$

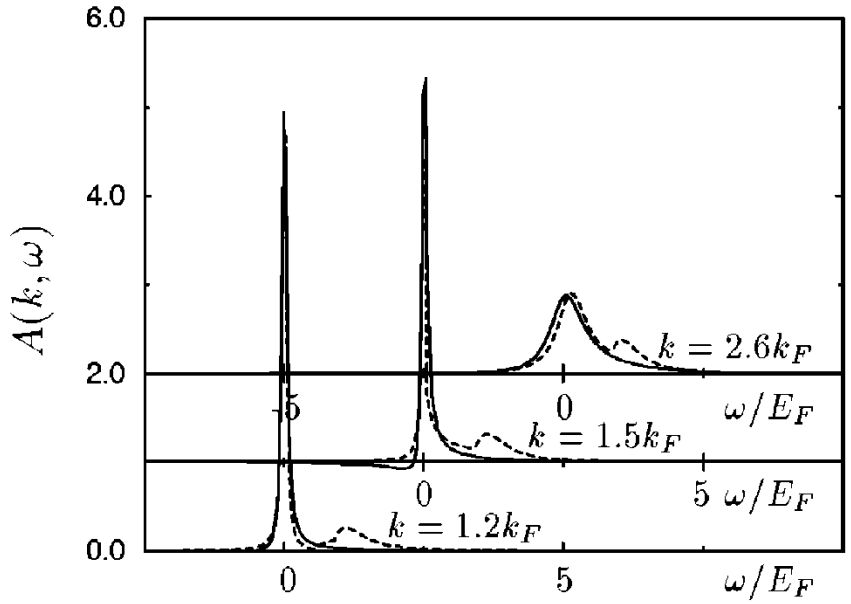
*L. Campbell, L. Hedin, J. J. Rehr, and W. Bardyszewski, Phys. Rev. B **65**, 064107 (2002)

Implementation in FEFF

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*



Multi-electron excitations

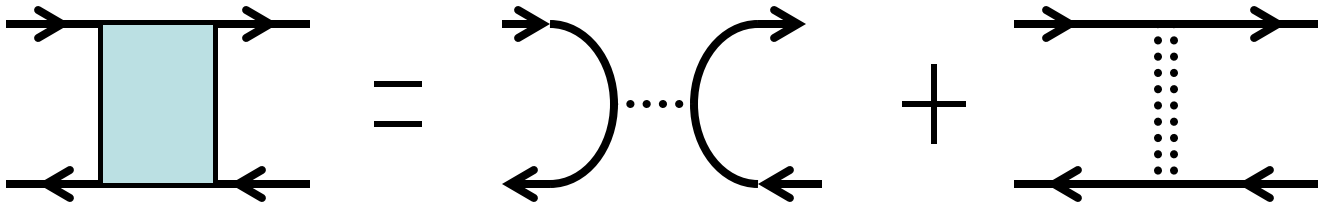
→ **satellites in spectral funcion**

S_0^2 **= 0.9**

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

III. GW/Bethe-Salpeter Equation*

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



Ingredients: Particle-Hole Hamiltonian

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

Σ GW self-energy

$V_{eh} = V_x + W$ Particle-hole interaction

A. AI2NBSE code

Optical-UV Spectra

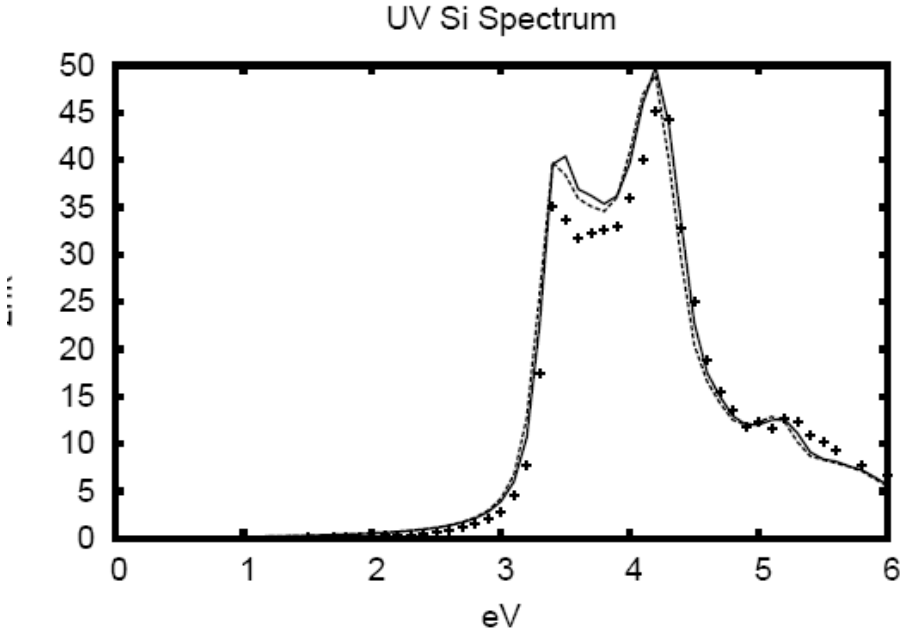
(ABINIT + NIST BSE
+ MPSE + interface):

PHYSICAL REVIEW B 78, 205108 (2008)

Optical to UV spectra and birefringence of SiO_2 and TiO_2: First-principles calculations with excitonic effects

H. M. Lawler,[1] J. J. Rehr,[1] F. Vila,[1] S. D. Dalosto,[1,2] E. L. Shirley,[2] and Z. H. Levine[2]
[1]*Department of Physics, University of Washington, Seattle, Washington 98195, USA*
[2]*National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA*
(Received 11 July 2008; revised manuscript received 13 October 2008; published 12 November 2008)

A first-principles approach is presented for calculations of optical, ultraviolet spectra including excitonic effects. The approach is based on Bethe-Salpeter equation calculations using the NBSE code combined with ground-state density-functional theory calculations from the electronic structure code ABINIT. Test calculations for bulk Si are presented, and the approach is illustrated with calculations of the optical spectra and birefringence of α-phase SiO_2 and the rutile and anatase phases of TiO_2. An interpretation of the strong birefringence in TiO_2 is presented.



UW / NIST Collaboration

Plane-wave, pseudo-potential code

cf. EXC, YAMBO, BerkeleyGW, etc.

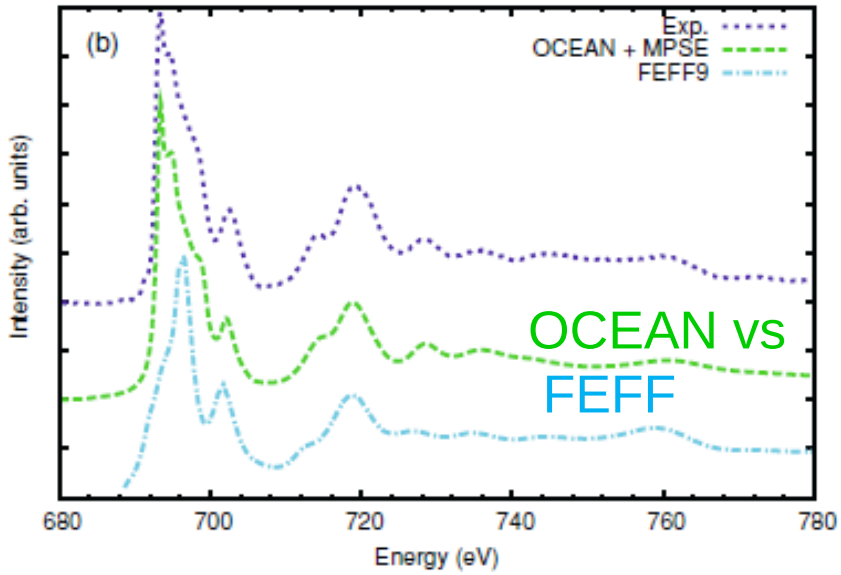
B. OCEAN* Core-GW/BSE Code

PHYSICAL REVIEW B 83, 115106 (2011)

Bethe-Salpeter equation calculations of core excitation spectra

J. Vinson, J. J. Rehr, and J. J. Kas
Department of Physics, University of Washington, Seattle, Washington 98195, USA

E. L. Shirley
National Institute of Standards and Technology (NIST), Gaithersburg, Maryland 20899, USA



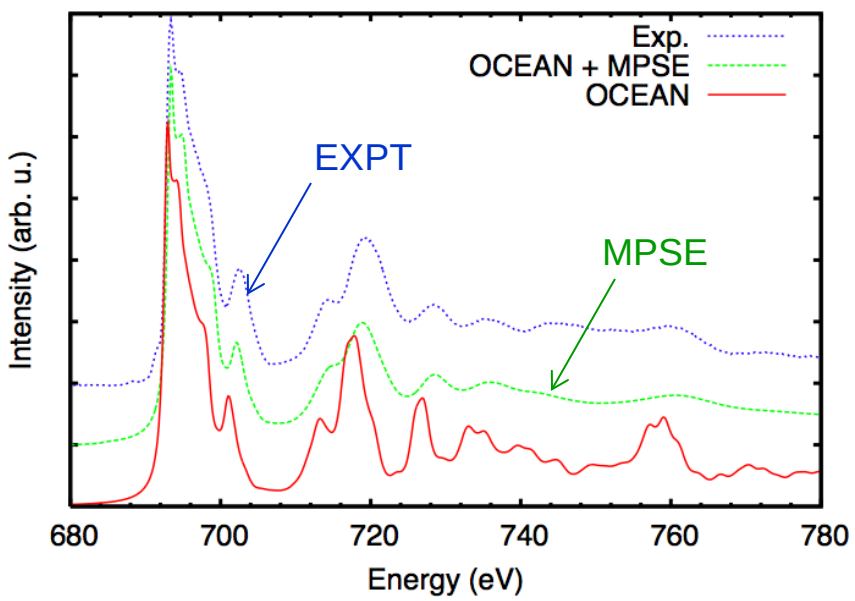
*Obtaining Core Excitations from ABINIT and NBSE

PW-PP + PAW
+ MPSE + NBSE

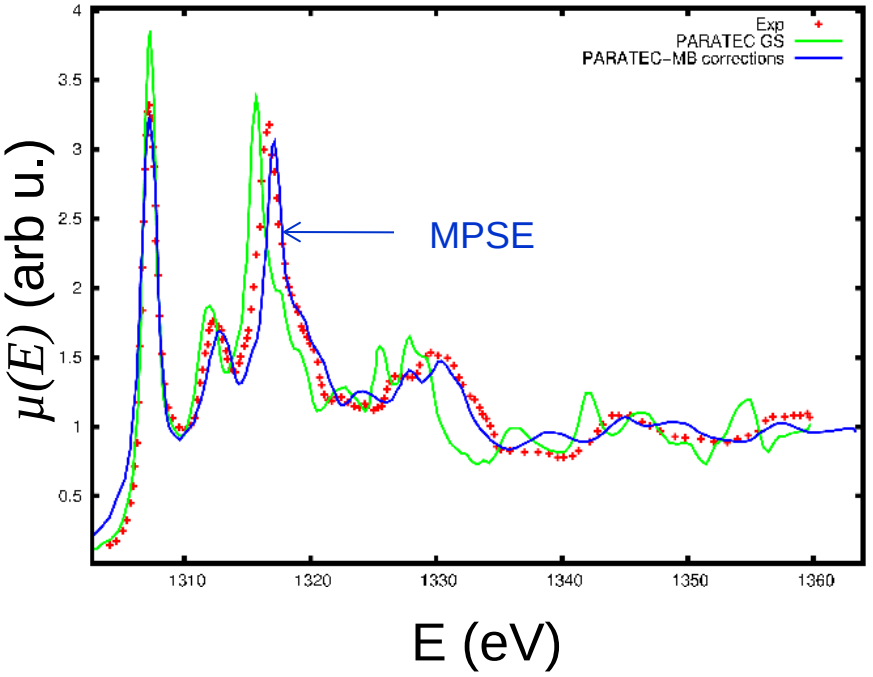
Phys. Rev. B83, 115106 (2011)

Effect of Self-energy in BSE and ΔSCF-DFT*

LiF (BSE < OCEAN)



$MgAl_2O_4$ < ΔSCF-DFT



*J. J. Kas, J. Vinson, N. Trcera, D. Cabaret, E. L. Shirley, and J. J. Rehr, Journal of Physics: Conference Series **190**, 012009 (2009)

Application: Water & Ice (AI2NBSE + OCEAN)

Theoretical optical and x-ray spectra of liquid and solid H_2O

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

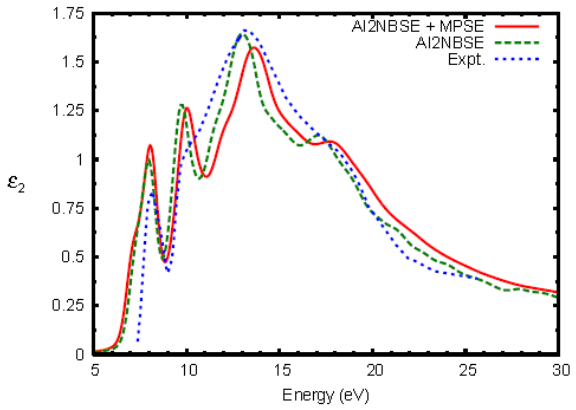
[1]*Dept. of Physics, Univ. of Washington Seattle, WA 98195*

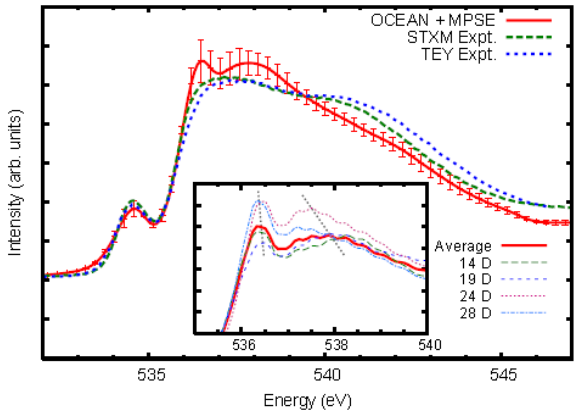
[2]*National Institute of Standards and Technology, Gaithersburg, MD 20899*

(Dated: July 11, 2011)

Theoretical optical and x-ray spectra of model structures of water and ice are calculated using a many-body perturbation theory, Bethe-Salpeter equation (BSE)approach implemented in the valence- and core-excitation codes AI2NBSE and OCEAN. These codes use *ab initio* density-functional theory wave functions from a plane-wave, pseudopotential code, quasi-particle self-energy corrections, and a BSE treatment of particle-hole interactions. The approach improves on independent-particle methods through the inclusion of a complex, energy-dependent self-energy and screened particle-hole interactions to account for inelastic losses and excitonic effects. These many-body effects are found to be crucial for quantitative calculations of ice and water spectra.

‹ 17 molecule MD snapshots





Optical Spectra

O K-edge XAS

OCEAN L-edge Spectra – Multiplet effects*

Bethe–Salpeter treatment of X-ray absorption including core-hole multiplet effects

Eric L. Shirley*

J. Elec.Spect. Rel. Phen. **144**, 1187(2005)

a lá E. Shirley:
BSE + KS crystal potential
ab initio – no parameters

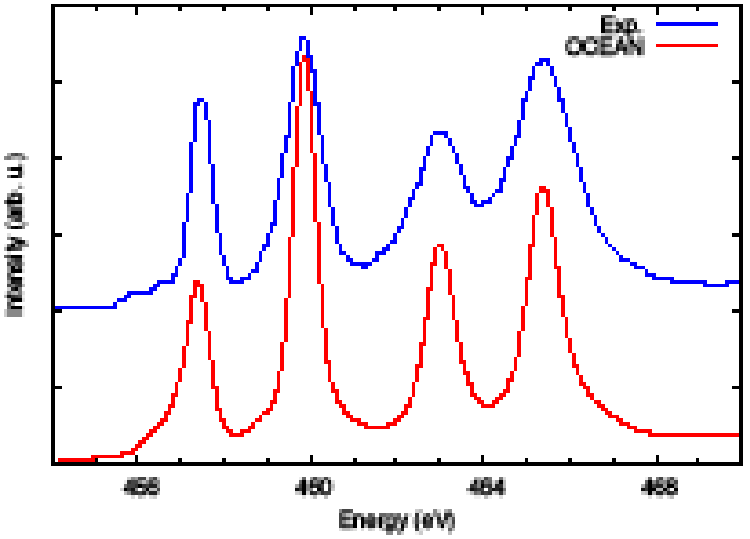
$$H_{BSE} = H_h + H_e + H_{eh}$$

$$H_h = -\epsilon_\alpha + L \cdot S(p)$$

$$H_e = \frac{p^2}{2m} + L \cdot S(d) + H_{KS}^{xtal}$$

$$H_{eh} = V_\alpha(r) + g(i,j)$$

Ti $L_{2,3}$ edge SrTiO3



cf. De Groot et al – Atomic multiplet model + crystal-field parameters

$$H_{at} = H_{av} + L \cdot S(p)$$
$$+L \cdot S(d) + H_{xtalfield} + g(i,j)$$

IV. Extensions for correlated systems
a) Hubbard-model corrections

PHYSICAL REVIEW B 85, 165123 (2012)

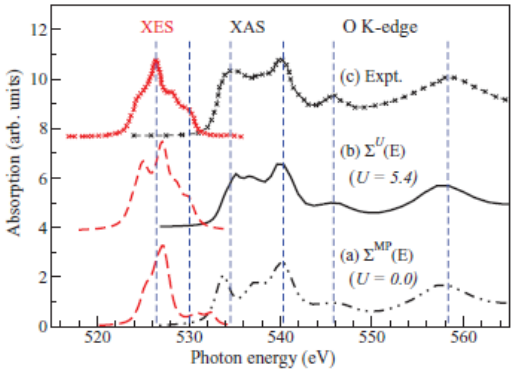
Hubbard model corrections in real-space x-ray spectroscopy theory

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

Hubbard U as self-energy correction estimated with cRPA

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

O K-edge MnO



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

Extensions

b) Charge-Transfer Excitations*

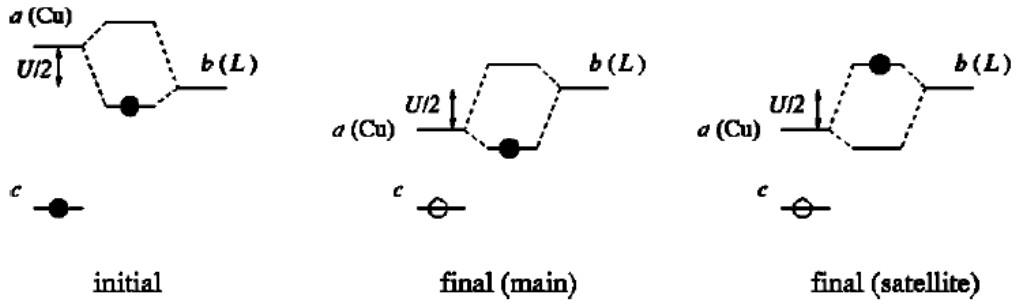
PHYSICAL REVIEW B VOLUME 60, NUMBER 11 15 SEPTEMBER 1999-I

Transition from the adiabatic to the sudden limit in core-level photoemission: A model study of a localized system

J. D. Lee and O. Gunnarsson
Max-Planck Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany

L. Hedin
Max-Planck Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany and Department of Theoretical Physics, University of Lund, Sölvegatan 14A, S-223 62 Lund, Sweden

(Received 23 April 1999)



*a lá Lee, Gunnarsson, & Hedin. (1999)

3-Level system +
Quasi-boson model

Core |c>

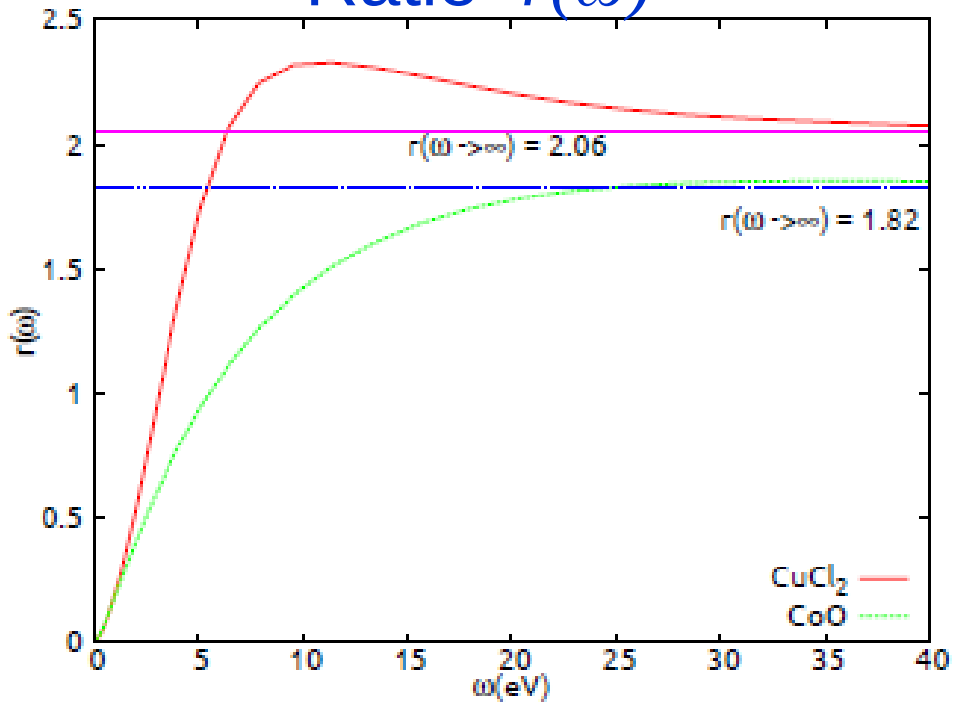
Localized |a>

Ligand |b>

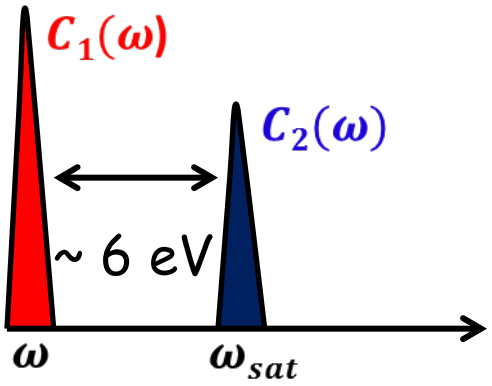
Double pole intrinsic spectral function

$$A(\omega) = C_1(\omega)\delta(\omega) + C_2(\omega)\delta(\omega - \omega_{sat})$$

Ratio $r(\omega)$



$$r(\omega) = \frac{C_1(\omega)}{C_2(\omega)}$$

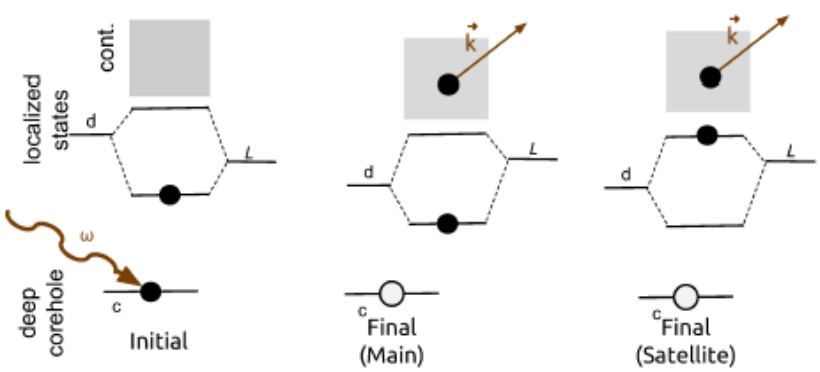


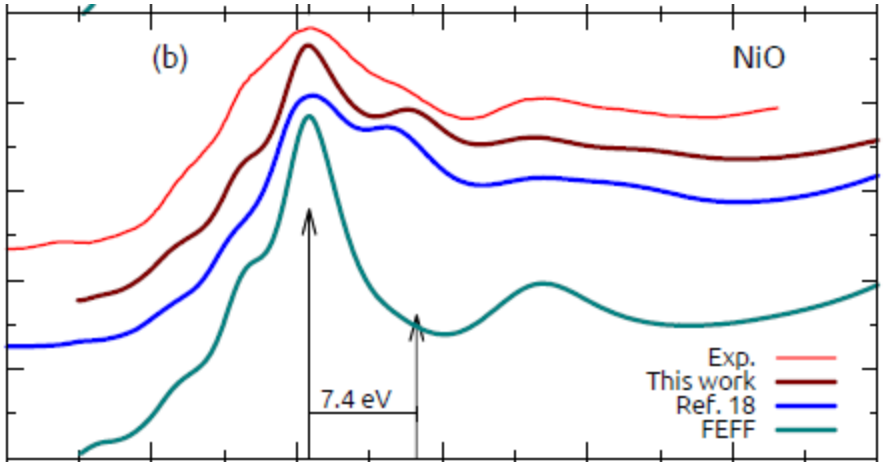
Example: CT satellites in transition metal oxides

Physical Review B **89**, 085123 (2014)

Charge transfer satellites in x-ray spectra of transition metal oxides

E. Klevak, J. J. Kas and J. J. Rehr
Department of Physics, University of Washington, Seattle, WA 98195
(Dated: January 23, 2014)





Cf. J.D.Lee, O.Gunnarsson ,and L.Hedin, Phys.Rev. B**60**,8034 (1999)

Extensions: RIXS and COMPTON Spectra

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*
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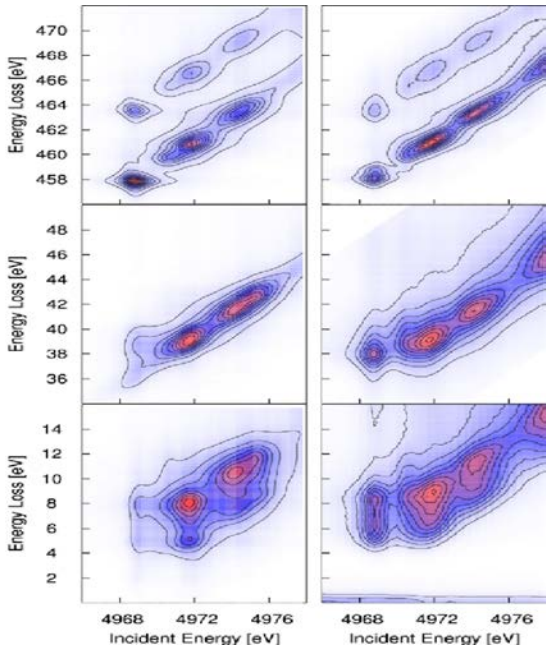
(Received 21 January 2011; revised manuscript received 7 April 2011; published 8 June 2011)

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.

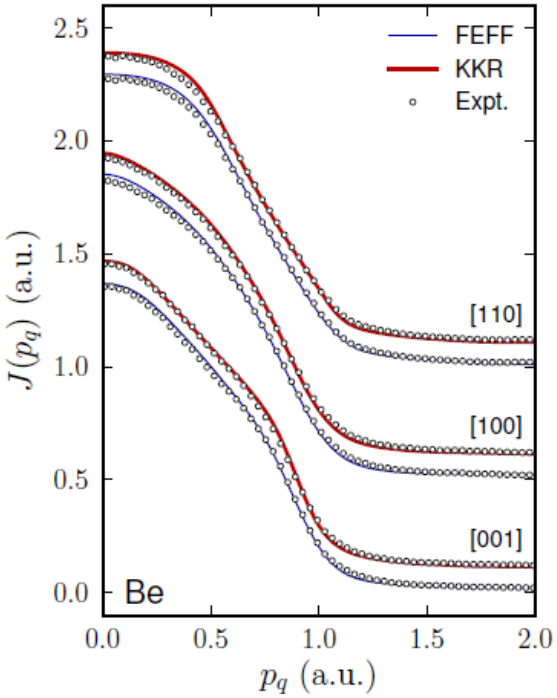


PHYSICAL REVIEW B **85**, 115135 (2012)

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.



User-friendly code GUI interfaces – JFEFF

New Developments in FEFF: FEFF9 and JFEFF

Proceedings of XAFS 15 in press 2012

Kevin Jorissen and John J. Rehr

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Abstract. The ab initio core-level spectroscopy code FEFF9 has seen many new developments in recent years. We describe the addition of new physics and new features designed to calculate more accurate spectra. We also present the user-friendly Java-based GUI JFEFF that simplifies running FEFF on platforms ranging from personal computers to high-performance parallel systems and virtual cloud platforms.

www.feffproject.org

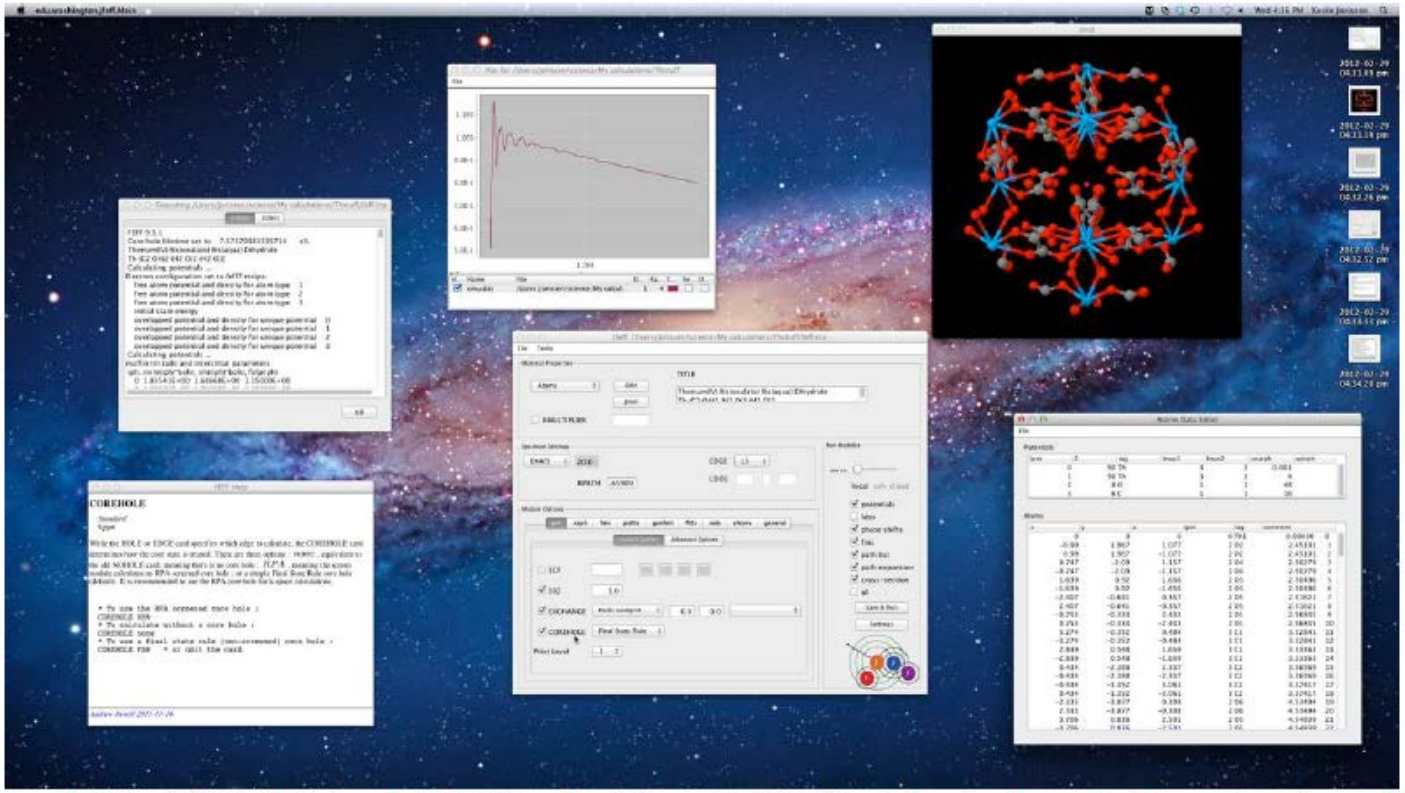


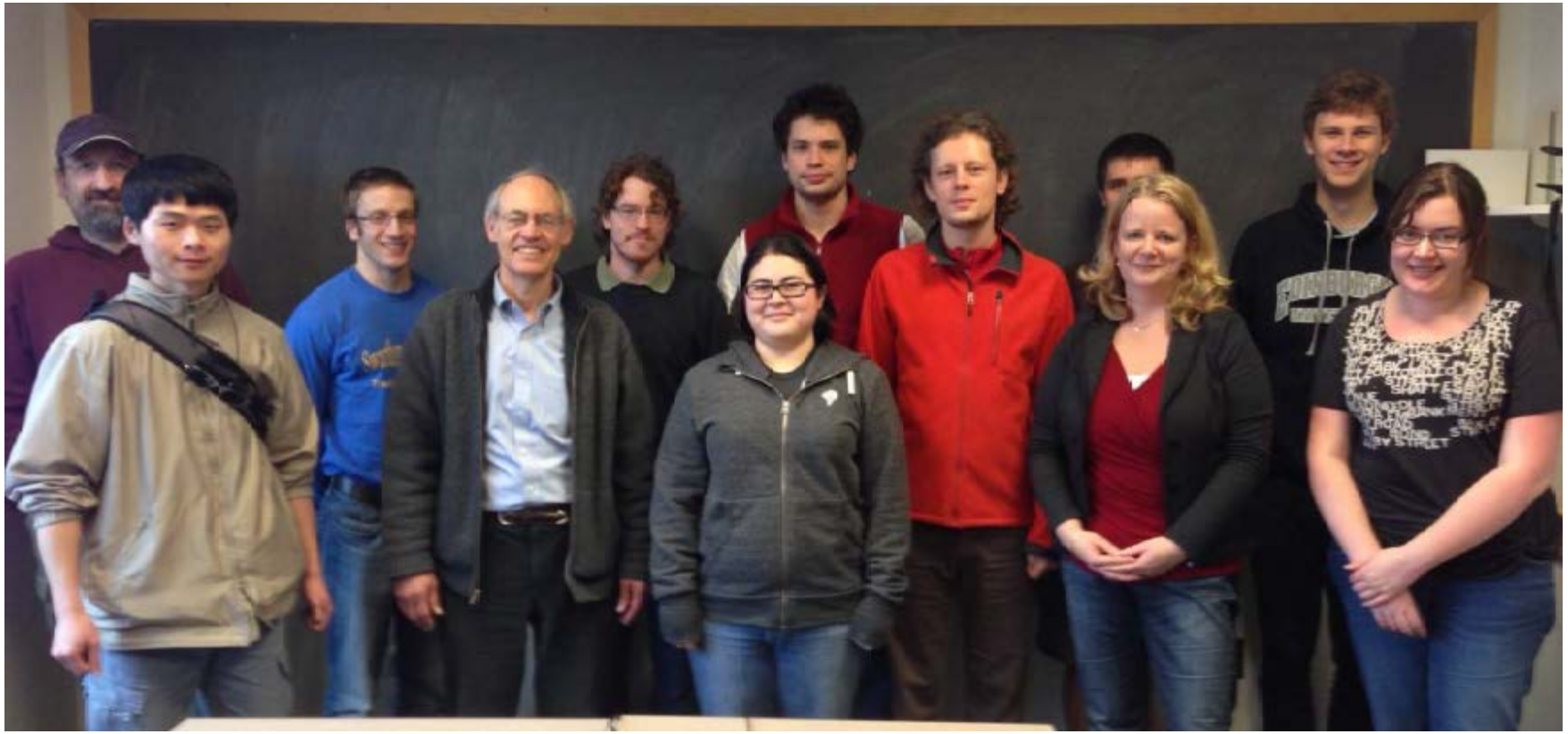
Figure 1 The JFEFF GUI for the FEFF9 code. The main JFEFF window is shown in the centre. Around it

Summary & Conclusions

Goals largely achieved - Core spectra understood in terms of excited state theory

- Ab initio RSGF and GW/BSE codes
- Ab initio many body corrections: core-hole, self energy, DW factors, and strong correlations
- Combined codes (**FEFF+OCEAN+AI2NBSE**) for **full spectrum** response UV-Vis-XAS

Acknowledgments: Rehr group & collaborators and
L Reining, M Guzzo, E Shirley, K Gilmore, et al.



Thanks to DOE BES and CMCSN and the ETSF for $ & €