2nd Introductory Training Day on Theoretical Spectroscopy

Tools for a Theoretical X-ray Beamline

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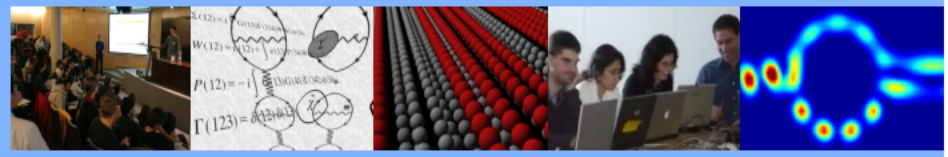
Ecole Polytechnique, Palaiseau, France 22 October 2010



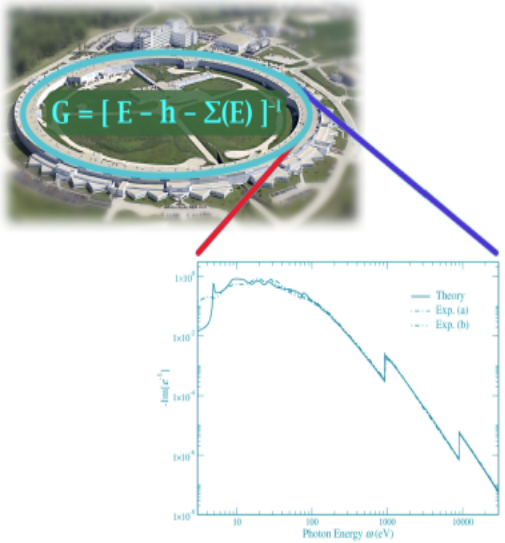
- About the ETSF
- Beamlines
  - Optics
  - Energy Loss Spectroscopy
  - Quantum Transport
  - Time Resolved Spectroscopy
  - Photoemission Spectroscopy
  - ***X-Ray Spectroscopy***
  - Vibrational Spectroscopy
- Services
- Resources
- ETSF I3 project
- Press
- Impressum

Intranet

- Login

X-Ray Spectroscopy

X-ray Spectroscopy Beamline



What

- Core level X-ray absorption spectra (XAS): X-ray absorption fine structure (XAFS), X-ray absorption near edge structure (XANES), and X-ray magnetic circular dichroism (XMCD).
- X-ray scattering factors, X-ray emission spectra, non-resonant X-ray Raman scattering (XRS) and electron energy loss spectra (EELS).

Where

- Bulk, Surfaces and Nanostructures. Liquids.

How

- Real-space Green's function (RSGF) approaches including quasi-particle effects (GW), core-hole screening, and Debye-Waller factors.
- Additional many body effects treated with TDDFT, BSE, and spectral functions.

How to use ETSF services?

- Introduction Package for New Users.

Beamline Coordinator

Prof. John Rehr

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References

Tools for a Theoretical X-ray Beamline

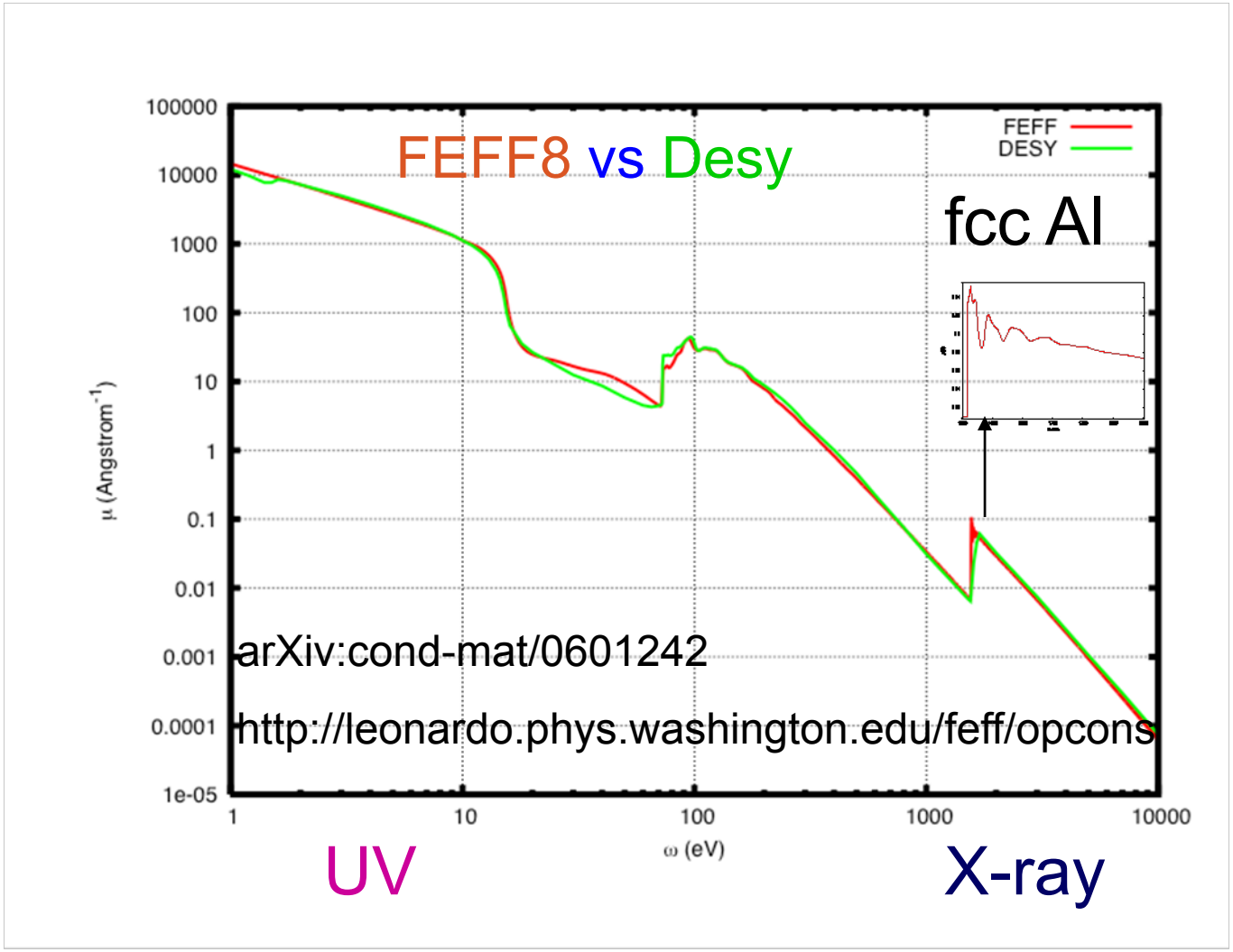
- **GOAL**: Next Generation Core-level Spectra
- *No* adjustable parameters
- Accuracy ~ experiment

- **TALK**:

1. **ETSF** Theoretical X-ray Beamline:
2. Tools for EXAFS and XANES, EELS, XMCD, …
3. DFT/MD-TOOLS
4. Next generation Theoretical tools:
   XAS, GW-BSE & RIXS

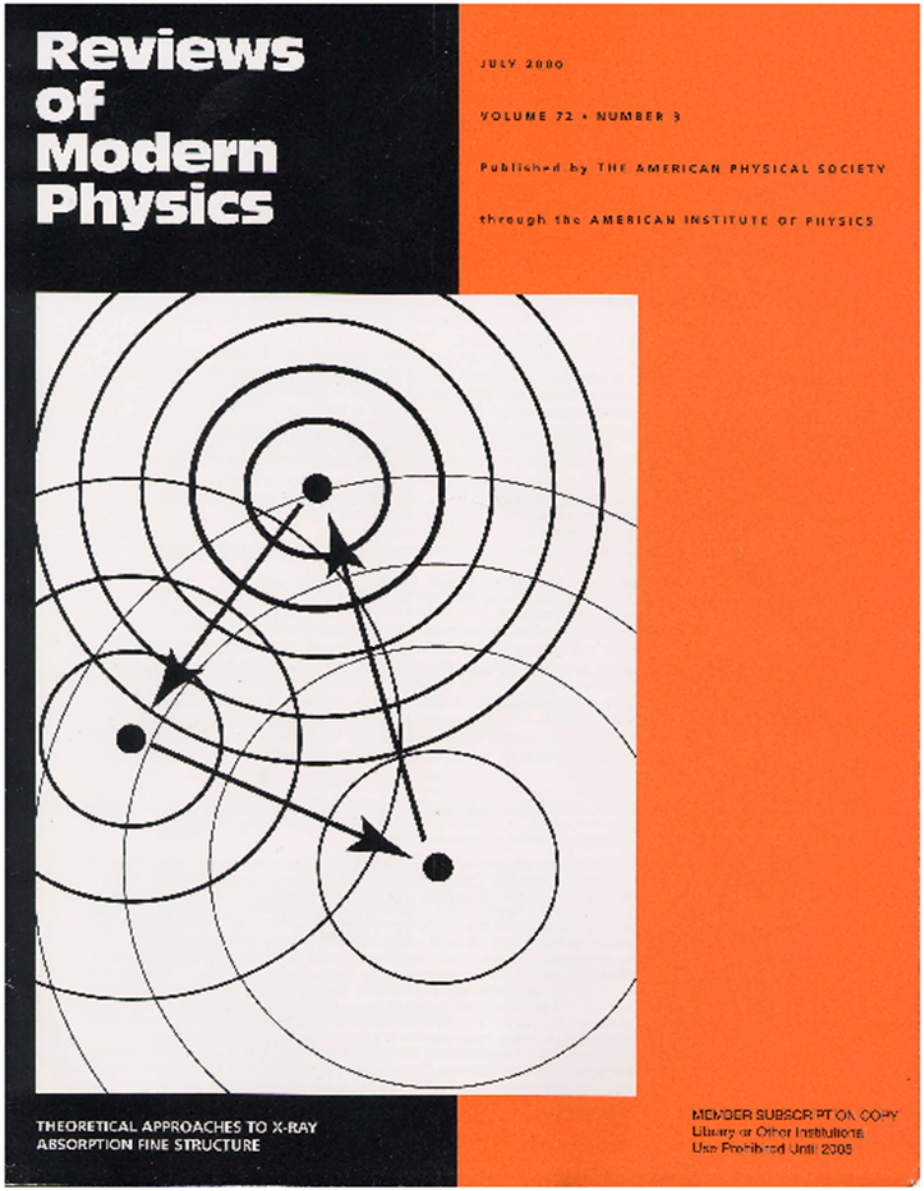
Need: Full spectrum theoretical tools

XAS, XES, RIXS etc.



Photon energy (eV)

2. Tools for EXAFS & XANES



FEFF codes

Real-space Green's function theory

JFEFF GUI

J. J. Rehr & R.C. Albers

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

Wave-function vs Green's functions

Real-space Green's Function Code

No **wave functions!**

- Golden rule via Wave functions

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

- Golden rule via Green's functions

Efficient!

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

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

Implementation: FEFF8

Real Space Green's Function code

PHYSICAL REVIEW B VOLUME 58, NUMBER 12 15 SEPTEMBER 1998-II

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

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MST-11, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

B. Ravel
Ceramics Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

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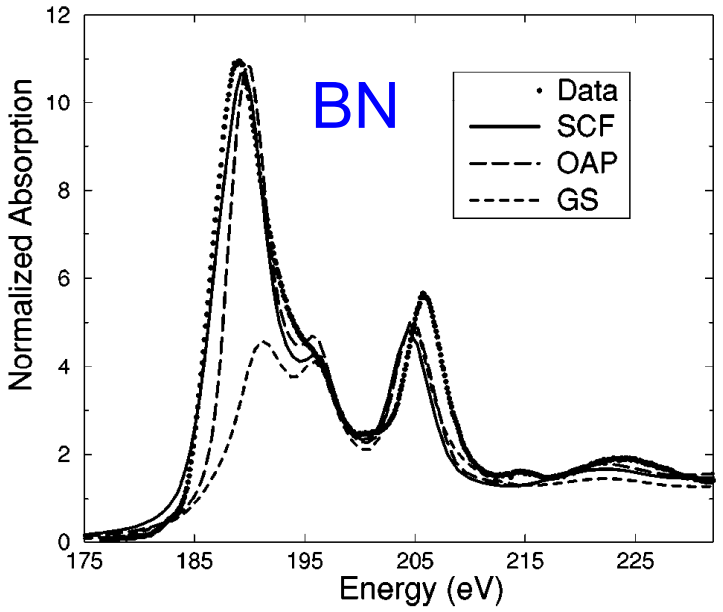
S. D. Conradson
MST-11, Los Alamos National Laboratory, Los Alamos, New Mexic

89 atom cluster

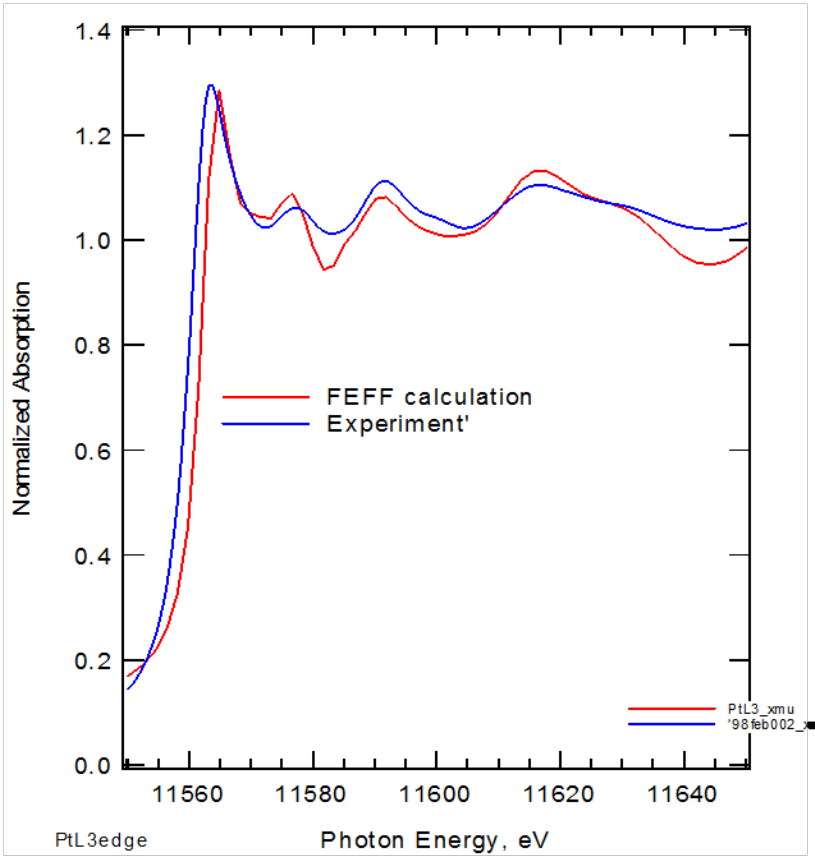
Core-hole, SCF potentials

Essential!

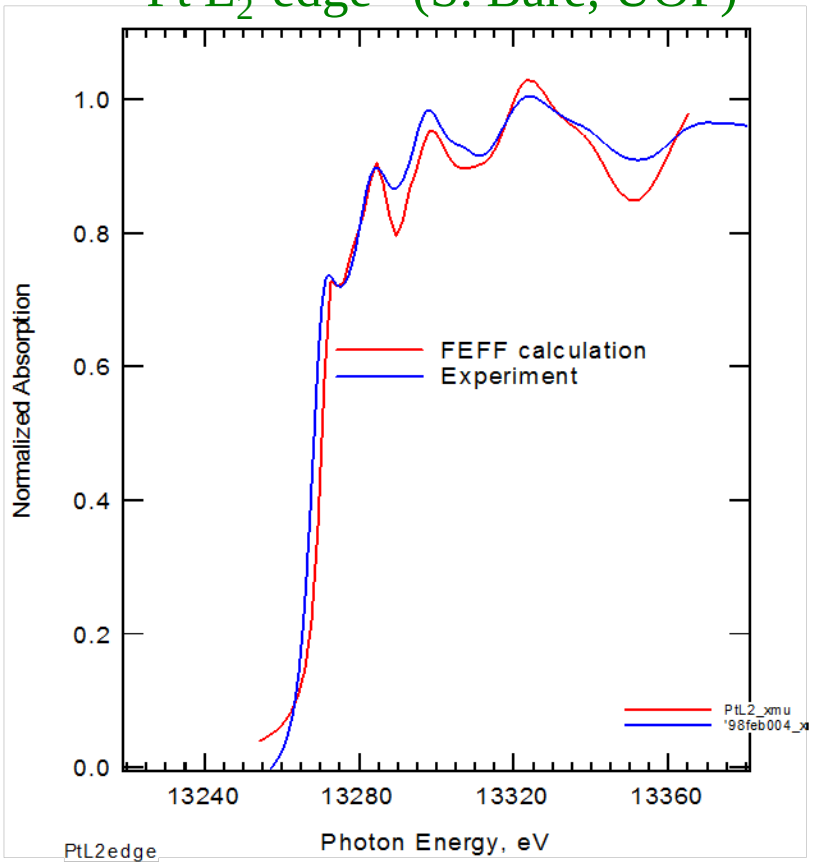


Example: Pt L_{23} XAS FEFF8 vs. experiment

Pt L_3-edge



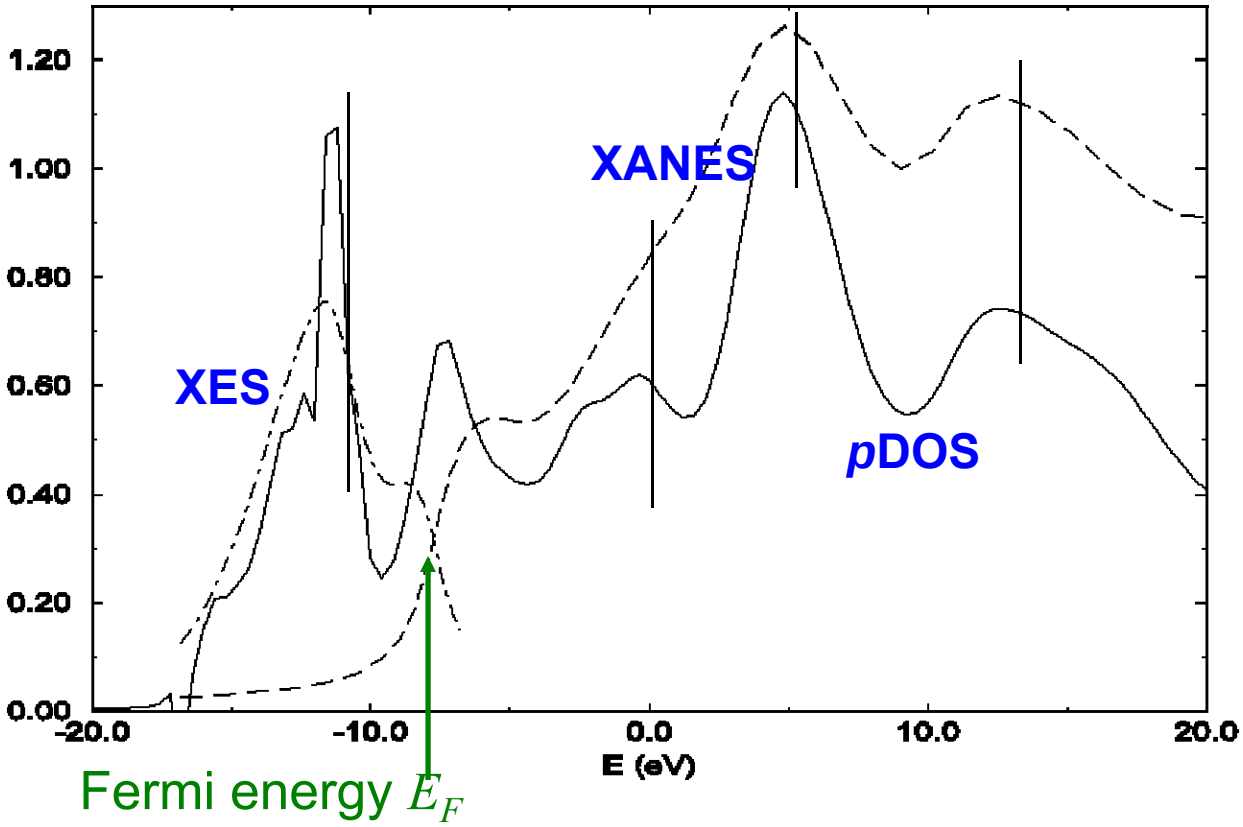
Pt L_2-edge (S. Bare, UOP)



Good agreement: *Relativistic* FEFF8 code reproduces all spectral features, ***including absence of white line at L_2-edge***.

XANES **vs** Projected Density of States (*LDOS*)

Cu *p*DOS vs XANES and XES



Final state energy E

FAST! Parallel Computation

PHYSICAL REVIEW B, VOLUME 65, 104107

Parallel calculation of electron multiple scattering using Lanczos algorithms

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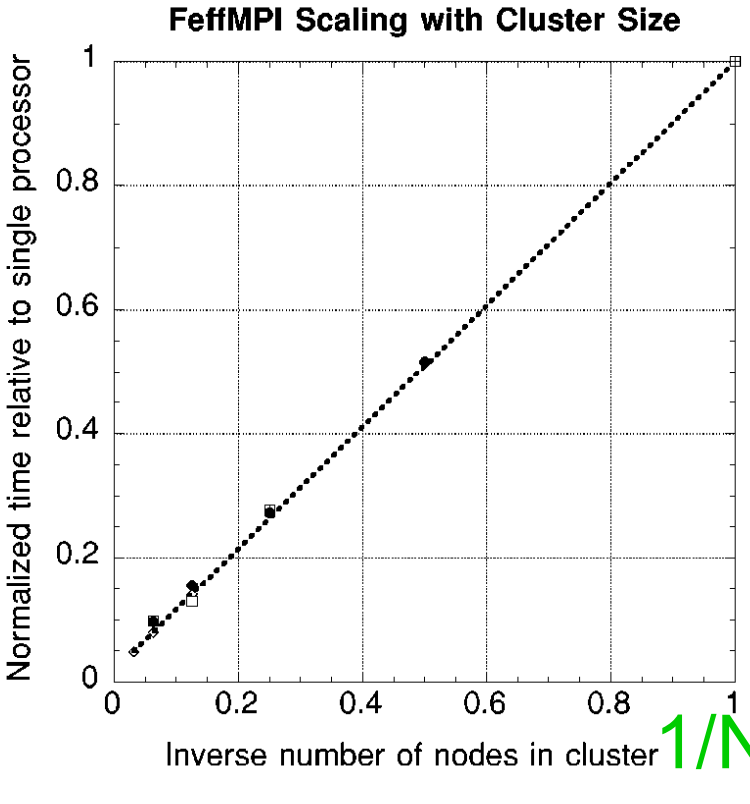
[1]*Department of Physics, University of Washington, Seattle, Washington 98195*
[2]*National Institute of Standards and Technology, Gaithersburg, Maryland 20899*



MPI: "Natural parallelization"

Each CPU does few energies

Lanczos: Iterative matrix inverse

Smooth crossover between

XANES and EXAFS!

$1/N_{CPU}$

DFT Tools: Real-time DFT/MD-XAS

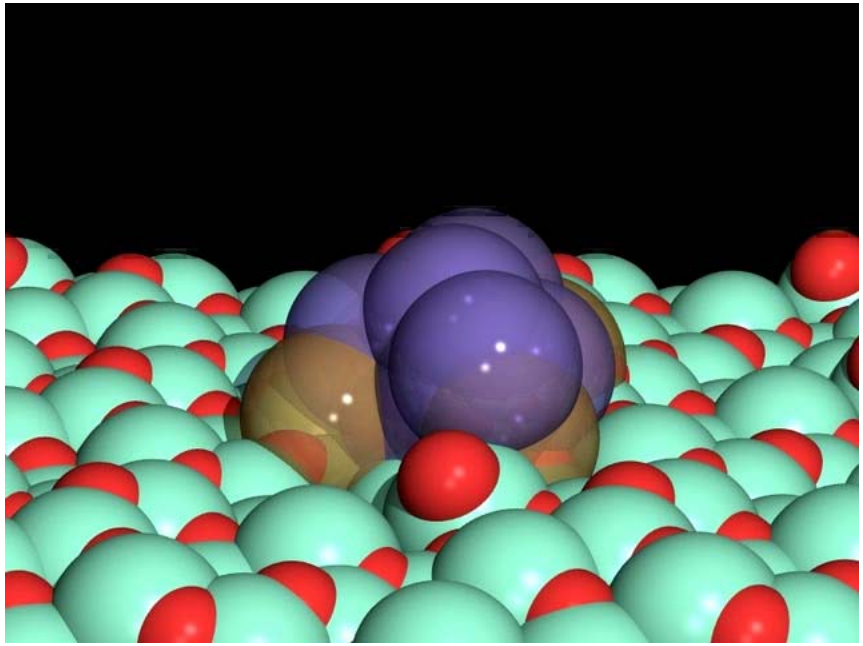
Nano-scale Pt catalysts*

Explains

unusual
properties* of

Pt_{10} /γ-Al_2O_3

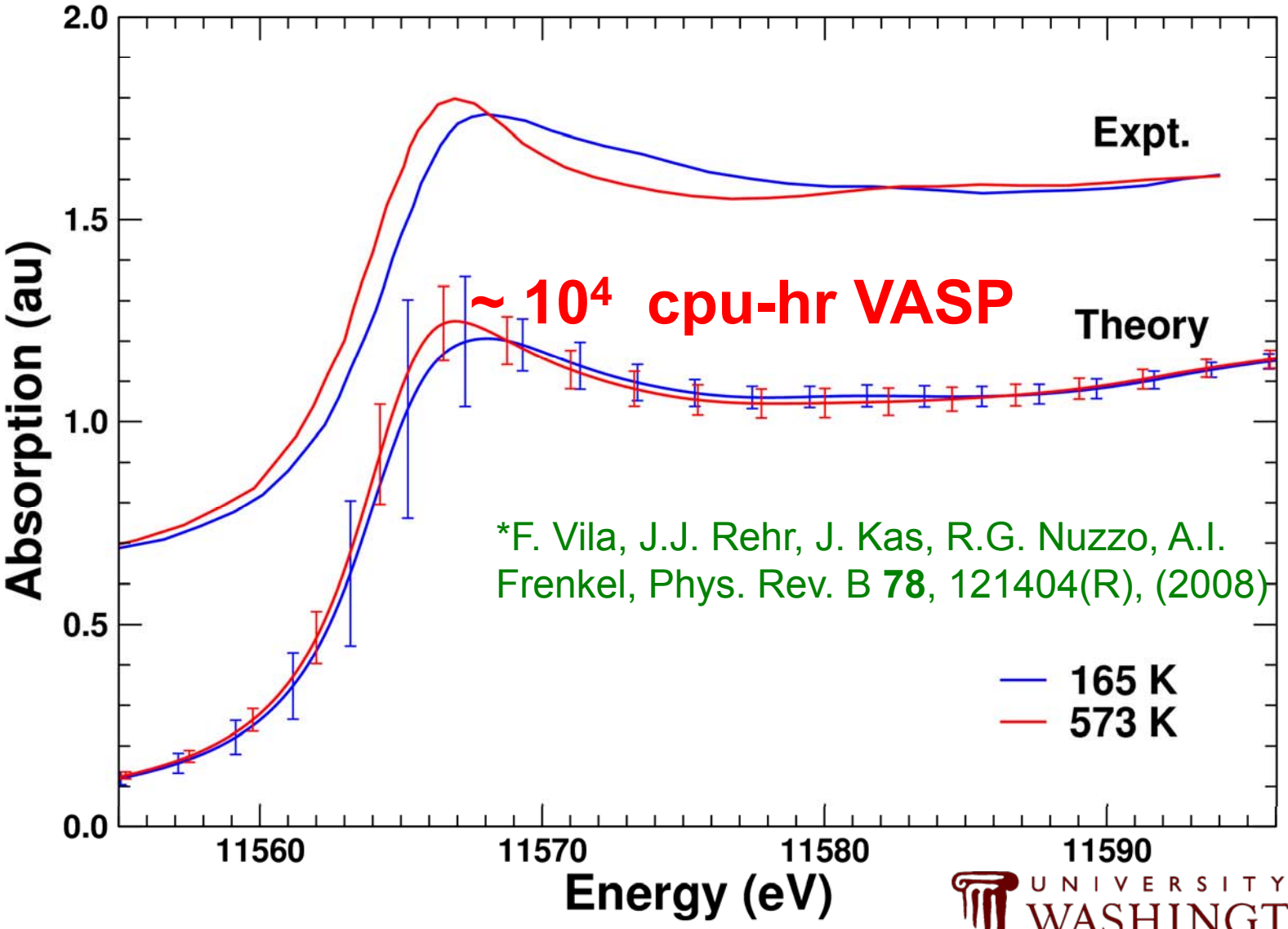
NTE, disorder,
red-shift



metallic Pt Al
oxidized Pt O

*Kang, Menard, Nuzzo, and **Frenkel,** J. Am. Chem. Soc. **128**, 12068 (2006)

Expt. vs DFT/MD structure +FEFF XAS Theory*



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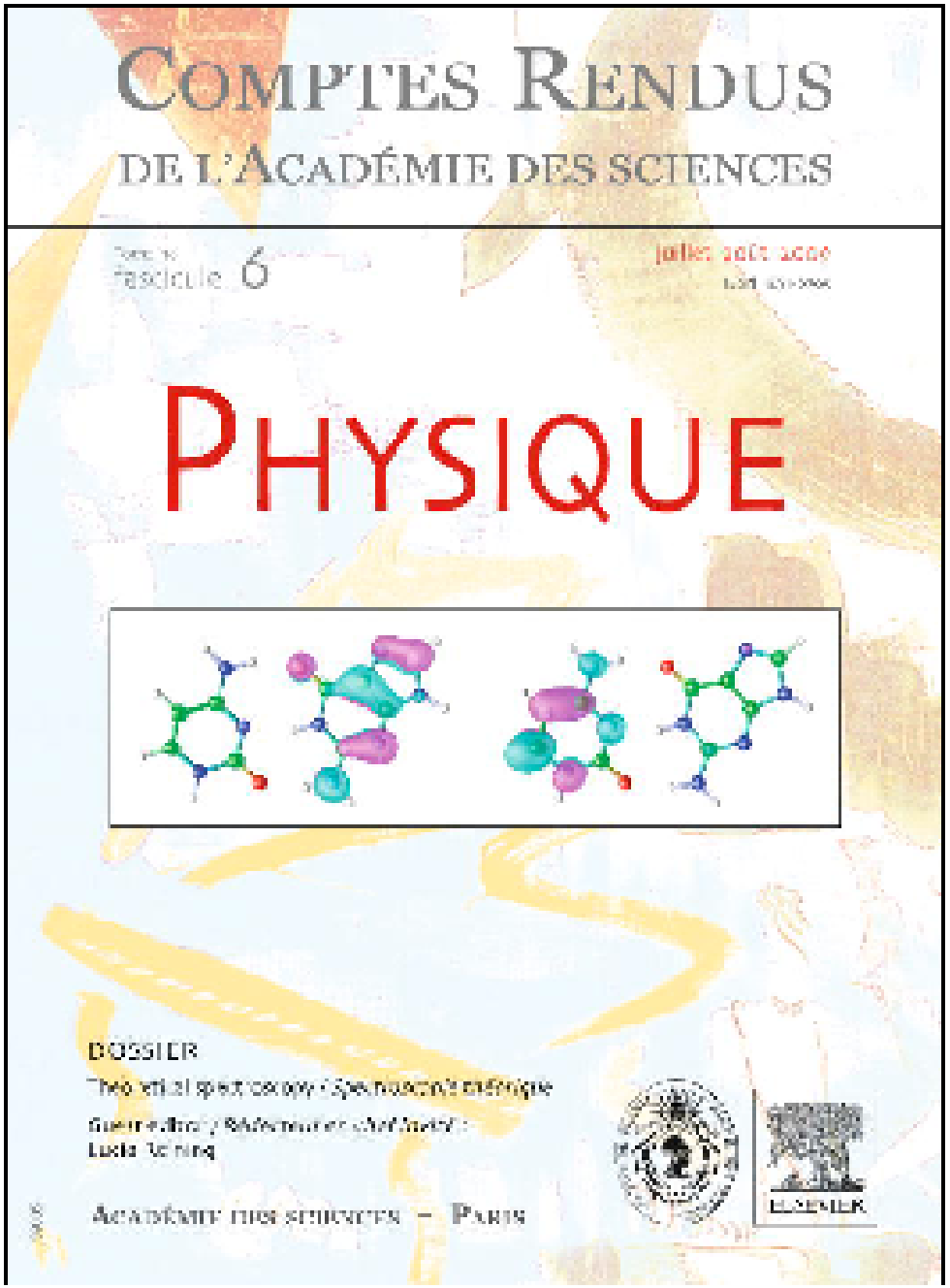


4. Next generation tools

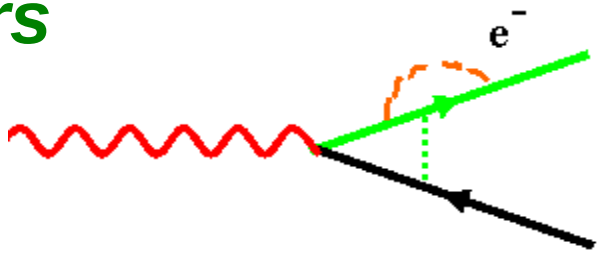
FEFF9, OCEAN

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

in Theoretical Spectroscopy
L. Reining (*Ed*) (2009)

Next generation tools for core-level spectra*

GOAL: ***no adjustable parameters***



A. Multi-electron excitations Quasi-boson

B. Core-hole effects BSE

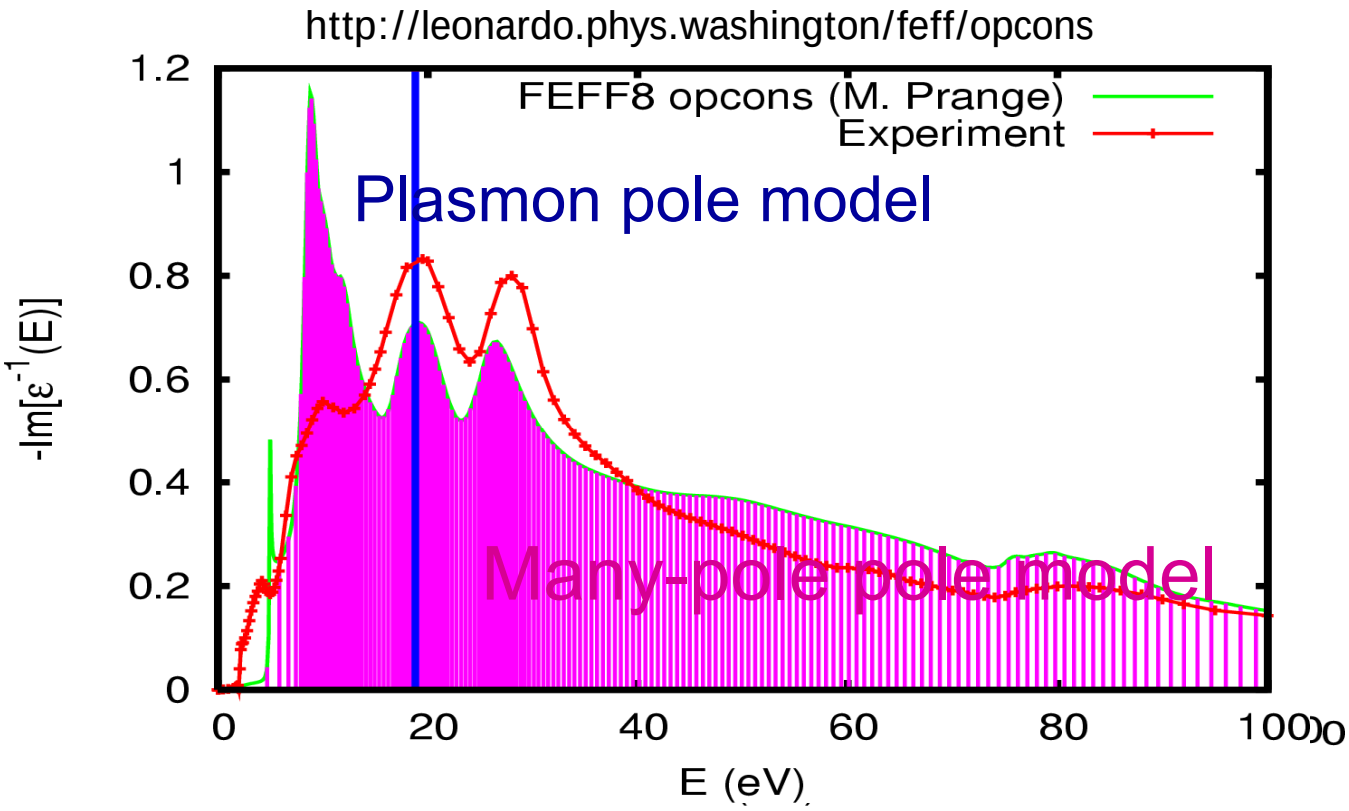
C. Vibrational effects Debye Waller factors

Implementation *FEFF9, OCEAN*

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

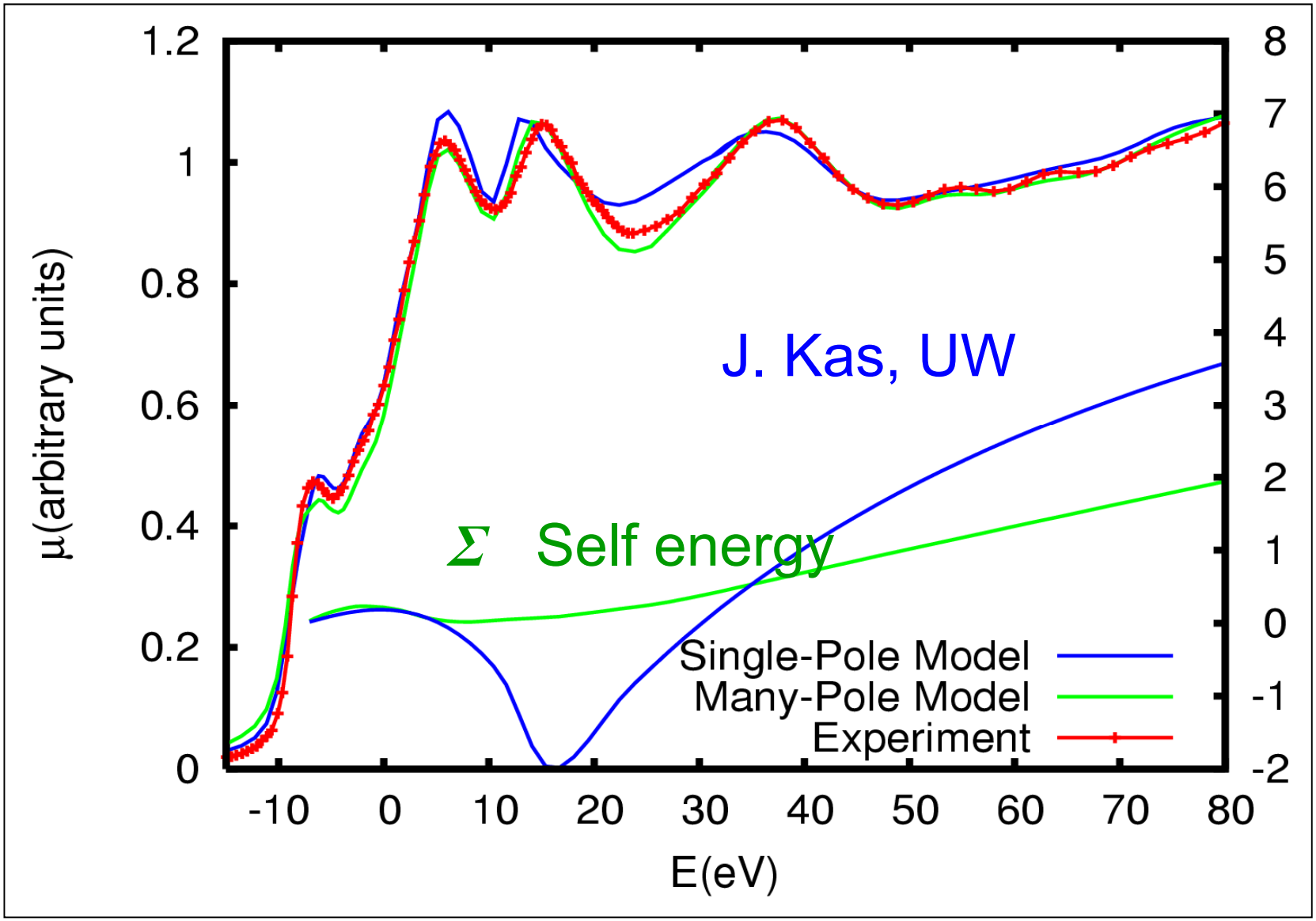
Many-pole self-energy model*

- Sum of single pole self-energies



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

Application: Improved Cu K Edge XANES



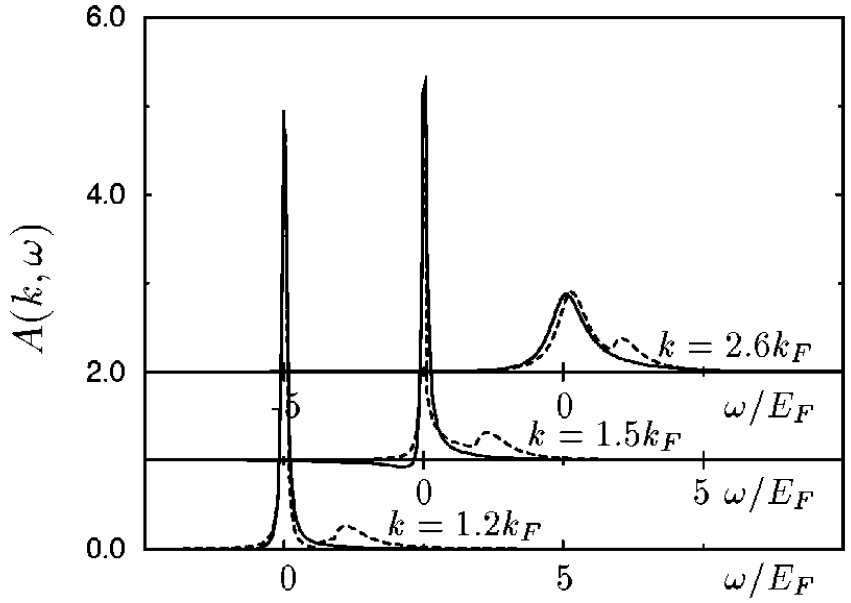
Intrinsic losses: Multi-electron Excitations S_0^2

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 $A(k,\omega)$



Multi-electron excitations

→ satellites in $A(k,\omega)$

Explains intrinsic losses

S_0^2**=0.9**

Beyond quasiparticles!

Quasi-Boson Theory of Inelastic Loss*

Excitations - plasmons, electron-hole pairs ... are **bosons**

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

- 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: $V_{vc} = -\Sigma_n V_{bb}^n \left(a_n^\dagger + a_n \right)$

"GW++" Same ingredients as GW self-energy

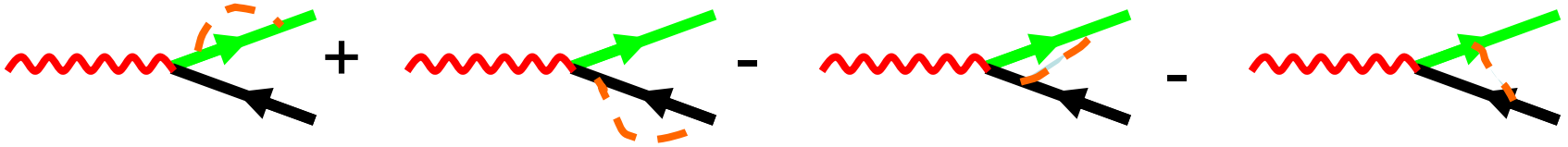
$V^n \rightarrow$ **-Im** $\varepsilon^{-1}(\omega_n, q_n)$ fluctuation potentials

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

Effective GW++ Green's Function $g_{eff}(\omega)$

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

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



Extrinsic + Intrinsic - 2 x Interference

Damped ***qp*** Green's function $g'(\omega) \equiv [\omega - h' - \Sigma(\omega) + i\gamma]^{-1}$

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

Vibrations: XAS Debye Waller Factors

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)

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

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

$$\rho(\omega^2) = \langle Q_i | \delta(\omega^2 - D) | Q_i \rangle$$

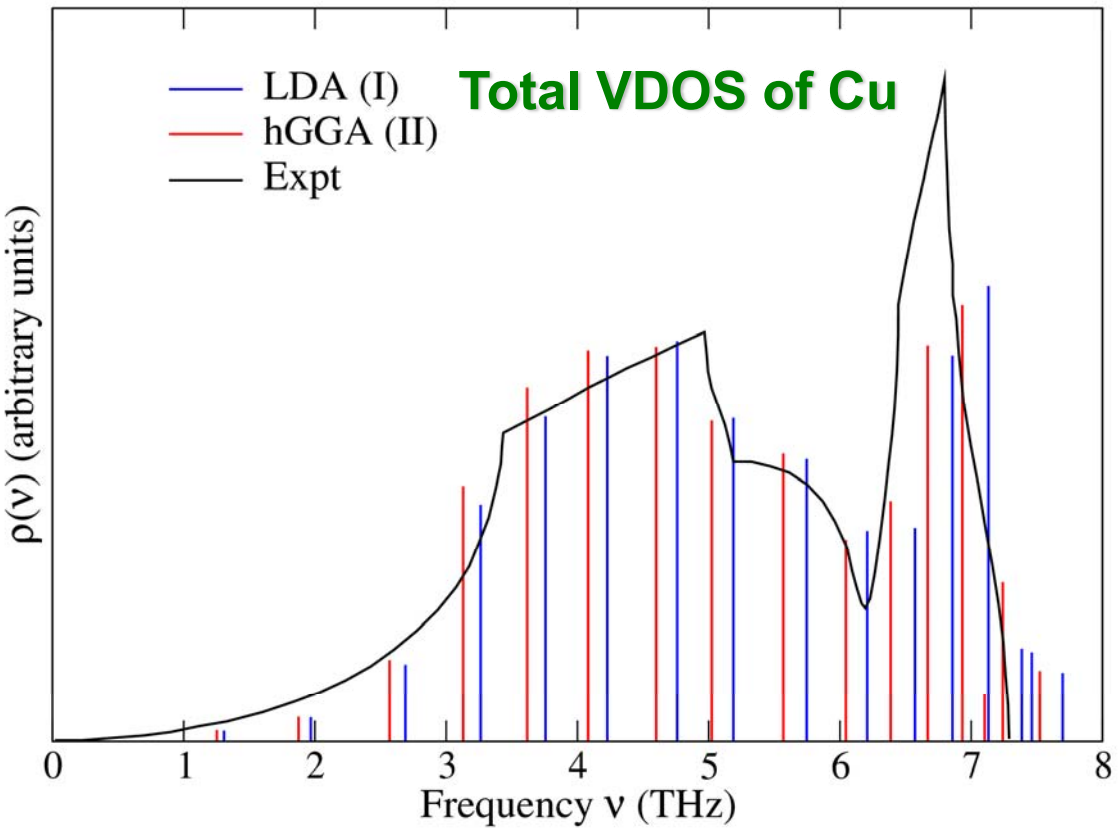
many pole VDOS

$$= \{6-\text{step Lanczos recursion}\}$$

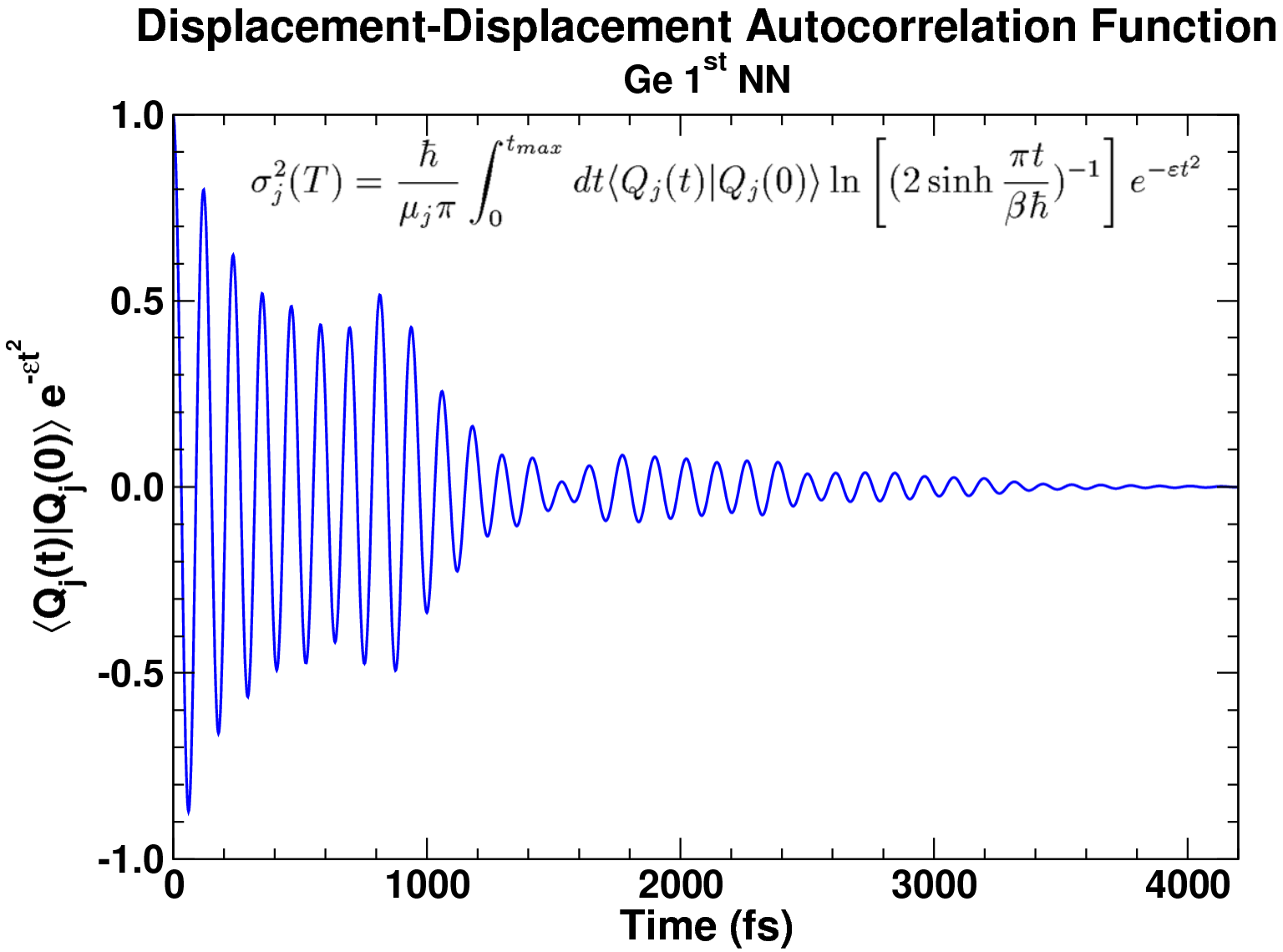
$$D_{jl\alpha,j'l'\beta} = \frac{1}{(m_j m_{j'})^{1/2}}\frac{\partial^2 E}{\partial u_{jl\alpha}\partial u_{j'l'\beta}}\left\{\begin{array}{c}\text{Dynamical Matrix}\\ \text{from ABINIT/Gaussian03}\end{array}\right.$$

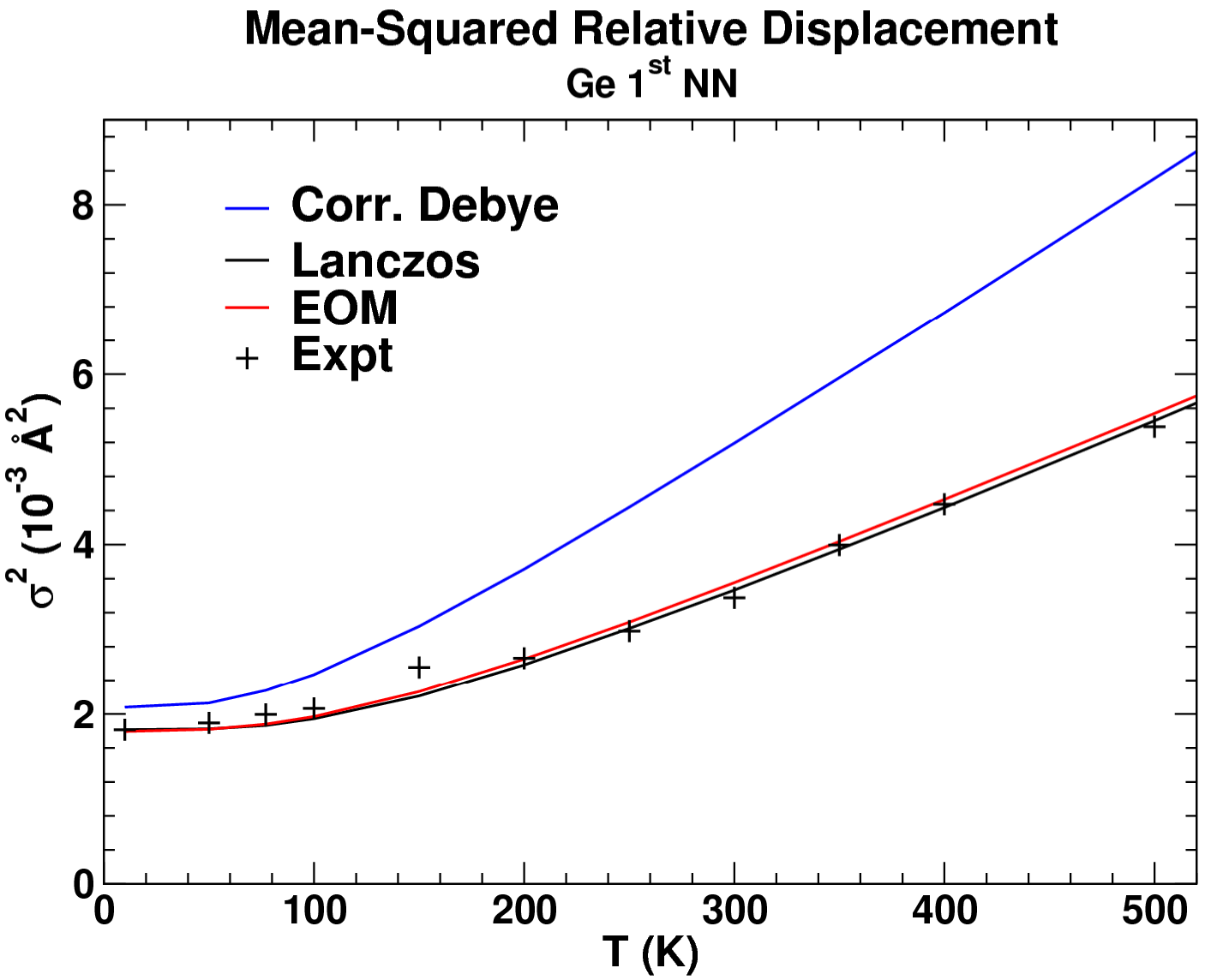
*Phys. Rev. B**76**, 014301 (2007)

A. Frequency Space: Lanczos many pole algorithm



B. Real-time (equation of motion) method




Mean-Squared Relative Displacement
Ge 1st NN
Corr. Debye
Lanczos
EOM
Expt
σ2 (10-3 Å2)
T (K)
0
2
4
6
8
0
100
200
300
400
500

ETSF- Project: F. Boscherini et al.

***Ab initio* analysis of the x-ray absorption spectrum of the myoglobin–carbon monoxide complex: Structure and vibrations**

G. Veronesi,[1,*] C. Degli Esposti Boschi,[2] L. Ferrari,[1] G. Venturoli,[3] F. Boscherini,[1,4,†] F. D. Vila,[5] and J. J. Rehr[5]
[1]*Department of Physics and CNISM, University of Bologna, viale C. Berti Pichat 6/2, I-40127 Bologna, Italy*
[2]*CNR, c/o CNISM, Department of Physics, University of Bologna, viale C. Berti Pichat 6/2, I-40127 Bologna, Italy*
[3]*Department of Biology and CNISM, University of Bologna, via Irnerio 42, I-40126 Bologna, Italy*
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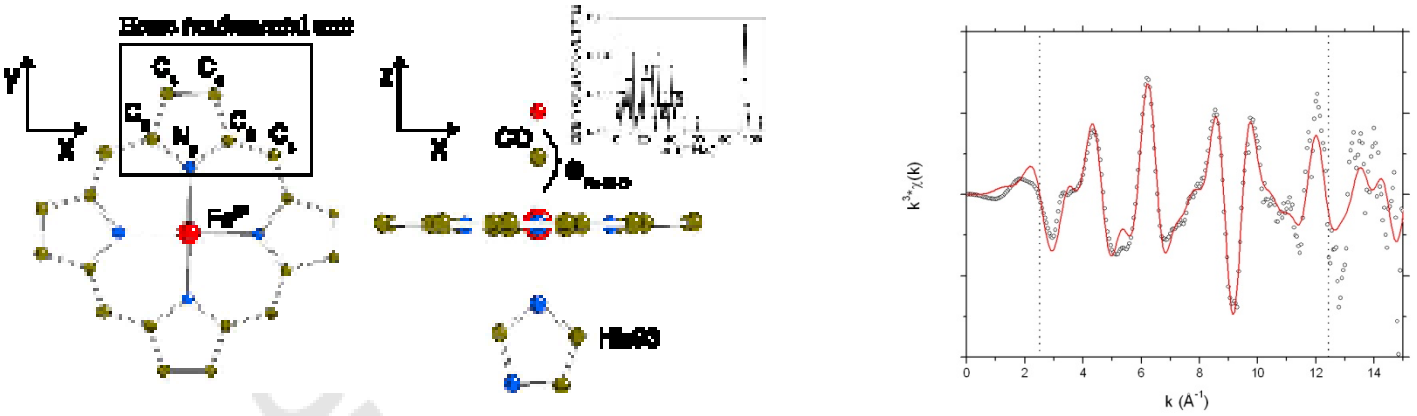
[5]*Department of Physics, University of Washington, Seattle, Washington 98195, USA*
(Received 13 April 2010)

We present a comparison between Fe *K*-edge x-ray absorption spectra of carbonmonoxy–myoglobin and its simulation based on density-functional theory determination of the structure and vibrations and spectral simulation with multiple-scattering theory. An excellent comparison is obtained for the main part of the molecular structure without any structural fitting parameters. The geometry of the CO ligand is reliably determined using a synergic approach to data analysis. The methodology underlying this approach is expected to be especially useful in similar situations in which high-resolution data for structure and vibrations are available.



G. Veronesi, C. Degli Esposti Boschi, L. Ferrari, G. Venturoli, F. Boscherini, F.D. Vila, and J.J. Rehr, Phys. Rev. B (R) **82**, 020101 (2010).

GW/BSE codes: AI2NBSE & OCEAN*

Bethe-Salpeter Equation Calculations 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 (NIST), Gaithersburg, MD 20899*

(Dated: September 29, 2010)

We present a hybrid approach for GW/Bethe-Salpeter Equation (BSE) calculations of core excitation spectra, including x-ray absorption (XAS), electron energy loss spectra (EELS), and non-resonant inelastic x-ray scattering (NRIXS). 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 BSE solver; and a many-pole GW self-energy model to account for final-state broadening and self-energy shifts. Multiplet effects are also accounted for. The approach is implemented using an interface dubbed OCEAN (Obtaining Core Excitations using ABINIT and NBSE). To demonstrate the utility of the code we present results for the K-edges in LiF as probed by XAS and NRIXS, the K-edges of KCl as probed by XAS, the Ti $L_{2,3}$-edge in $SrTiO_3$ as probed by XAS, and the Mg $L_{2,3}$-edge in MgO as probed by XAS. We compare the results to experiments and results obtained using other theoretical approaches.

PACS numbers: 78.70.Dm, 78.20.Bh, 71.15.Qe

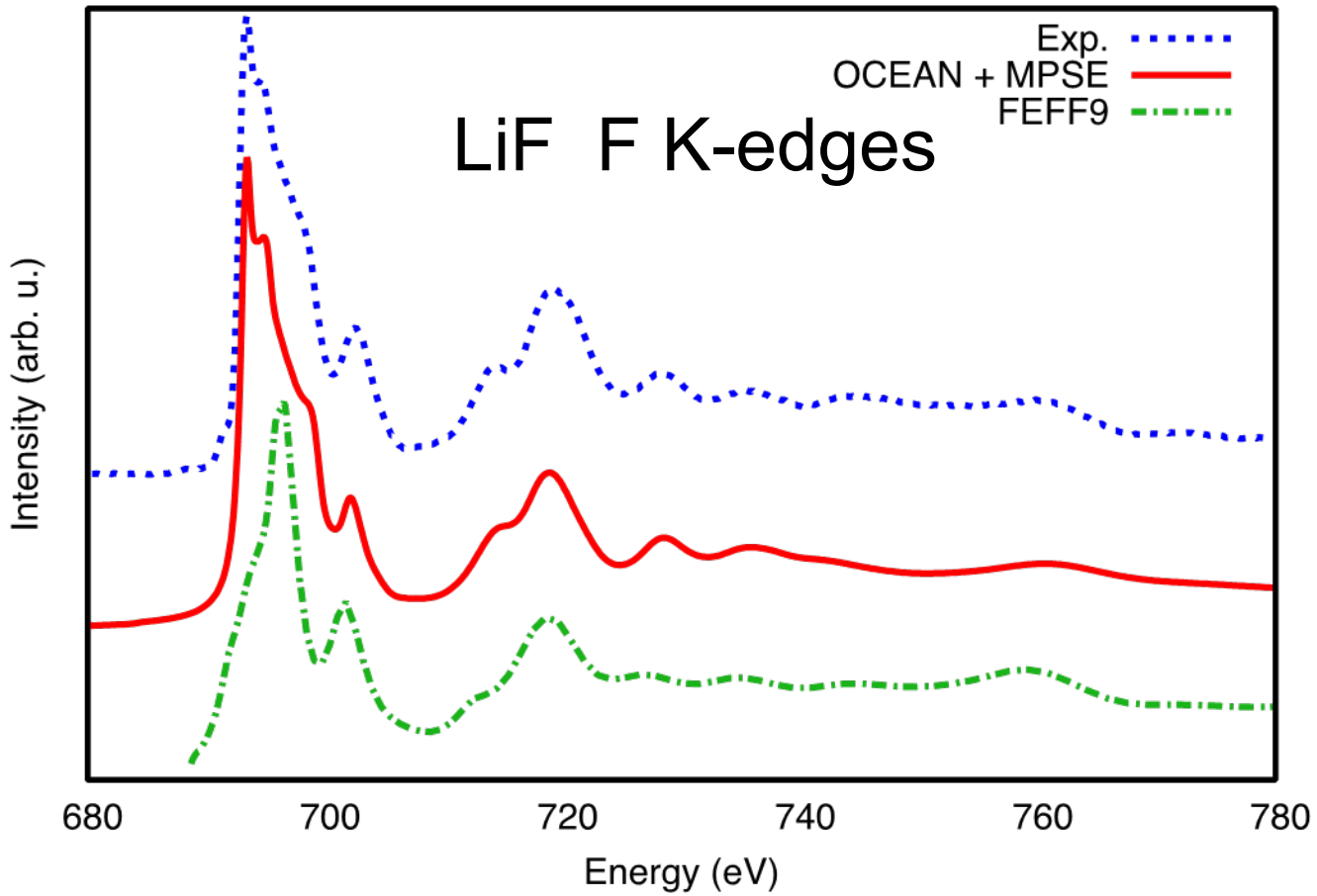
*arXiv:1010.0025 Submitted to Phys Rev B (Sept. 2010)

UNIVERSITY OF WASHINGTON + NIST

OCEAN: XAS, XES & RIXS

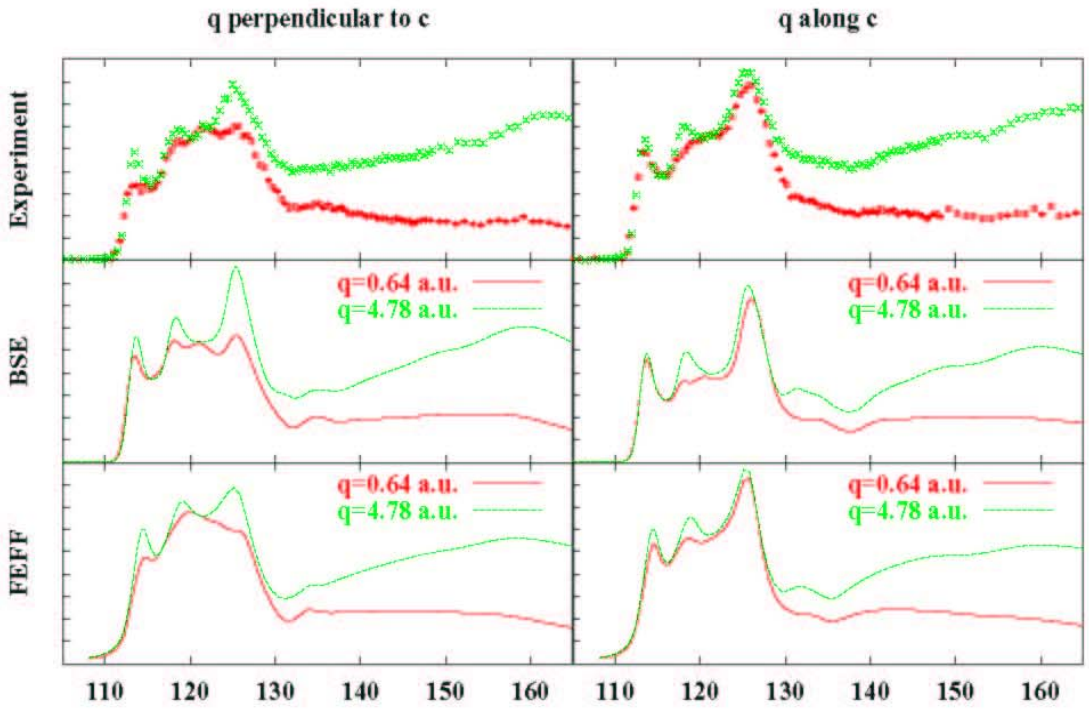
- Plane-wave, pseudo-potential DFT < ABINIT
- PAW transition matrix
- RPA screened core-hole
- Bethe-Salpeter Eq. including multiplet effects
- Many-pole GW self-energy

GW/BSE XANES


Exp.
OCEAN + MPSE
FEFF9
LiF F K-edges
Intensity (arb. u.)
680
700
720
740
760
780
Energy (eV)

Inelastic X-ray Scattering (NRIXS)

Be K-edge XRS/NRIXS: FEFF vs BSE vs Expt



Expt

BSE*

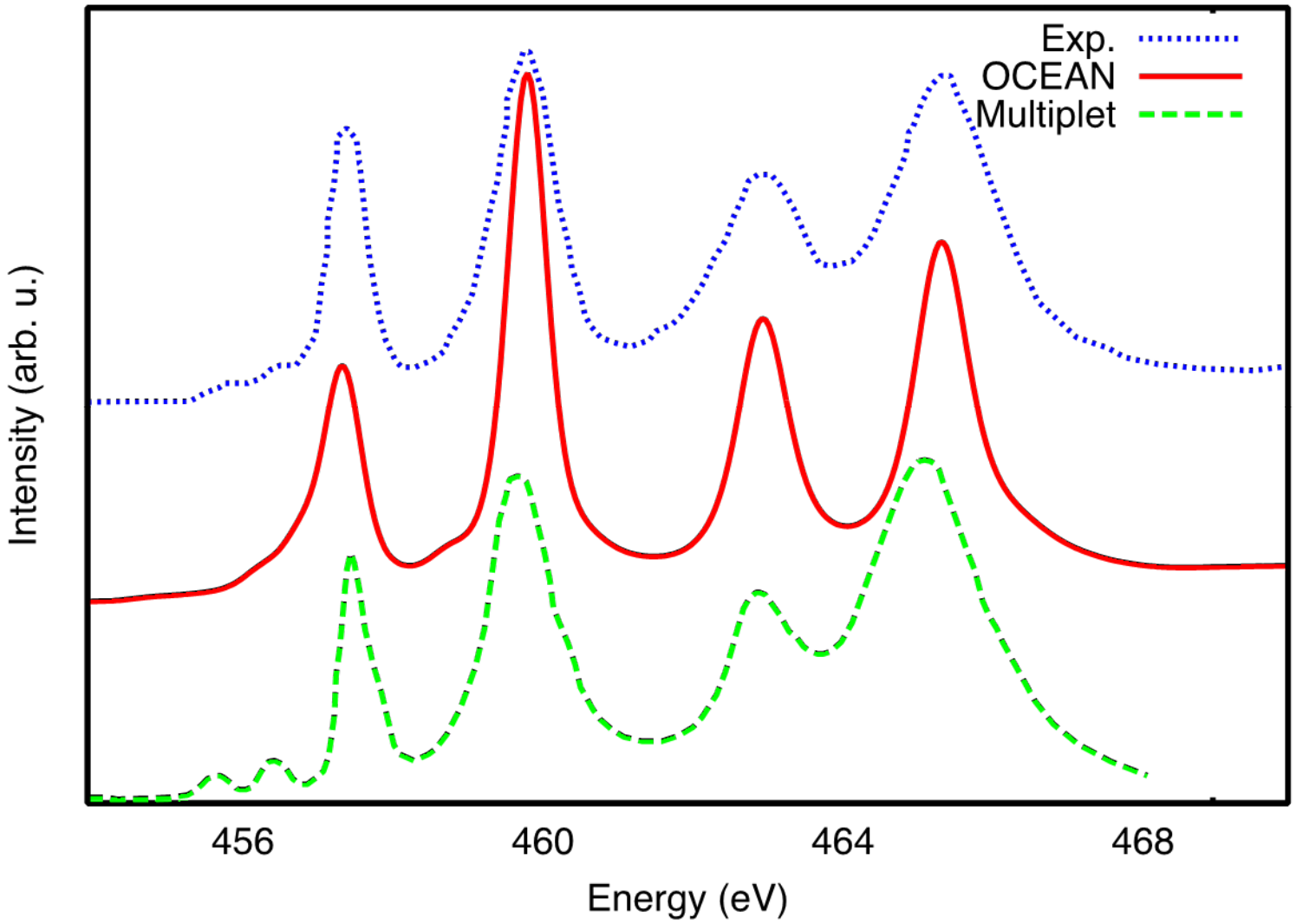
$f_{eff}(\boldsymbol{q})$

Experiment: C. Sternemann et al., Phys. Rev. B **68**, 035111 (2003).

* BSE: J. A. Soininen and E. L. Shirley, Phys. Rev. B **64**, 165112 (2001).

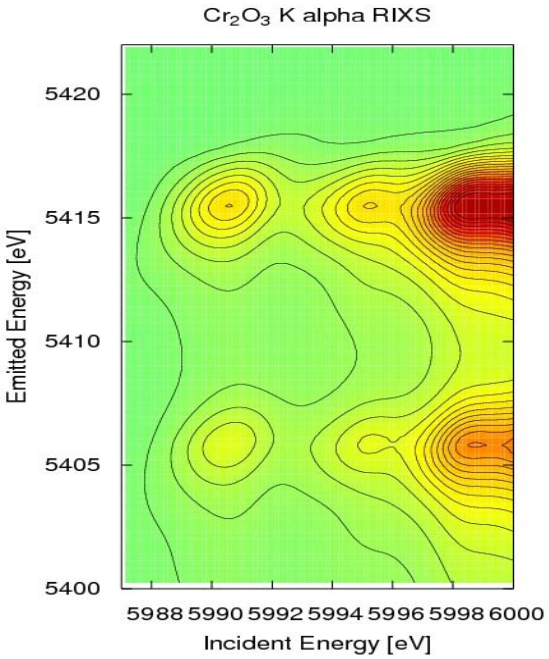
L_{23} Multiplets < OCEAN

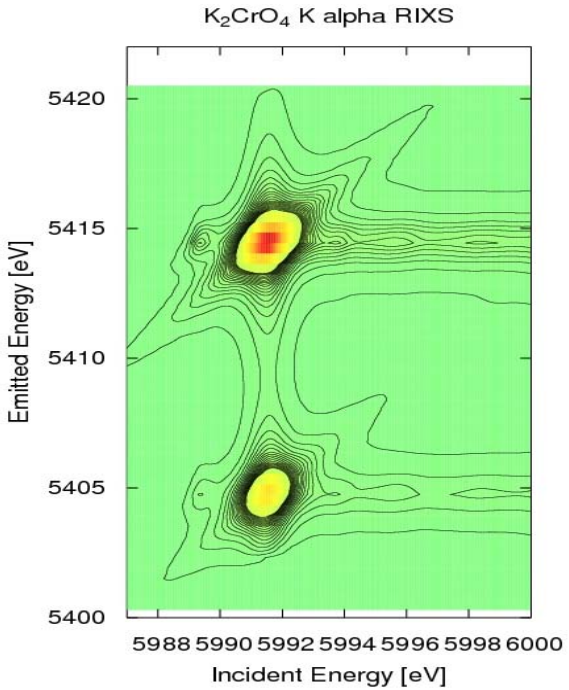
$SrTiO_3$ Ti L_{23}-edge



Developmental – RIXS*

$$\frac{d^2\sigma}{d\Omega d\omega} \propto \frac{\omega}{\Omega} \int d\omega_1 d\omega_2 \, A_{\text{eff}}(\Omega - \omega + \omega_1, \omega_2) \frac{a(\omega_1 - \tilde{E}) \mu(\Omega - \omega + \omega_1 - \omega_2)}{|\omega + \omega_2 + E' - \omega_1 - i\Gamma_b|^2}. \quad (1)$$





*J. Kas & JJR

Acknowledgments

Rehr Group

- J. Kas (UW)
- F. Vila (UW)
- K. Jorissen (UW)
- M. Prange (ORNL,UW)
- A. Sorini (SSRL/SLAC,UW)
- Y. Takimoto (ISSP,UW)

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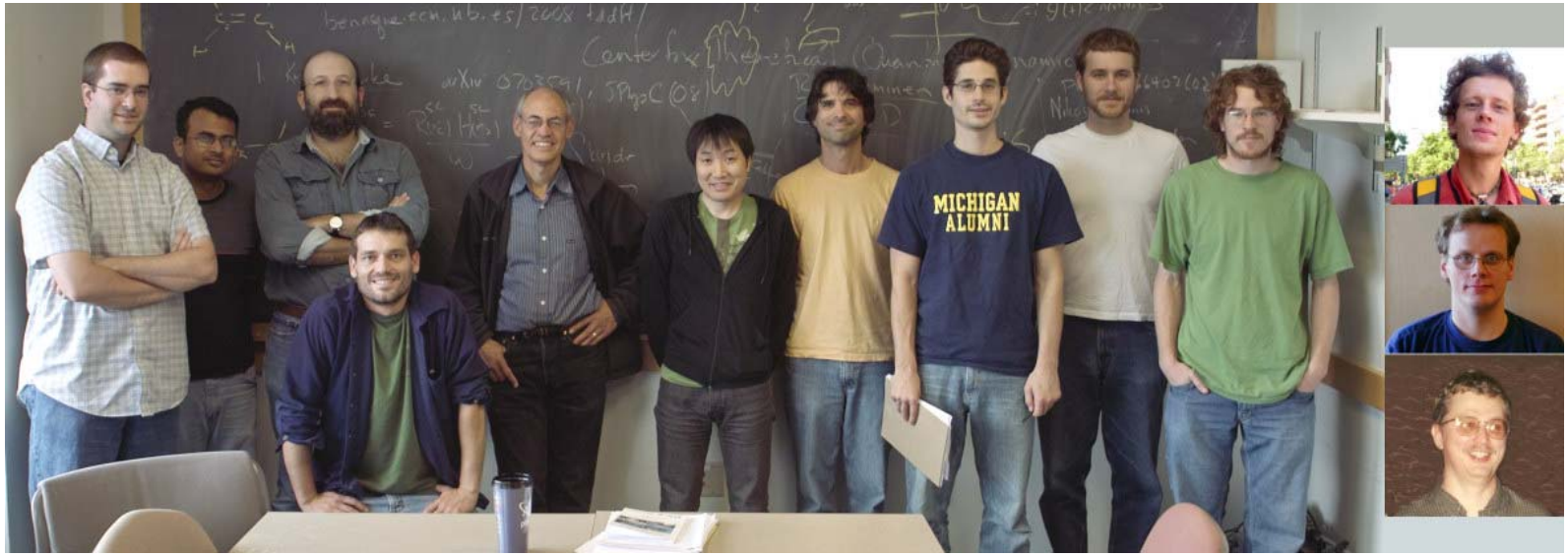
R.C. Albers (Los Alamos))
E. Shirley (NIST)
A. Soininen (U. Helsinki)



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