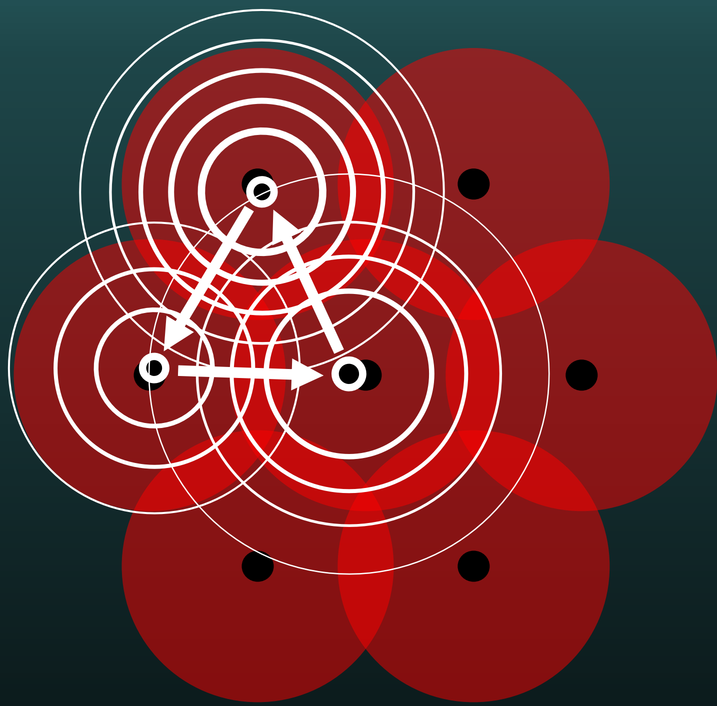
M&M Conference Columbus, OH 24-28 June, 2016

Theory and Parameter Free Calculations of EELS and X-ray Spectra



J.J. Rehr[1], J. J. Kas[1], K. Jorissen[2], and F. Vila[1]

[1]Department of Physics, University of Washington, [2]Amazon Web Services
Seattle, WA

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Theory and Parameter Free Calculations of EELS and X-ray Spectra

- **GOAL**: Ab initio theory & interpretation of core level EELS & XAS

IR $\rightarrow$ VIS $\rightarrow$ UV $\rightarrow$ X-ray

- **TALK**: Advanced Codes & Workflow tools

Theory: FEFF/Green's function + OCEAN/BSE

If I can’t calculate it,

I don’t understand it.

(Often attributed to R. P. Feynman)

Challenge:

Full spectrum electron- and X-ray spectra

DEUTSCHES ELEKTRONEN-SYNCHROTRON DESY

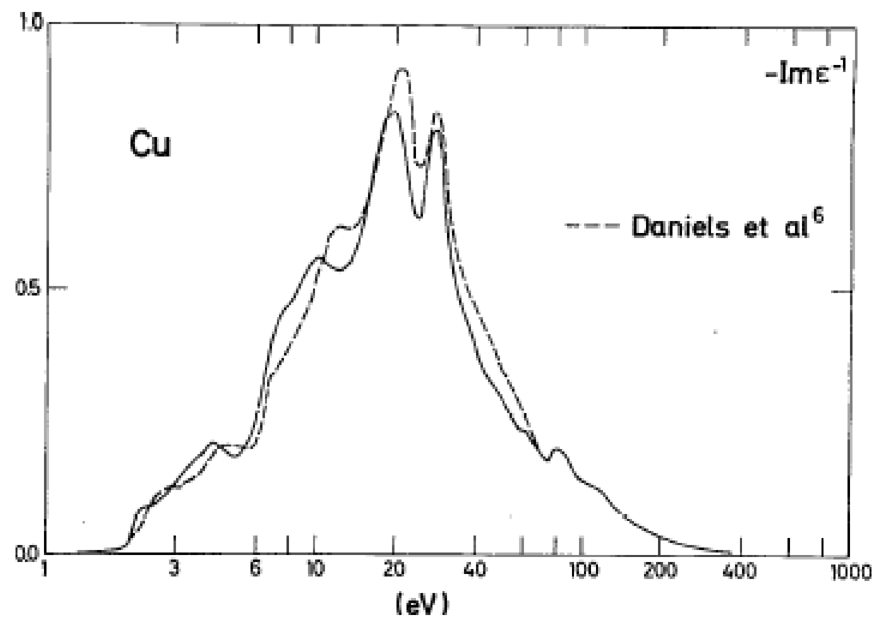
DESY SR-74/7
May 1974

May 1974

Optical Constants from the Far Infrared to the X-Ray Region:
Mg, Al, Cu, Ag, Au, Bi, C, and Al_2O_3

by

H.-J. Hagemann, W. Gudat, and C. Kunz



Cu loss function

Challenge:

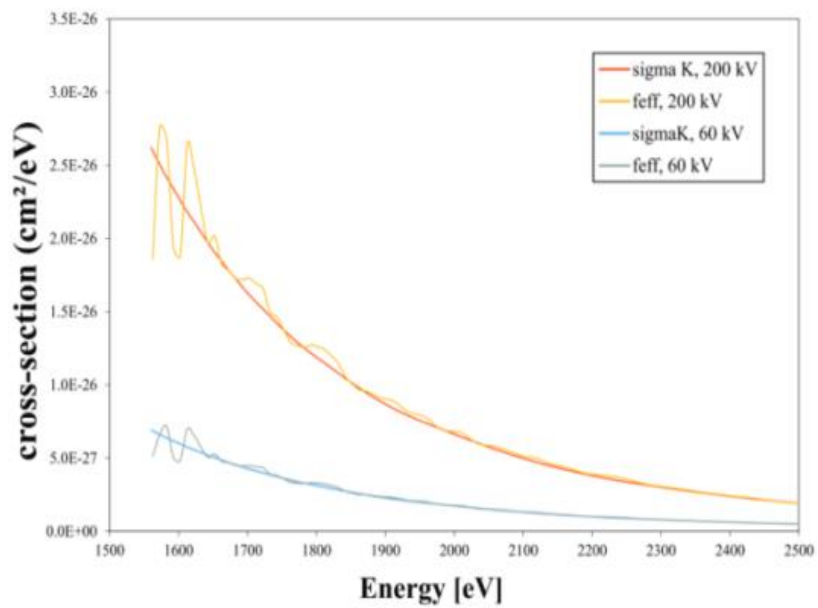
Improve on Hydrogenic model of EELS*

Ultramicroscopy 4 (1979) 169–179

K-SHELL IONIZATION CROSS-SECTIONS FOR USE IN MICROANALYSIS

R.F. EGERTON
Physics Department, University of Alberta, Edmonton, Canada, T6G 2J1

Received 17 October 1978; in revised form 21 November 1978



L. Konrad *et al.*, MCM2015

*L. Pauling, Proc. Roy Soc. A London 114, 181 (1927)

~ 35 years later: *Ab initio* optical constants*

PHYSICAL REVIEW B 80, 155110 (2009)

Real space calculation of optical constants from optical to x-ray frequencies

M. P. Prange,[1] J. J. Rehr,[1] G. Rivas,[2] J. J. Kas,[1] and John W. Lawson[3]
[1]*Department of Physics, University of Washington, Seattle, Washington 98195, USA*
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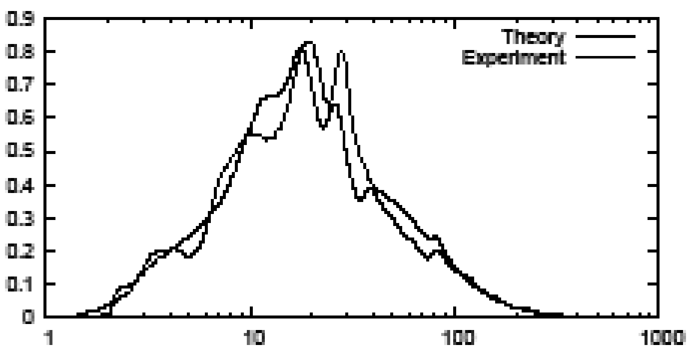
[3]*NASA Ames Research Center, Mail Stop 229-1, Moffett Field, California 94035, USA*
(Received 17 October 2008; revised manuscript received 20 July 2009; published 5 October 2009)



Cu loss function

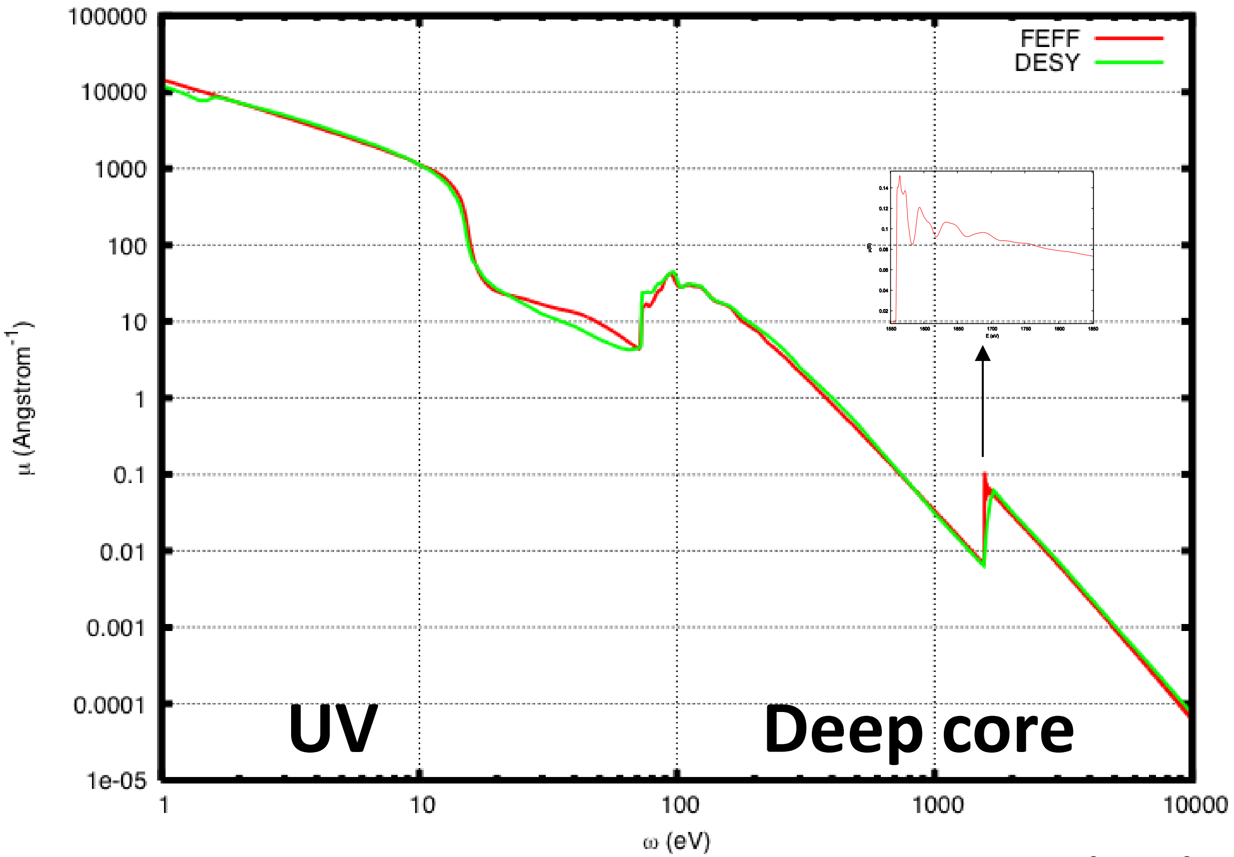
ω (eV)	ϵ_1	ϵ_2	n
.380000E+01	-.966246E+00	.492160E+01	.574110E+00
.390000E+01	-.874007E+00	.488653E+01	.583407E+00
.400000E+01	-.792192E+00	.485292E+01	.591411E+00
.410000E+01	-.725534E+00	.482128E+01	.597428E+00
.420000E+01	-.673854E+00	.479077E+01	.601251E+00
.430000E+01	-.631718E+00	.475174E+01	.602230E+00
.450000E+01	-.564064E+00	.467822E+01	.602254E+00
.475000E+01	-.527798E+00	.459519E+01	.595553E+00
.500000E+01	-.570524E+00	.447607E+01	.569409E+00
.550000E+01	-.597635E+00	.414935E+01	.511810E+00
.600000E+01	-.627088E+00	.377460E+01	.443231E+00

*http://feffproject.org/feff/desy

Optical constants

Dielectric function	$\epsilon = \epsilon_1 + i\epsilon_2$
Energy Loss (EELS)	$-\mathrm{Im}\,\epsilon^{-1}$
Absorption coefficient	μ
Refractive index	$n + i\,k$
Reflectivity	R
X-ray scattering factors	$f = f_0 + f_1 + i\,f_2$
Hamaker constants	$\epsilon(i\omega)$

Broad Spectrum Calculations:
Theory vs. Expt.



Photon energy or Energy Loss (eV)

http://feffproject.org/feff/desy

EELS Theory *a lá* Fermi's golden rule

$$\frac{\partial^2\sigma}{\partial E\partial\Omega}(E,\boldsymbol{Q}) = \xi\sum_{I,F}\frac{k_F}{k_I}|\langle I\; k_I|V|k_F F\rangle|^2\,\delta(E_I - E_F) \approx S(q,\omega)$$

$V = 1/|r - r'|$ Coulomb interaction

Dynamic Structure Factor ~ Loss function

$$S(q,\omega) \sim Im\,\epsilon^{-1}(\boldsymbol{q},\omega)$$

Computational bottleneck:

Too many states!

All state k_F, k_I (probe) and F, I (sample) contribute

Paradigm shift: Real-space Green's Function Approach

Golden rule *via* wavefunctions

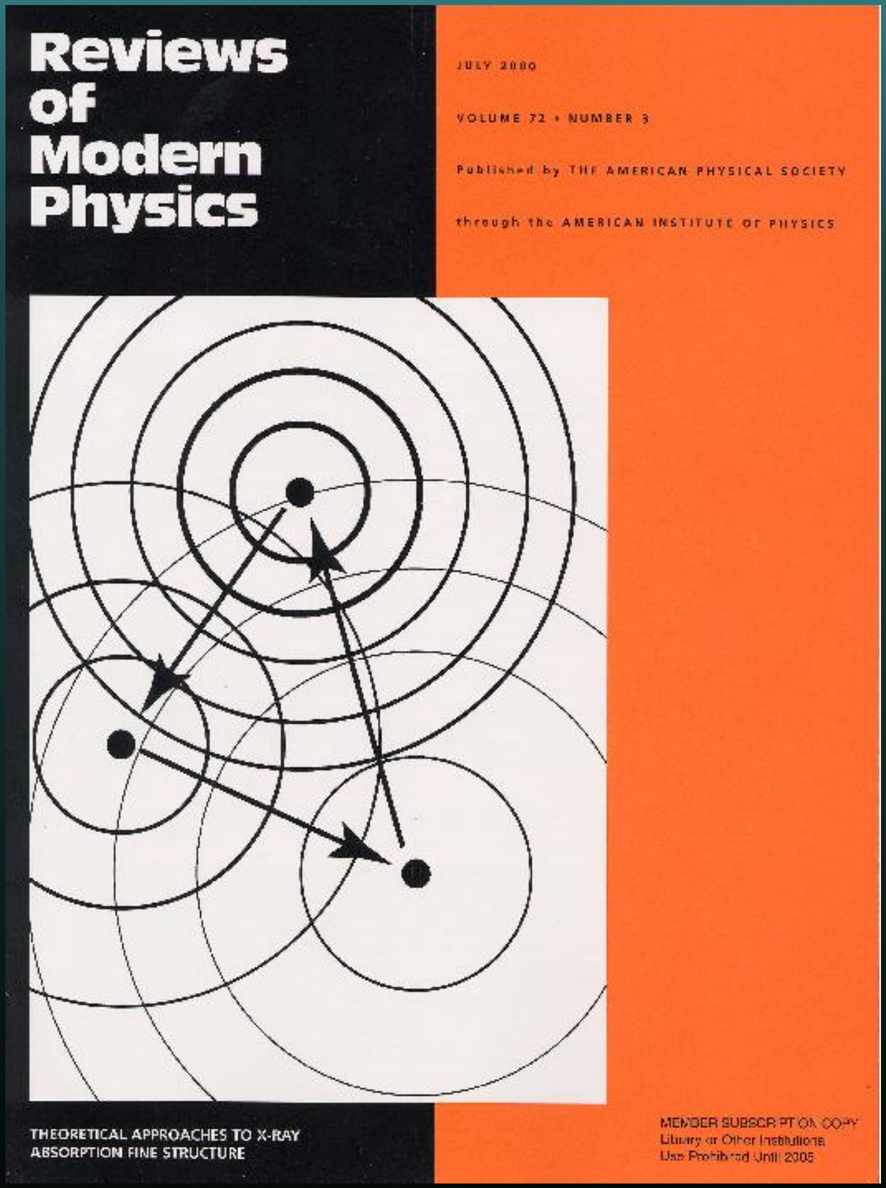
$$\mu(E) \sim \sum_f |\langle i|\hat{\epsilon}\cdot\mathbf{r}|f\rangle|^2\, \delta(E - E_f)$$

Golden rule via Green's functions: $G = 1/(E - h - \Sigma)$

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

Efficient:

No sums over final states!



XAS & EELS

Real-space Green's function theory

J. J. Rehr & R.C. Albers,
Rev. Mod. Phys. **72**, 621 (2000)

http://feffproject.org/feff/desy

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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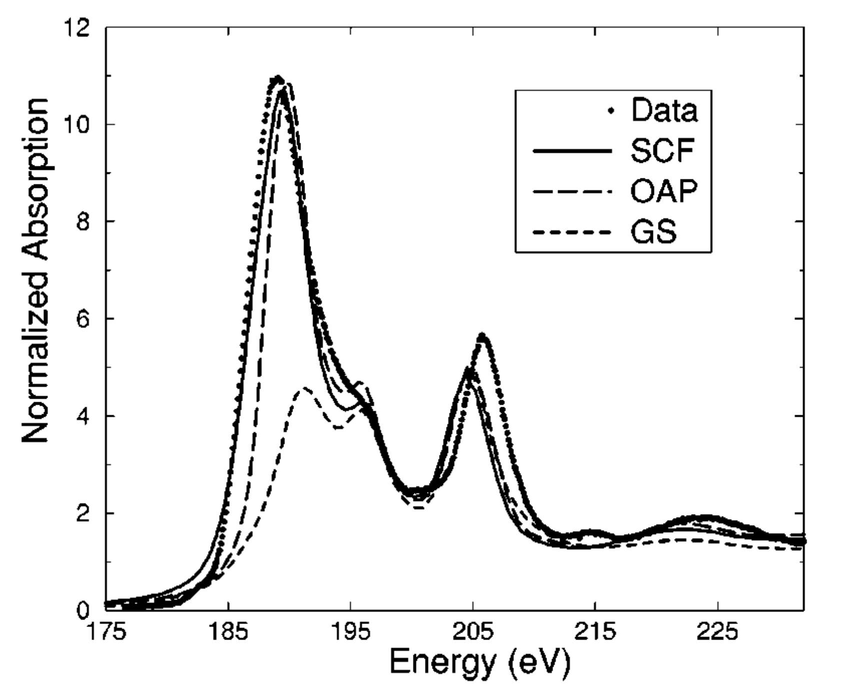
FEFF8

Core-hole
SCF potentials
Self-energy
DW factors
Efficient Core level spectra:
EELS, XAS, XES



89 atom BN cluster

Parallel (MPI) FEFF

PHYSICAL REVIEW B, VOLUME 65, 104107

Parallel calculation of electron multiple scattering using Lanczos algorithms

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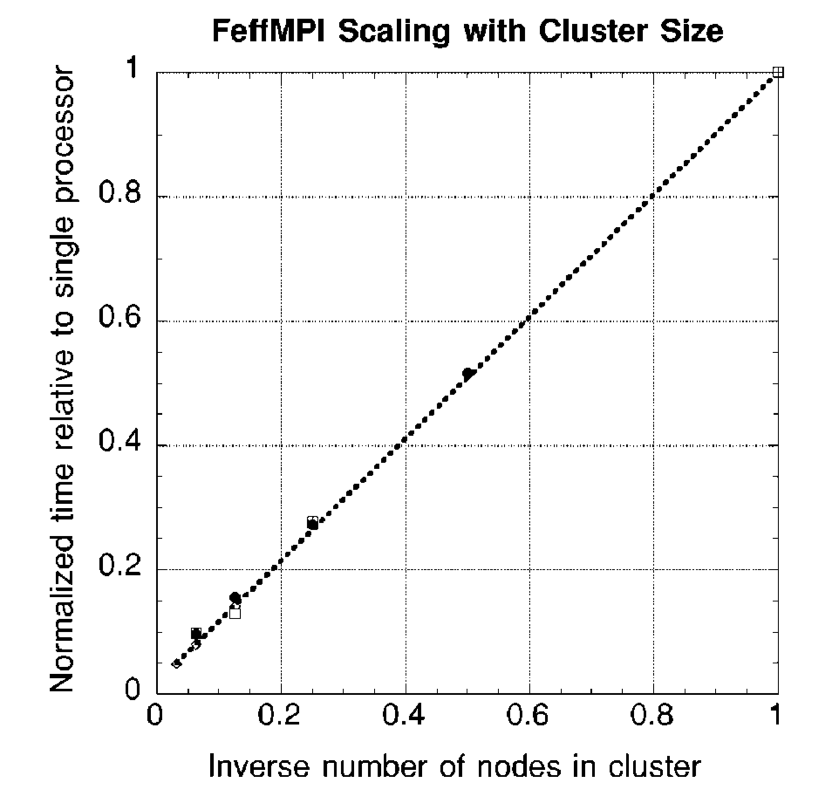
[1]*Department of Physics, University of Washington, Seattle, Washington 98195*
[2]*National Institute of Standards and Technology, Gaithersburg, Maryland 20899*



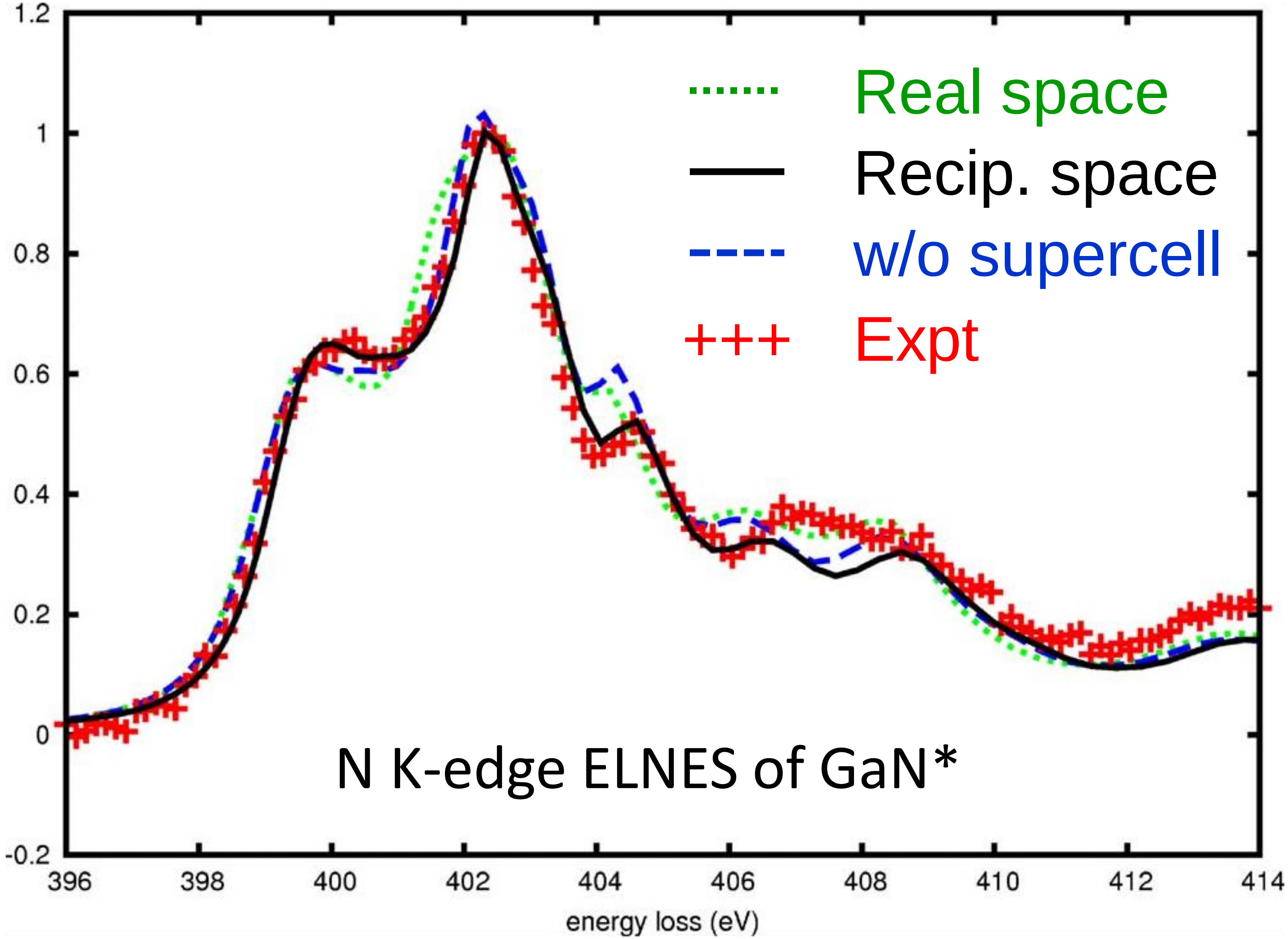
$$\mu(E) \sim -\frac{1}{\pi}\,\mathrm{Im}\langle i|\hat{\epsilon}\cdot\mathbf{r}' G(\mathbf{r}',\mathbf{r},E)\hat{\epsilon}\cdot\mathbf{r}|i\rangle$$

MPI: "Natural parallelization"
Each proc. does a few energies

Needed for state-of-the-art XANES simulations

EELS in FEFF9: Impurity Green's function

EELS in periodic systems w/o supercell*



*K. Jorissen & J. J. Rehr Phys. Rev. B 81, 245124 (2010)

Relativistic corrections to EELS*

Relativistic Coulomb interaction

$$\frac{\partial^2\sigma}{\partial E\partial\Omega}(E,\boldsymbol{Q}) = \xi\frac{k'}{k}\frac{1}{(Q^2 - E/\hbar c)^2}\sum_{I,F}|\langle I\,|\boldsymbol{r}\cdot\boldsymbol{Q}'|F\rangle|^2\,\delta(E_I - E_F - E)$$

$$\frac{\partial^2\sigma}{\partial E\partial\Omega}(E,\boldsymbol{Q}) = f(Q)\sum_{i,j=1}^{3} Q'_i Q'_j \sigma_{ij}(E)$$

where $\boldsymbol{Q}' = \boldsymbol{Q} - Q_z\beta^2\boldsymbol{e}_z$

and the abs. tensor is $\sigma_{ij}(E) = \xi' E\sum_{I,F}\langle F|r_i|I\rangle\langle I|r_j|F\rangle\,\delta(E_I - E_F - E)$

*P. Schattschneider *et al.*, Phys. Rev. B 2005

Relativistic EELS

PHYSICAL REVIEW B **81**, 155108 (2010)

Multiple scattering calculations of relativistic electron energy loss spectra

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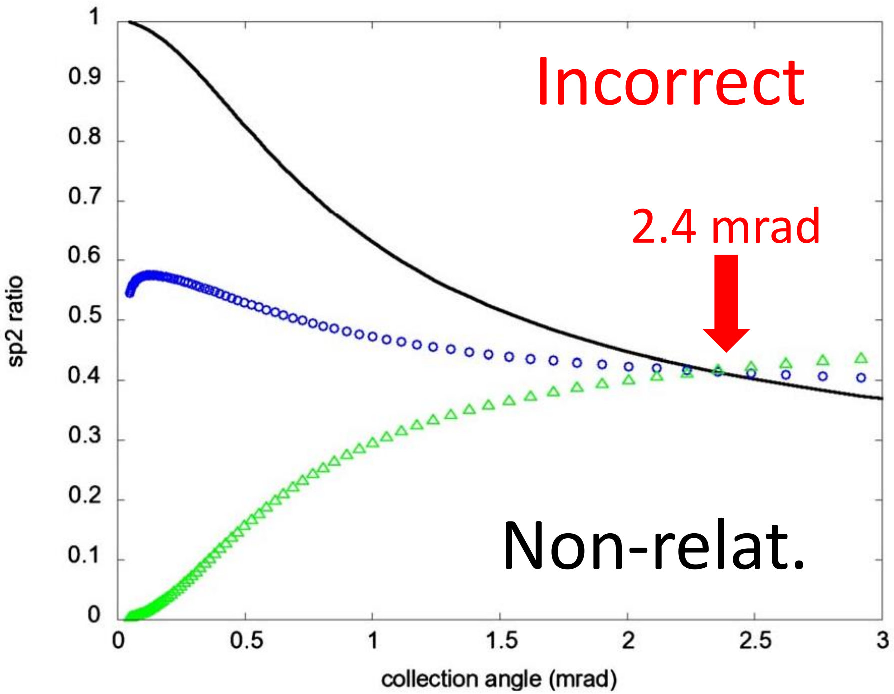
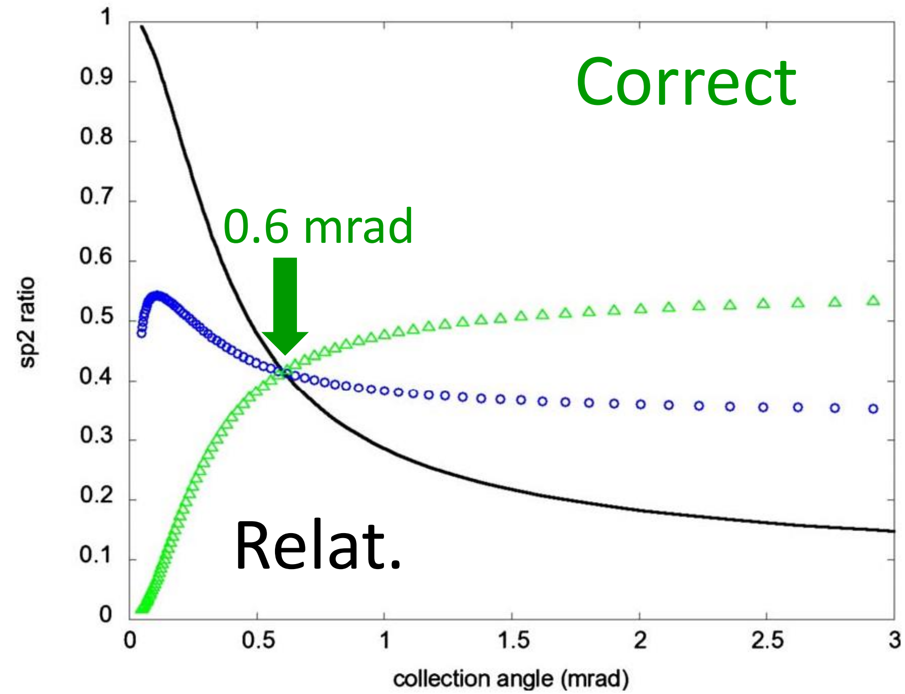
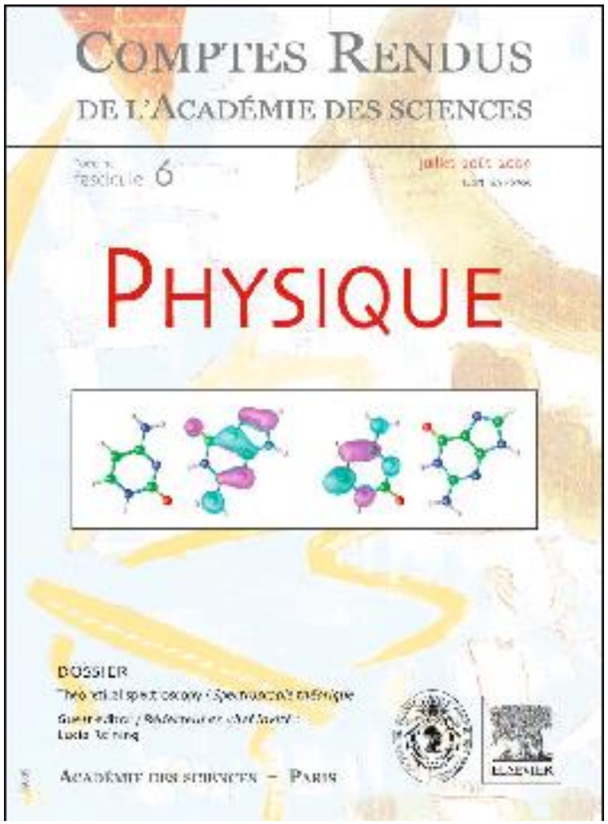
(Received 26 October 2009; revised manuscript received 30 March 2010; published 13 April 2010)





Relativistic Magic Angle in FEFF9 agrees with expt.

FEFF9: Advanced methods



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Available online at www.sciencedirect.com
ScienceDirect

C. R. Physique 10 (2009) 548–559

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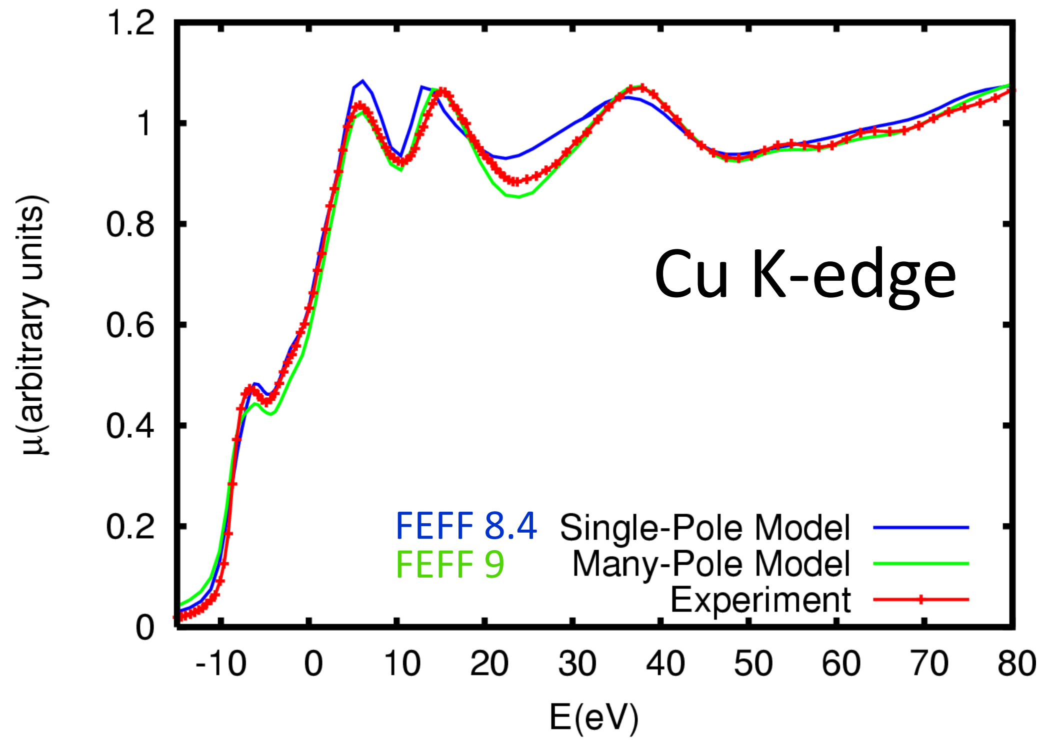
http://france.elsevier.com/direct/COMREN/

Theoretical spectroscopy / Spectroscopie théorique

Ab initio theory and calculations of X-ray spectra

John J. Rehr *, Joshua J. Kas, Micah P. Prange, Adam P. Sorini, Yoshinari Takimoto, Fernando Vila



FEFF9: Advanced methods

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

Parameter-free calculations of X-ray spectra with FEFF9

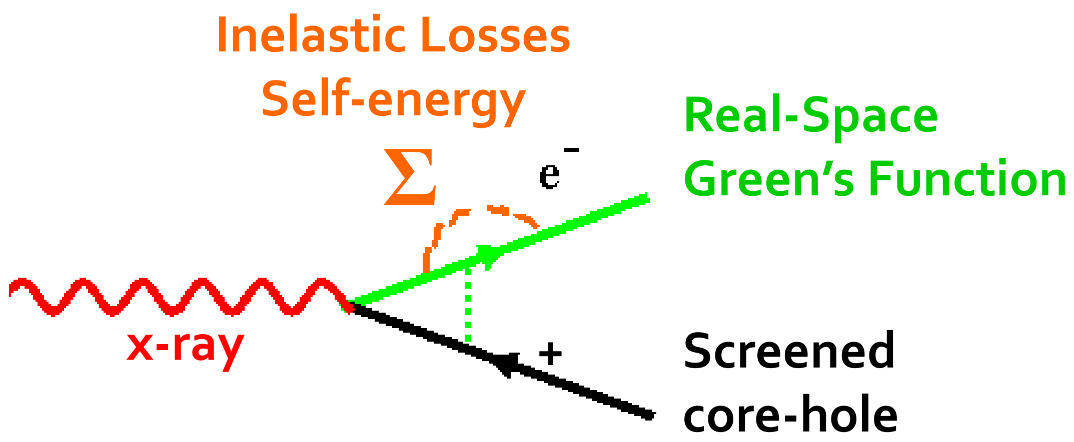
John J. Rehr,*[a] Joshua J. Kas,[a] Fernando D. Vila,[a] Micah P. Prange[bc] and Kevin Jorissen[a]

Received 15th December 2009, Accepted 27th April 2010
First published as an Advance Article on the web 6th May 2010
DOI: 10.1039/b926434e

 Phys. Chem. Chem. Phys., 2010, **12**, 5503–5513 | 5503

Ab initio:
- Mean free paths
- Self-energies
- Debye-Waller factors

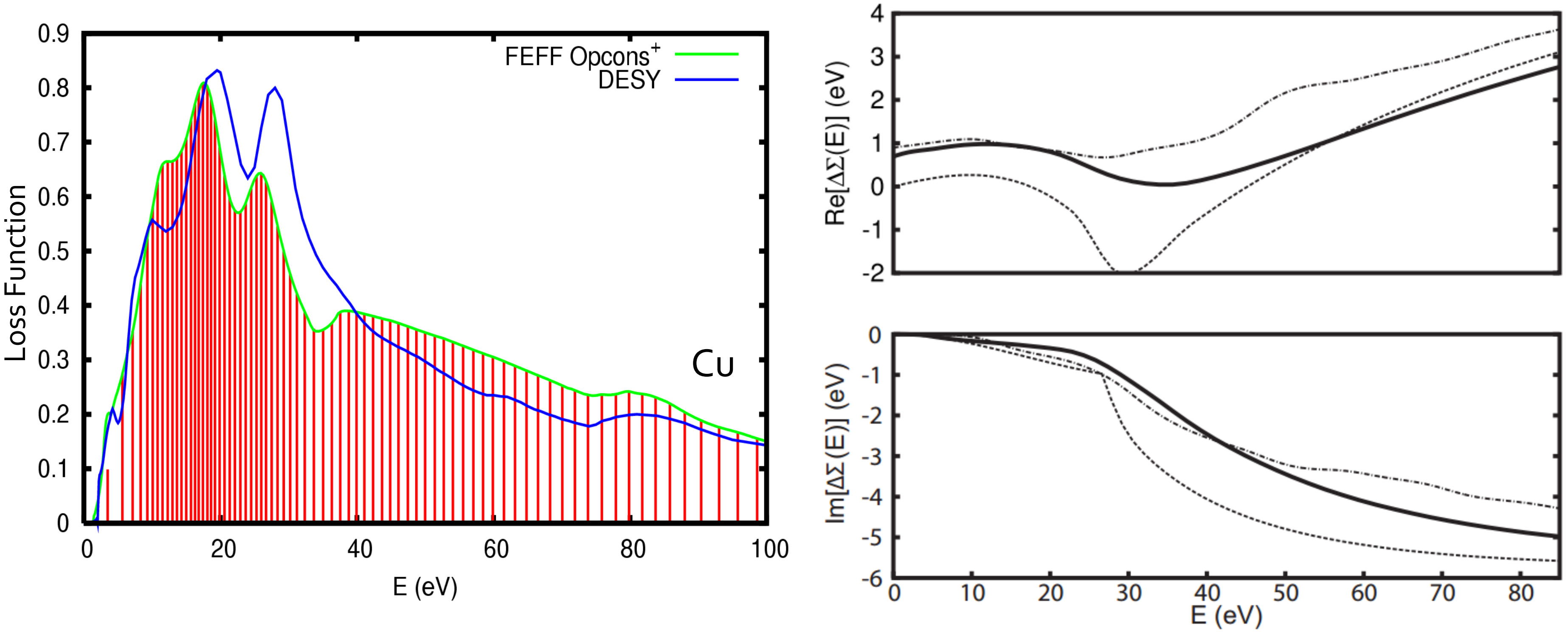
RPA core-hole screening
Multi-electron excitations



Many-Pole Self-Energy (MPSE)

Extension of Hedin-Lundqvist (HL) plasmon-pole (pp) GW SE model

Σ approximated as sum of PP models matched to loss function

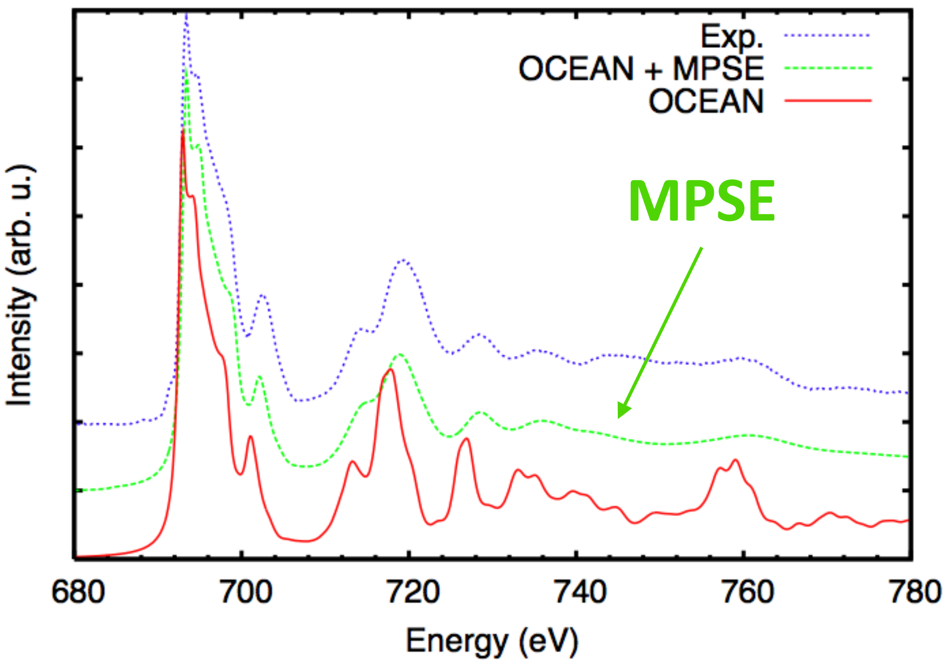


Many-pole (full) much better than HL (dashed) *vs* better theory (dot-dashed)

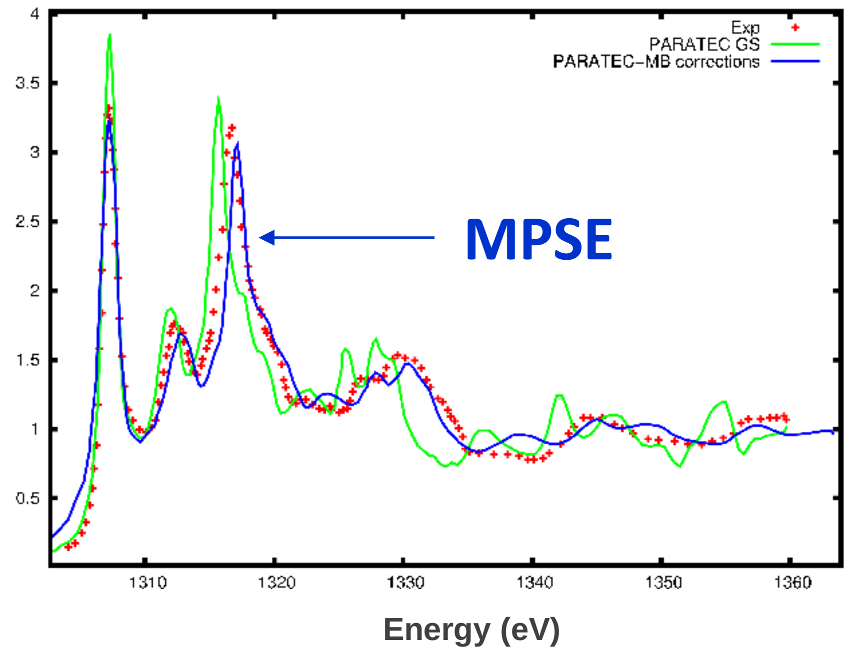
J. J. Kas et al., PRB 76, 195116 (2007)

MPSE corrections in BSE and DFT*

LiF (BSE+MPSE)



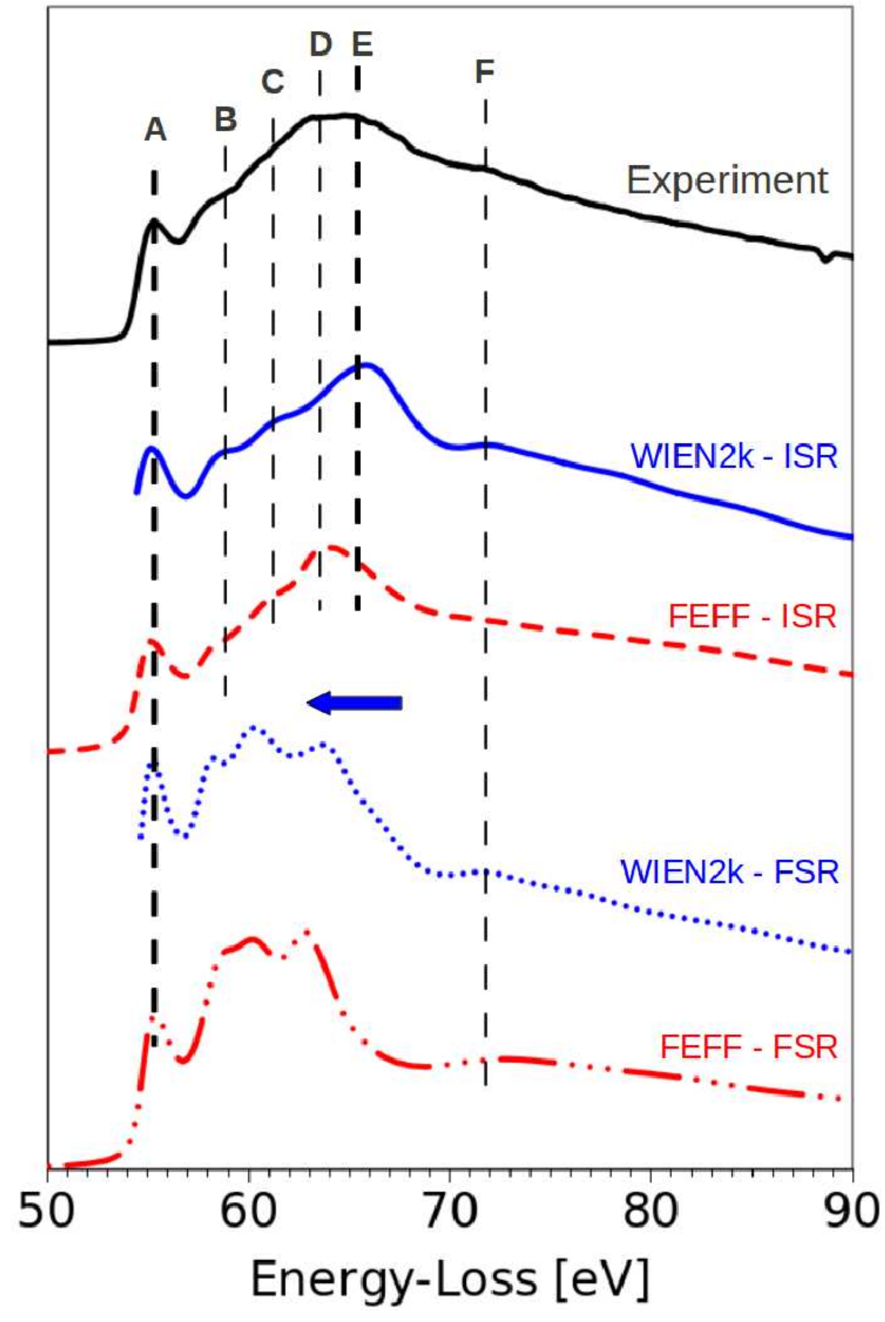
$MgAl_2O_4$ (ΔSCF-DFT+MPSE)



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

Question: Can we improve the theory?

V. Mauchamp, M. Jaouen, JJR, and J. J. Kas, U. Poiters, Preprint (2010)

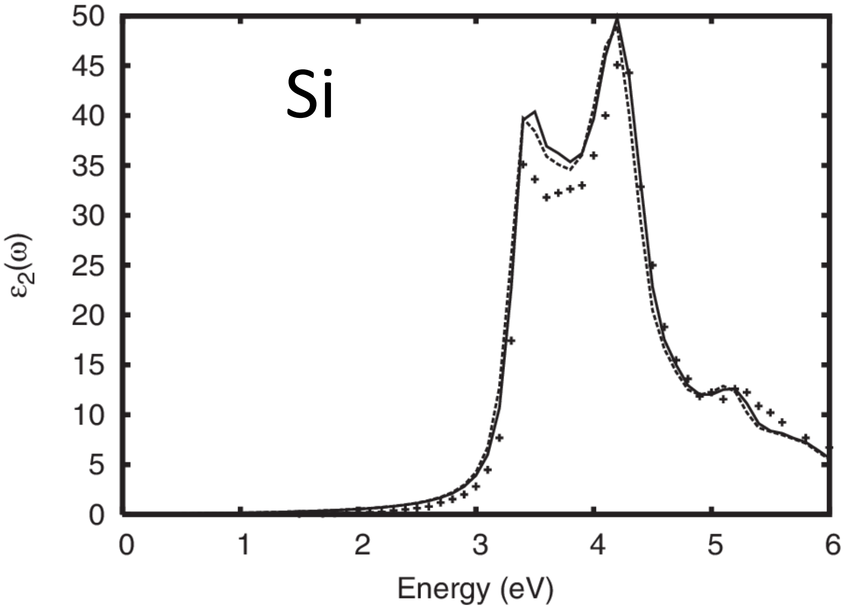


Answer: GW/BSE
Ab initio optical & low-loss spectra

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*



AI2NBSE:
Abinit+NIST BSE+UW MPSE

Plane-wave, pseudo-potential GW/BSE code

UW + NIST collaboration

Ab initio GW/BSE core-spectra:
ELNES & XANES

PHYSICAL REVIEW B 83, 115106 (2011)

Bethe-Salpeter equation calculations of core excitation spectra

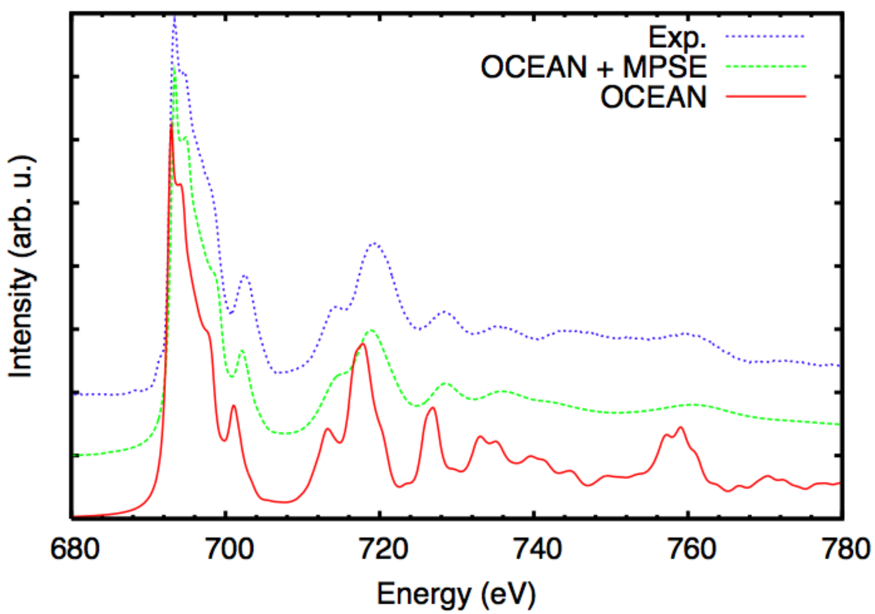
J. Vinson, J. J. Rehr, and J. J. Kas
Department of Physics, University of Washington, Seattle, Washington 98195, USA

E. L. Shirley
National Institute of Standards and Technology (NIST), Gaithersburg, Maryland 20899, USA
(Received 29 September 2010; published 4 March 2011)

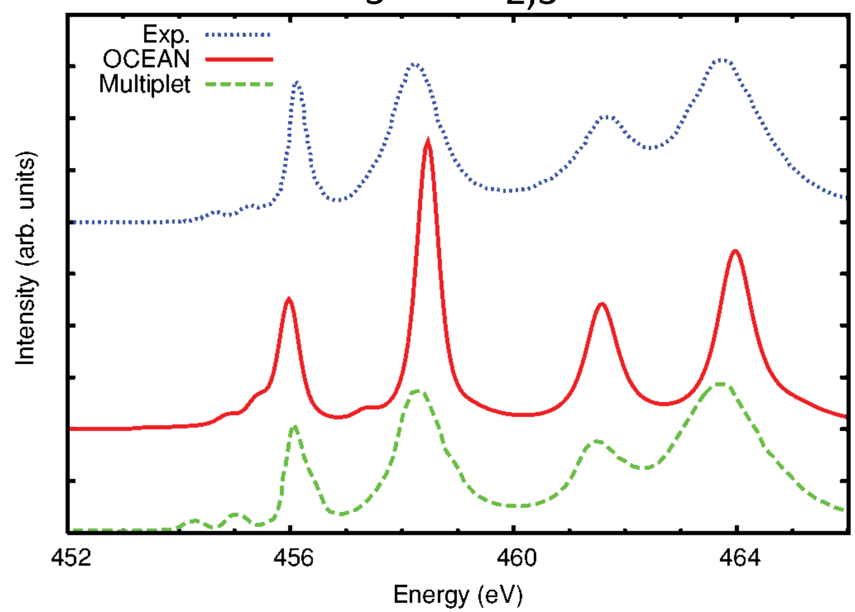
OCEAN: Obtaining Core Excitations from Abinit and NBSE

UW + NIST Collaboration

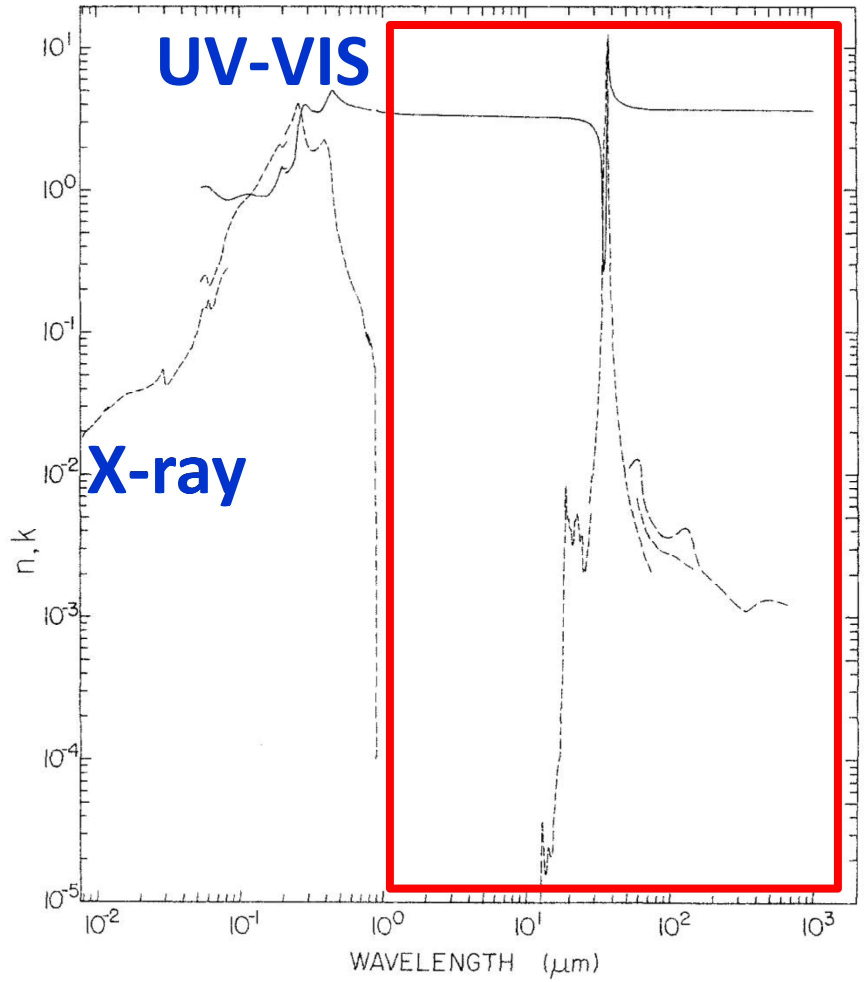
LiF: F K edge



$SrTiO_3$: Ti $L_{2,3}$ edge



Are we there yet?
Optical constants: THz to X-ray



Challenge:

Efficient phonon spectra

Can we compute vibrational properties ab initio?

Ab initio Debye Waller Factors: $\mathrm{e}^{-2\sigma_R^2 k^2}$

Projected Vibrational DOS: Use efficient pole model

$$\rho_R(\omega) = -\frac{2\omega}{\pi}\,\mathrm{Im}\left\langle 0\left|\frac{1}{\omega^2 - \mathbf{D} + i\varepsilon}\right|0\right\rangle \cong \sum_{v=1}^{N} w_v \delta(\omega - \omega_v)$$

EXAFS MSRDs:

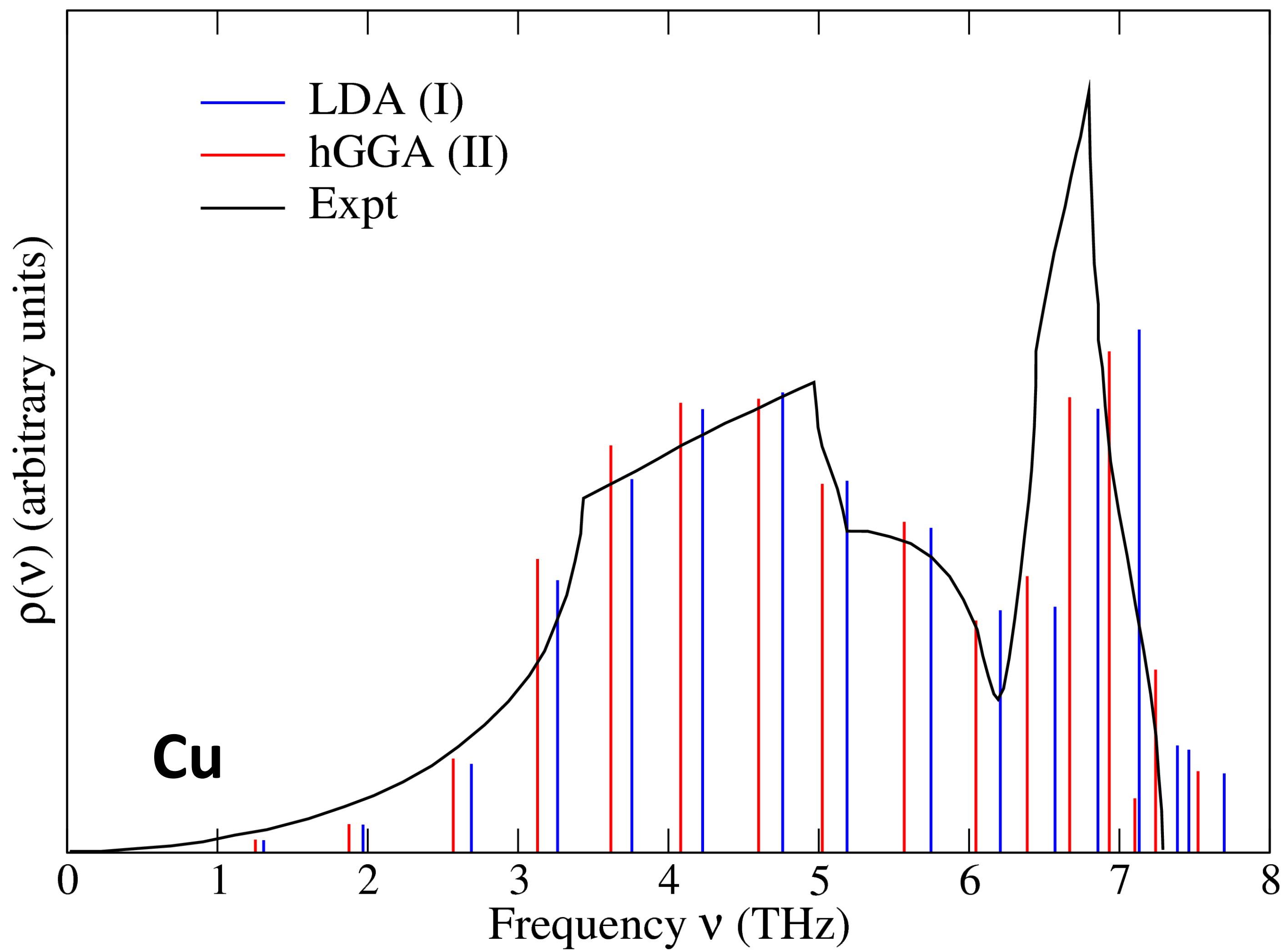
$$\sigma_R^2(T) = \frac{\hbar}{2\mu_R}\int_0^\infty \frac{1}{\omega}\coth\left(\frac{\beta\hbar\omega}{2}\right)\rho_R(\omega)\,d\omega$$

Helmholtz Free Energy:

$$F(T) = E + \, k_B T \sum_i^{N_{coor}} \int_0^\infty \ln\left[2\sinh\left(\frac{\beta\hbar\omega}{2}\right)\right]\,\rho_i(\omega)\,d\omega$$

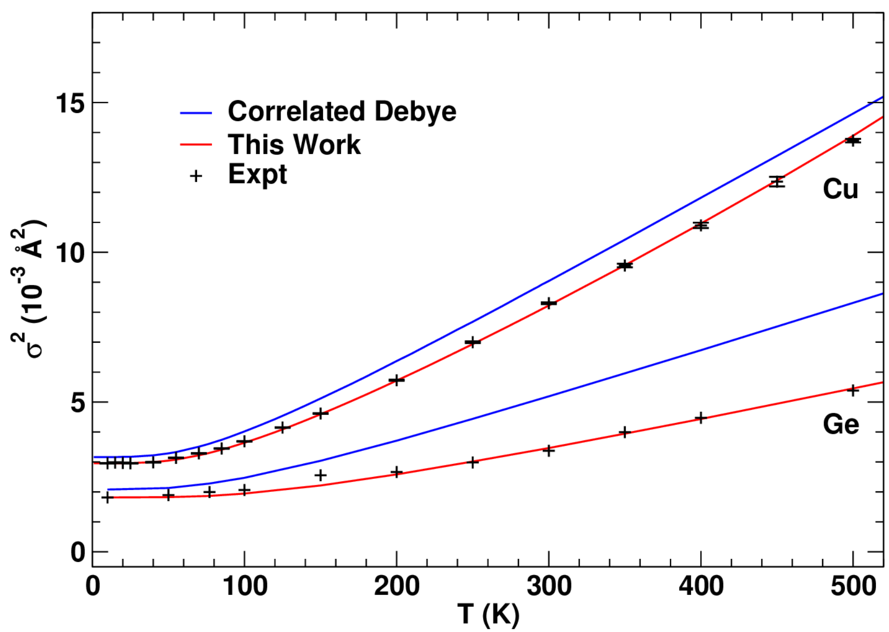
Vila et al, Phys. Rev. B 76, 014301 (2007)

Vibrational Density of States

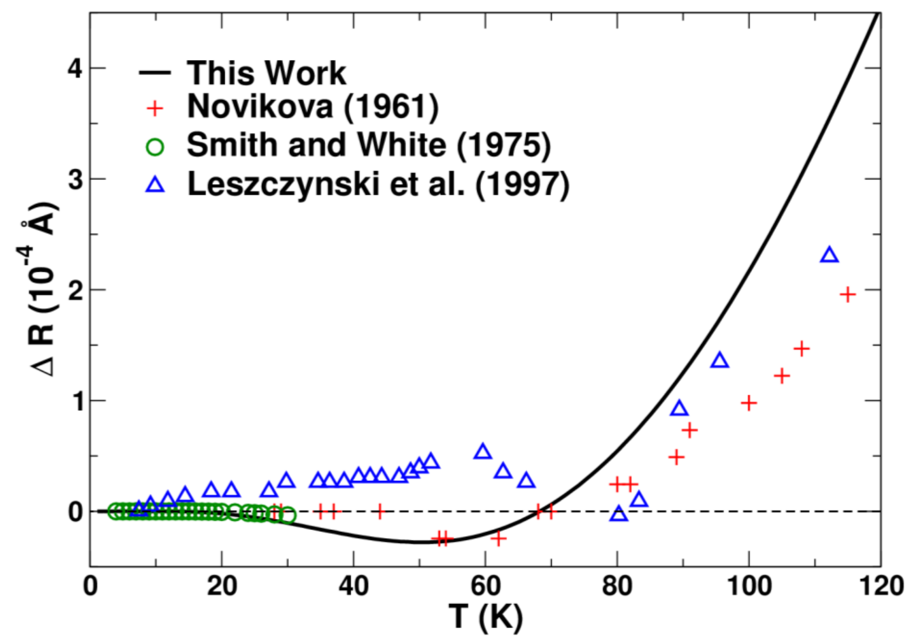


Typical Results

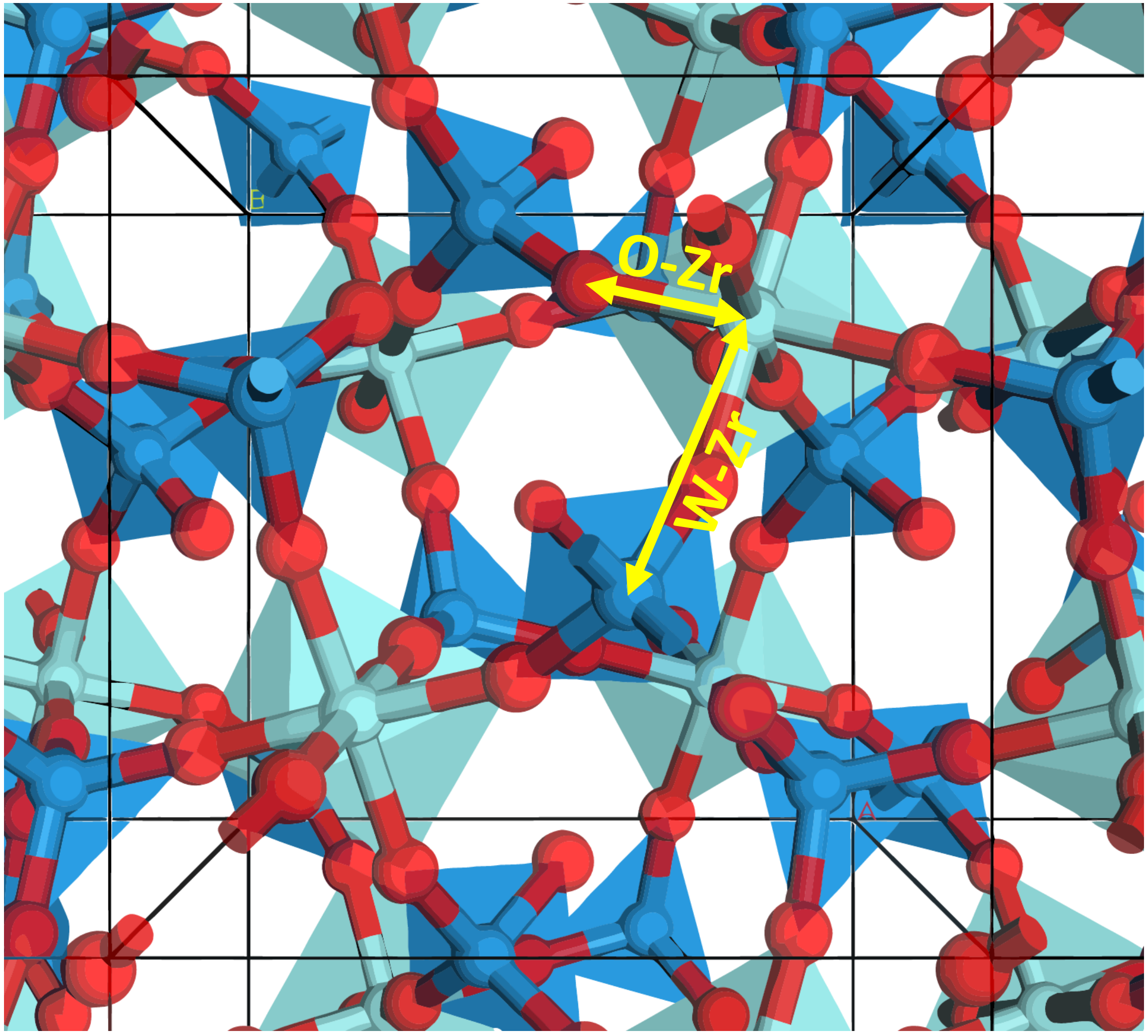
Cu and Ge: NN MSRD



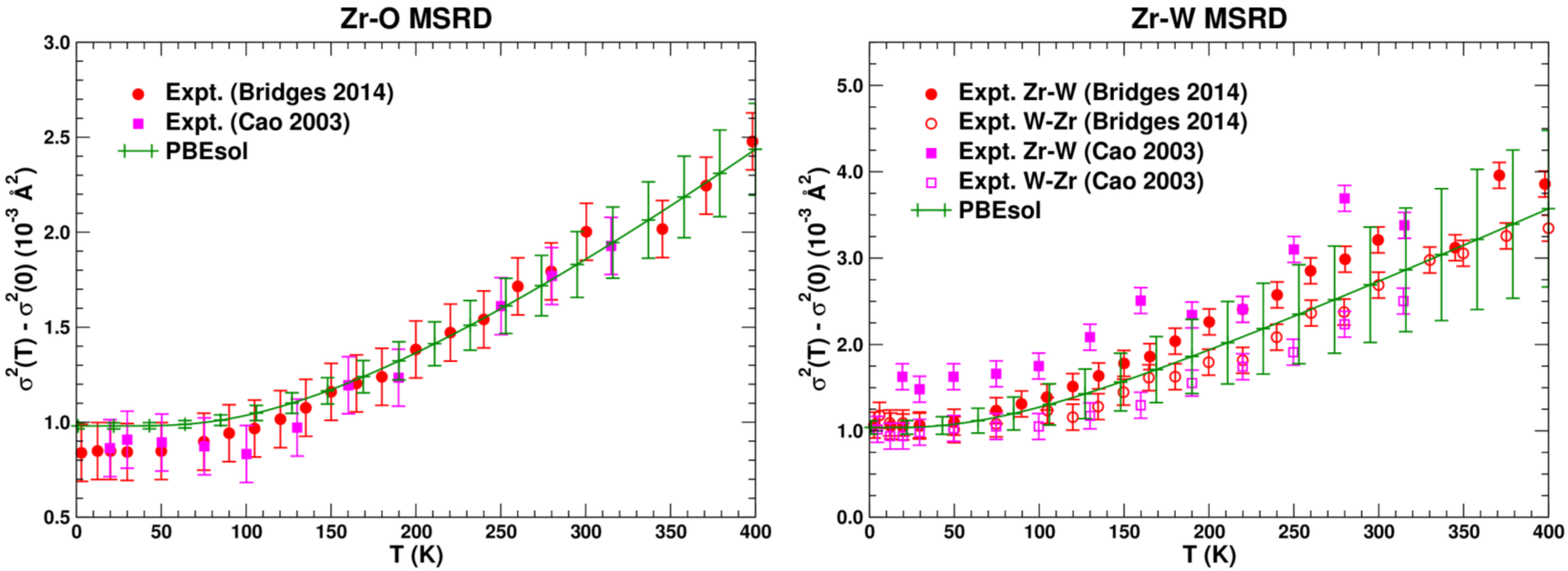
GaAs: Negative Thermal Expansion



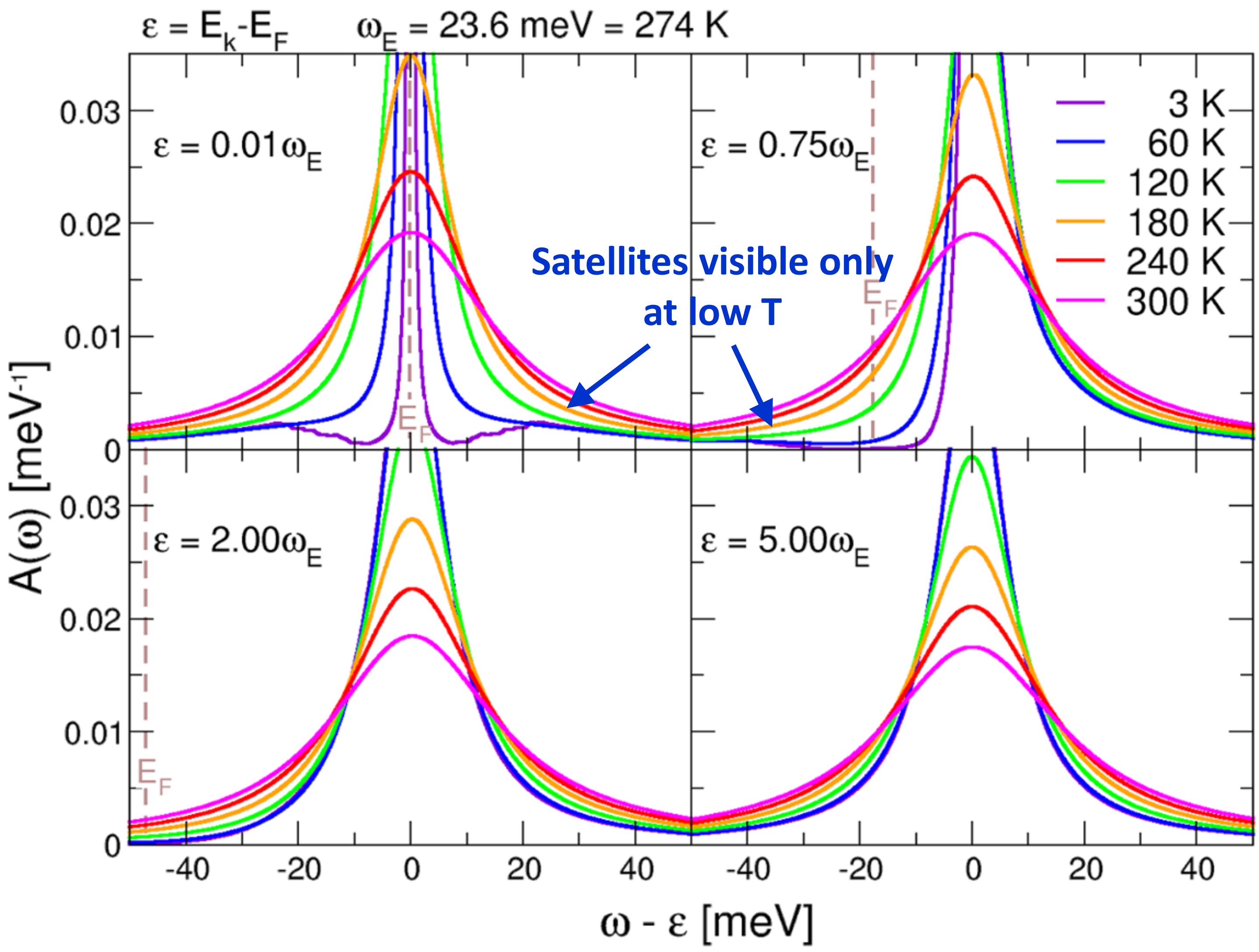
ZrW_2O_8: Complex unit cell



ZrW_2O_8: MSRDs



Phonon-contributions to final-state broadening in Cu



User-friendly Java GUI: JFEFF

15th International Conference on X-ray Absorption Fine Structure (XAFS15) IOP Publishing
Journal of Physics: Conference Series **430** (2013) 012001 doi:10.1088/1742-6596/430/1/012001

New Developments in FEFF: FEFF9 and JFEFF

Kevin Jorissen and John J. Rehr

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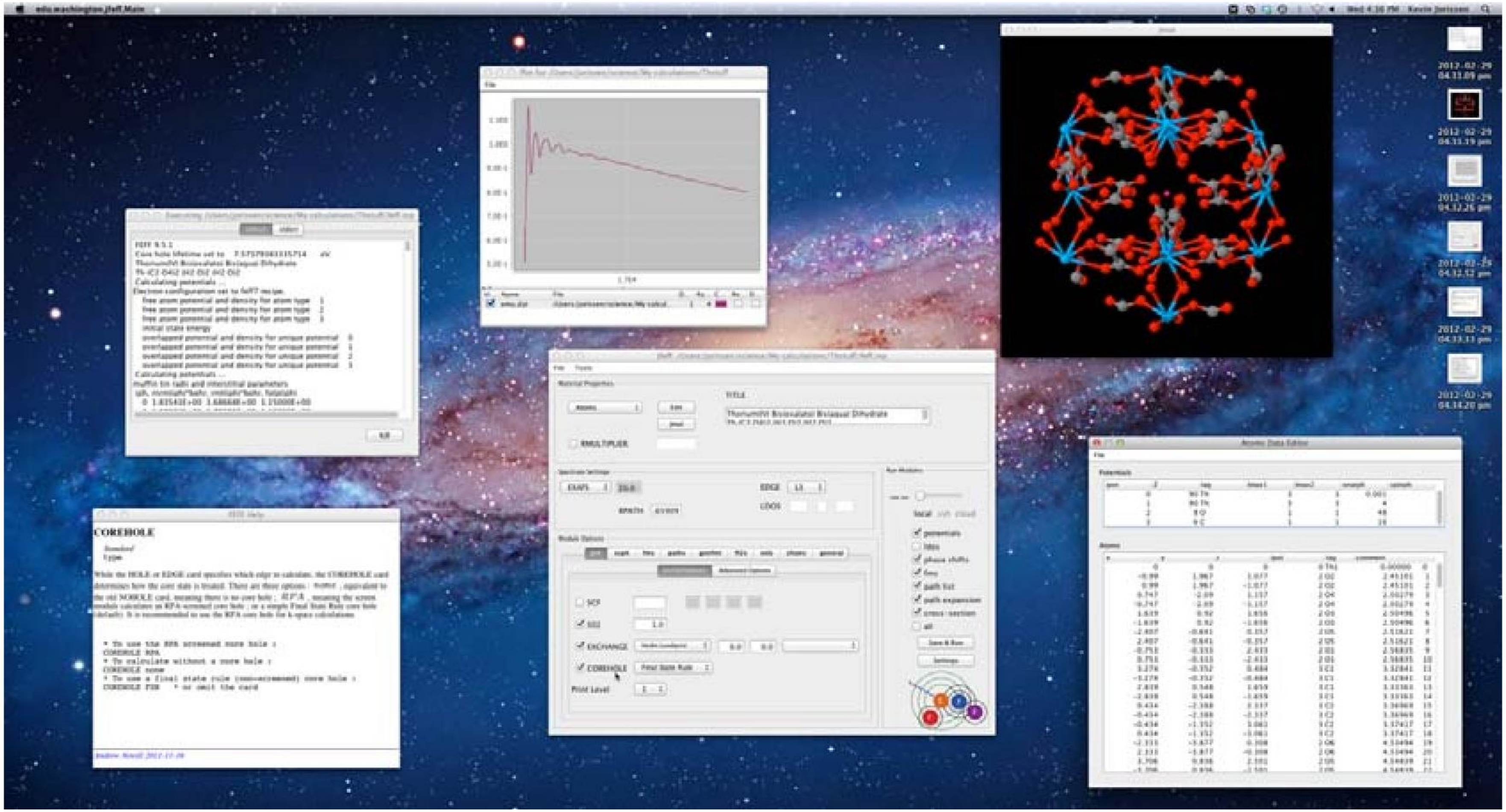
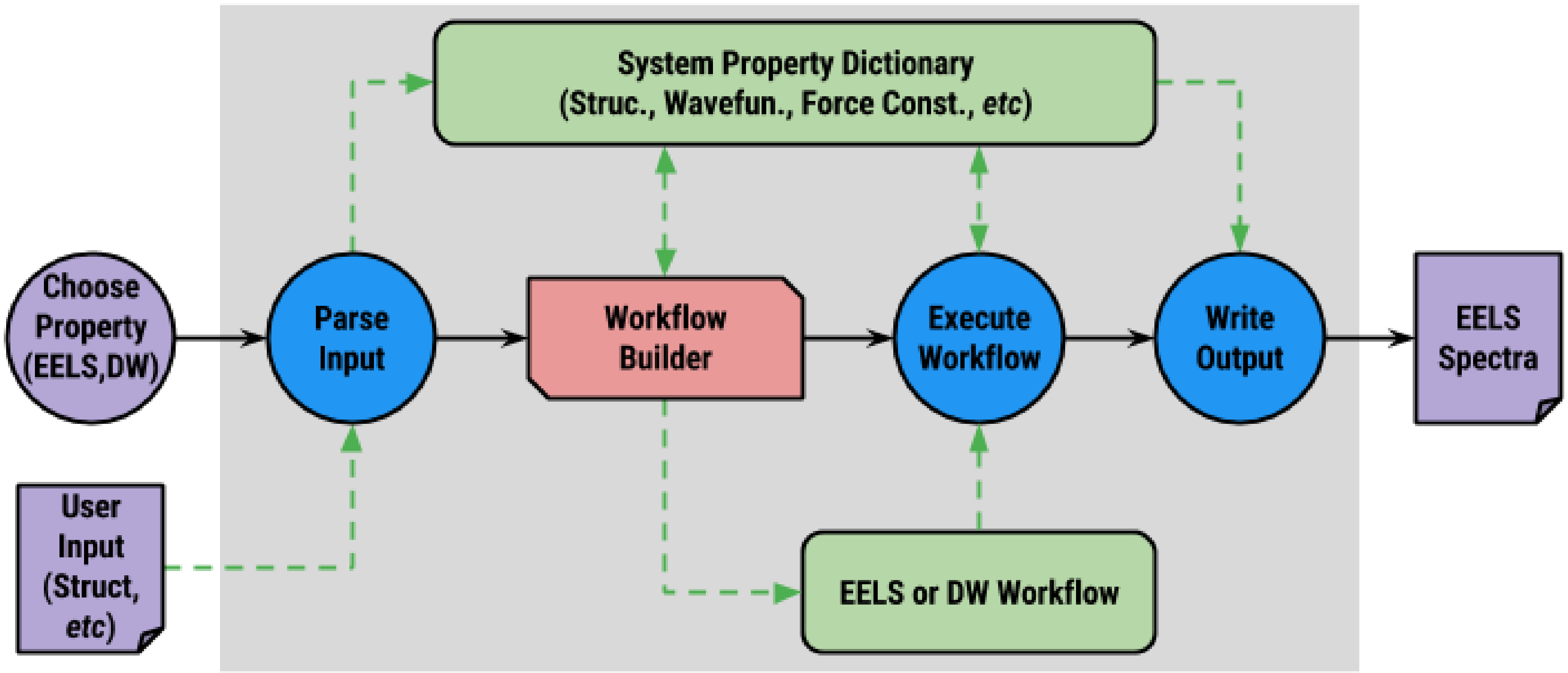
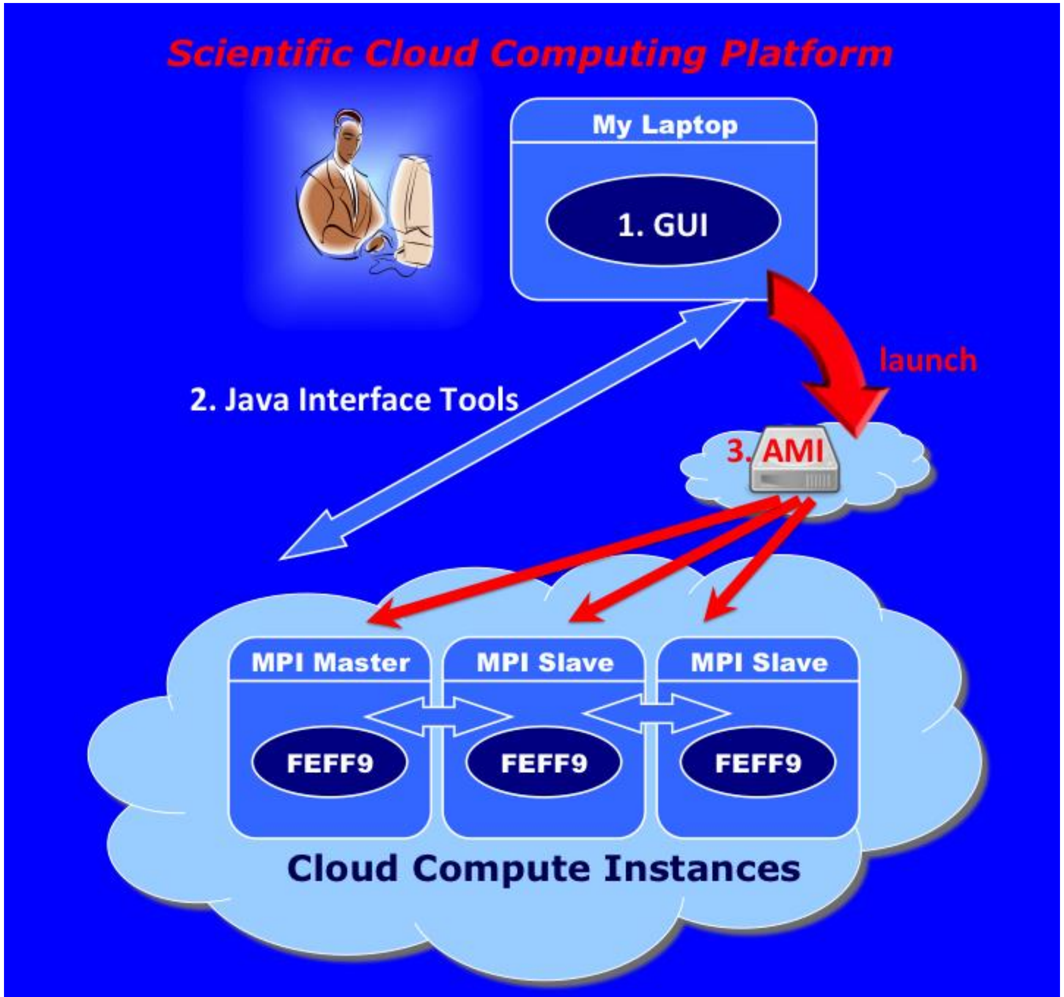


VESPA - Virtual EELS Software Package

Goal: Integrated EELS software for STEM using CORVUS Workflow Manager



Prototype: Virtual STEM in the Cloud
State-of-the-art EELS modeling



FEFF9+JFEFF

AI2NBSE and OCEAN

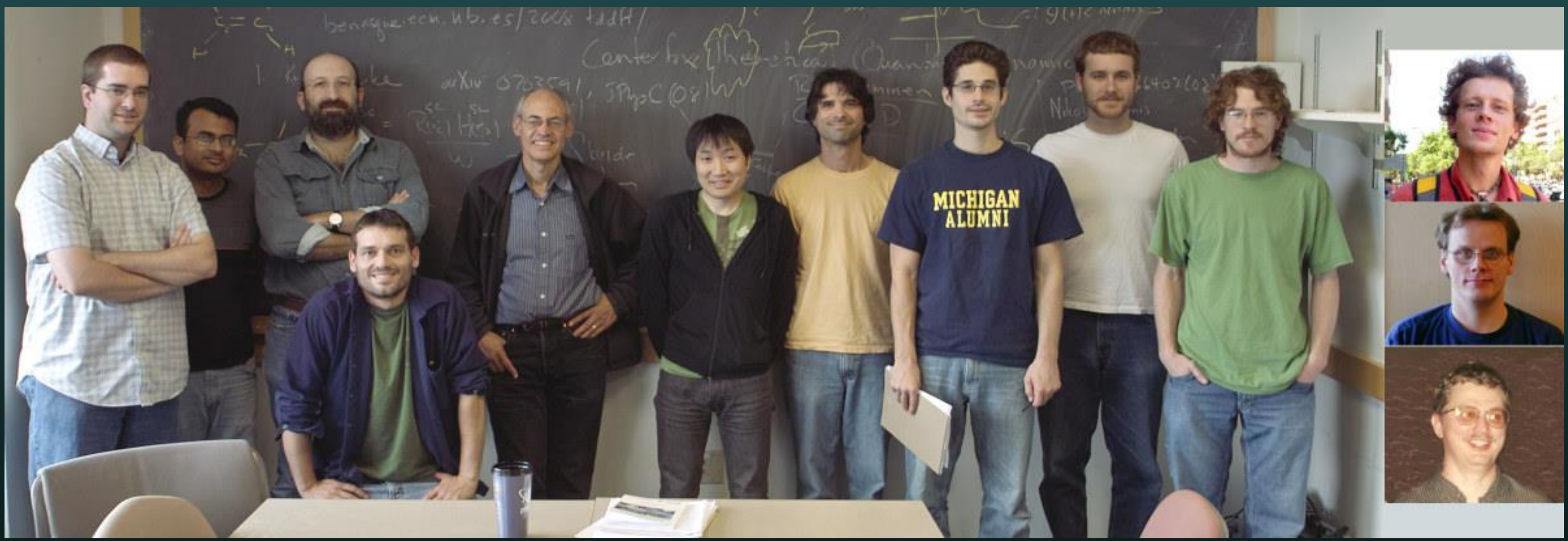
TELNES

Precompiled & Optimized on the Amazon EC2

CONCLUSIONS

- Goals:
  - Mostly achieved or in sight
- Complementary theoretical techniques:
  - Real-space
  - Supercell/reciprocal space
- Next generation theory & codes including:
  - Many-body effects
  - Relativistic effects
- Broad spectrum response:
  - IR → VIS → UV → X-ray

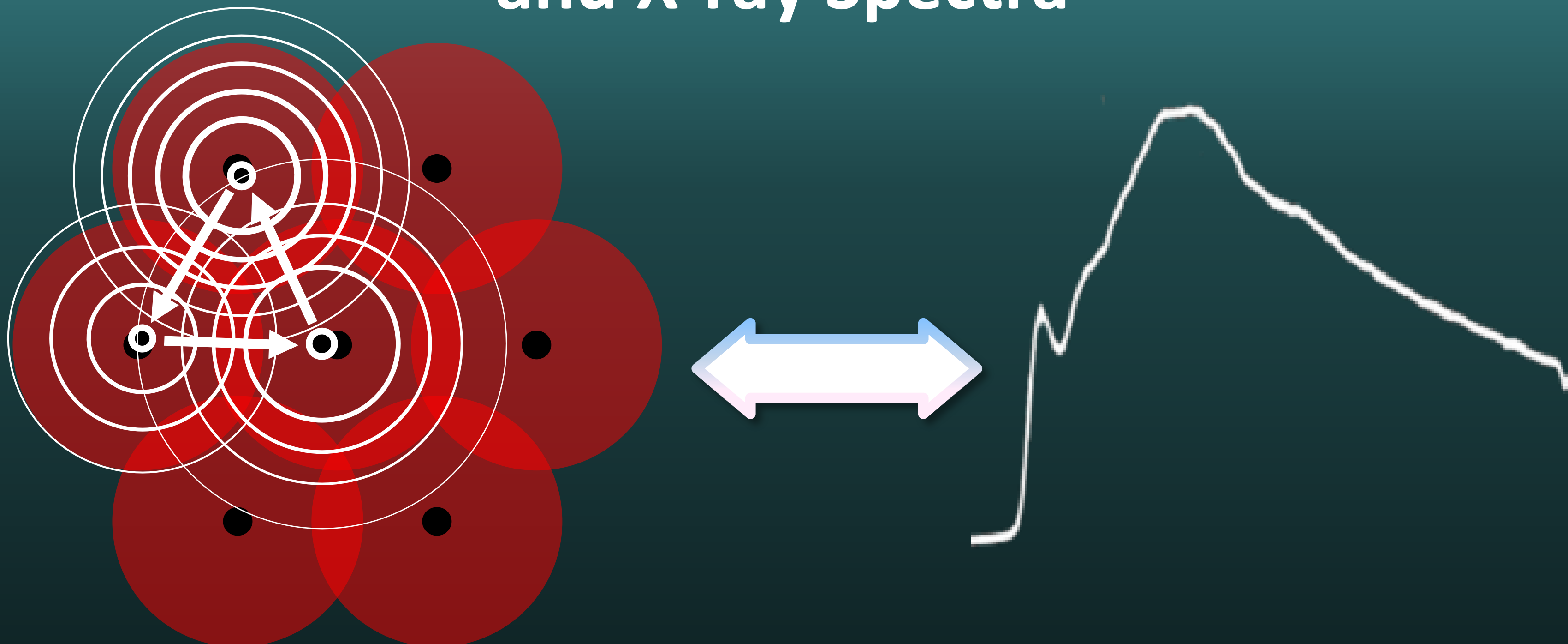
Acknowledgments: Thanks to DOE BES for $$ Rehr Group + L. Reining, M. Guzzo, E. Shirley, K. Gilmore, et al.



From left to right:

Ken Nagle
Towfiq Ahmed
Fernando Vila
Micah Prange
John Rehr
Yoshi Takimoto
Hadley Lawler
Adam Sorini
John Vinson
Josh Kas
Kevin Jorissen
Aleksi Soininen
Alex Ankudinov
(Shauna Story)
(Egor Clevac)

Theory and Parameter Free Calculations of EELS and X-ray Spectra



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Thank you!

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