Excitations in Condensed Matter: From Basic Concepts to Real Materials

KITP, UCSB October 5, 2009 - December 18, 2009

Real-space Green's function approach for electronic, vibrational and optical properties

J. J. Rehr
Department of Physics,
University of Washington
Seattle, WA, USA

Supported by DOE BES and NIST

Real-space Green's function approach

- **GOAL**: *ab initio* theory of electronic, vibrational, and optical properties

- "Pretty good theory"
- Broad spectrum VIS – X-ray
- Accuracy ~ experiment

- **TALK**:

I. **RSGF** approach

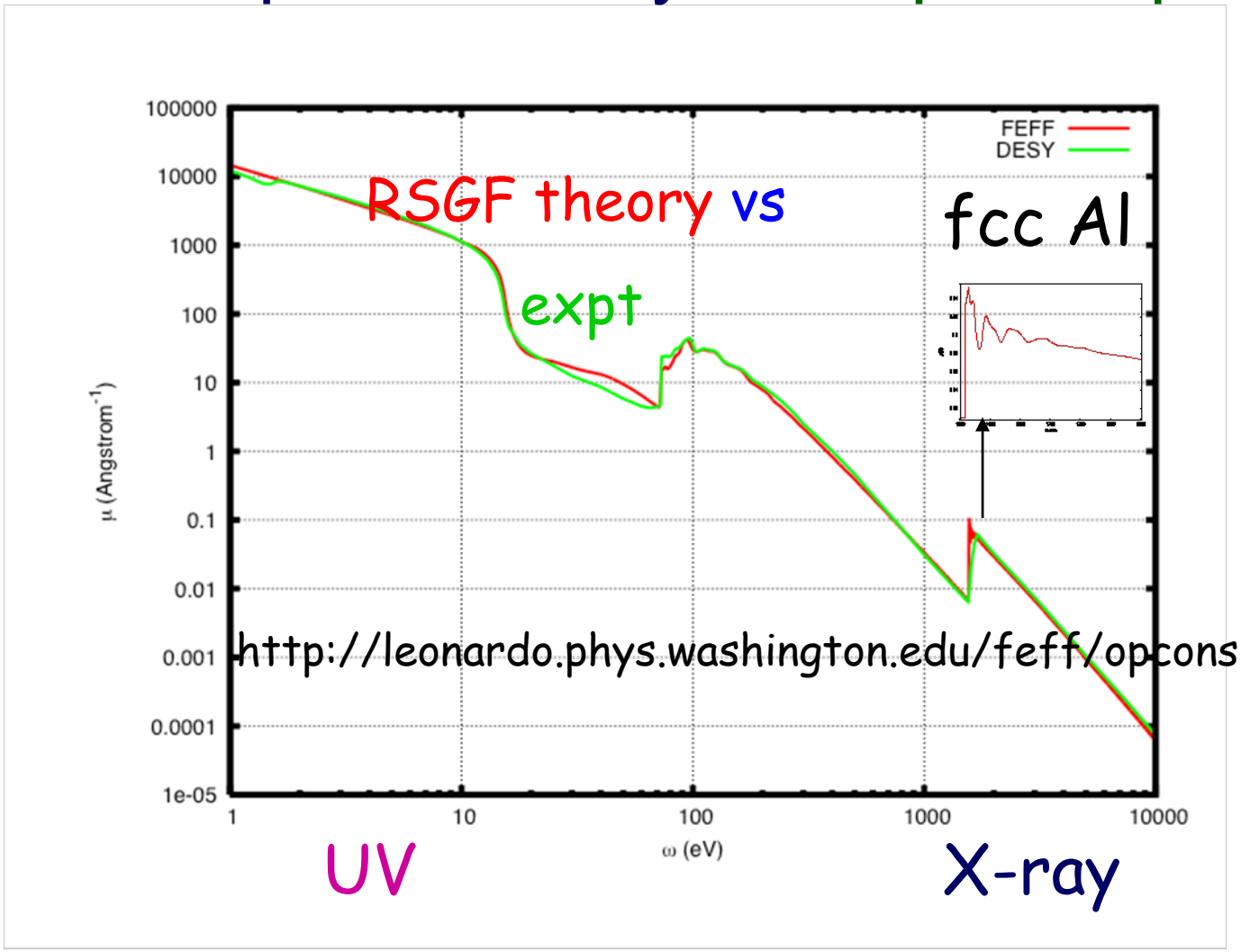
II. Parameter free theory No adjustable parameters

"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?"

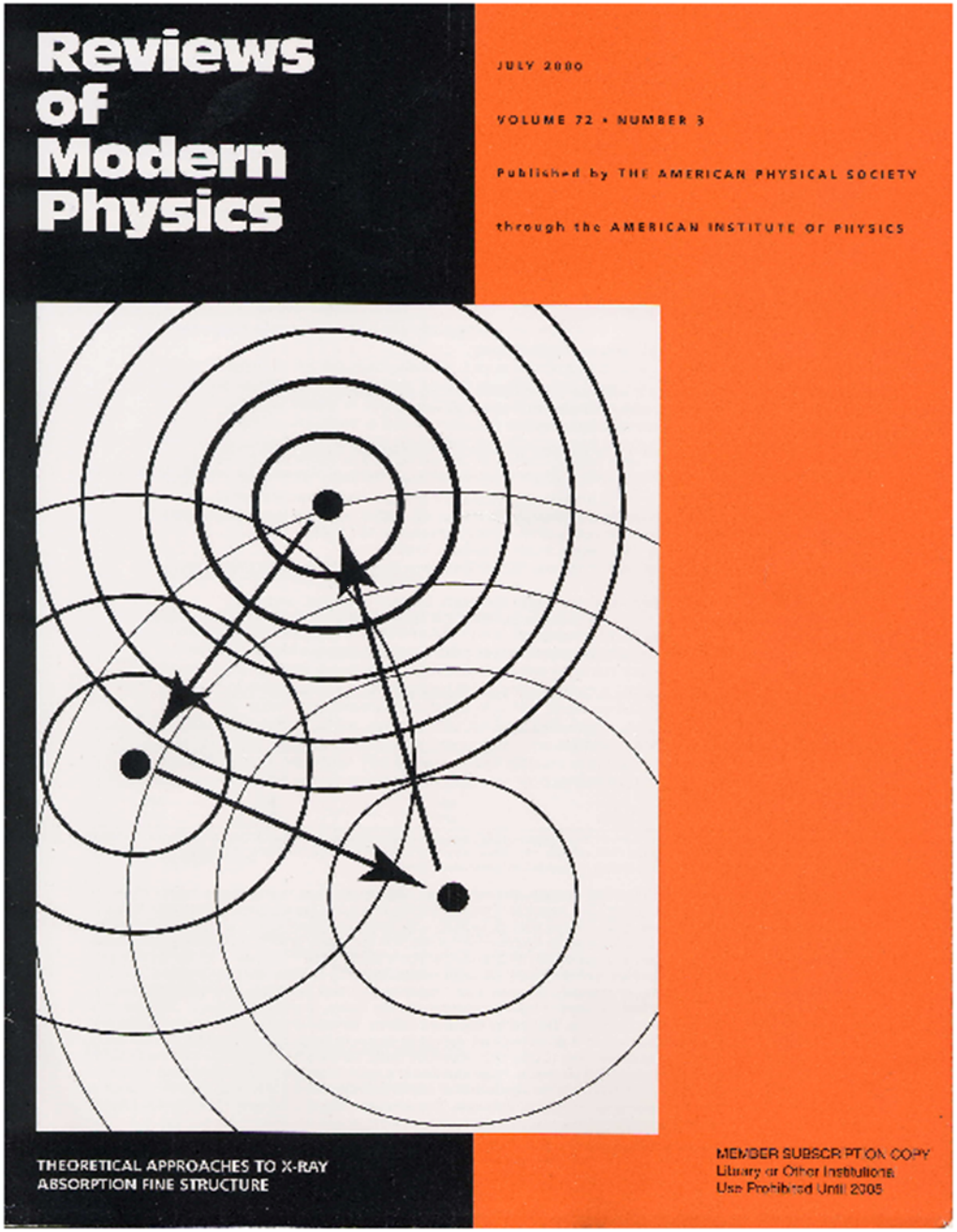
R. P. Feynman

Experiment vs Theory: Full spectrum

Optical - X-ray Absorption Spectra



Photon energy (eV)



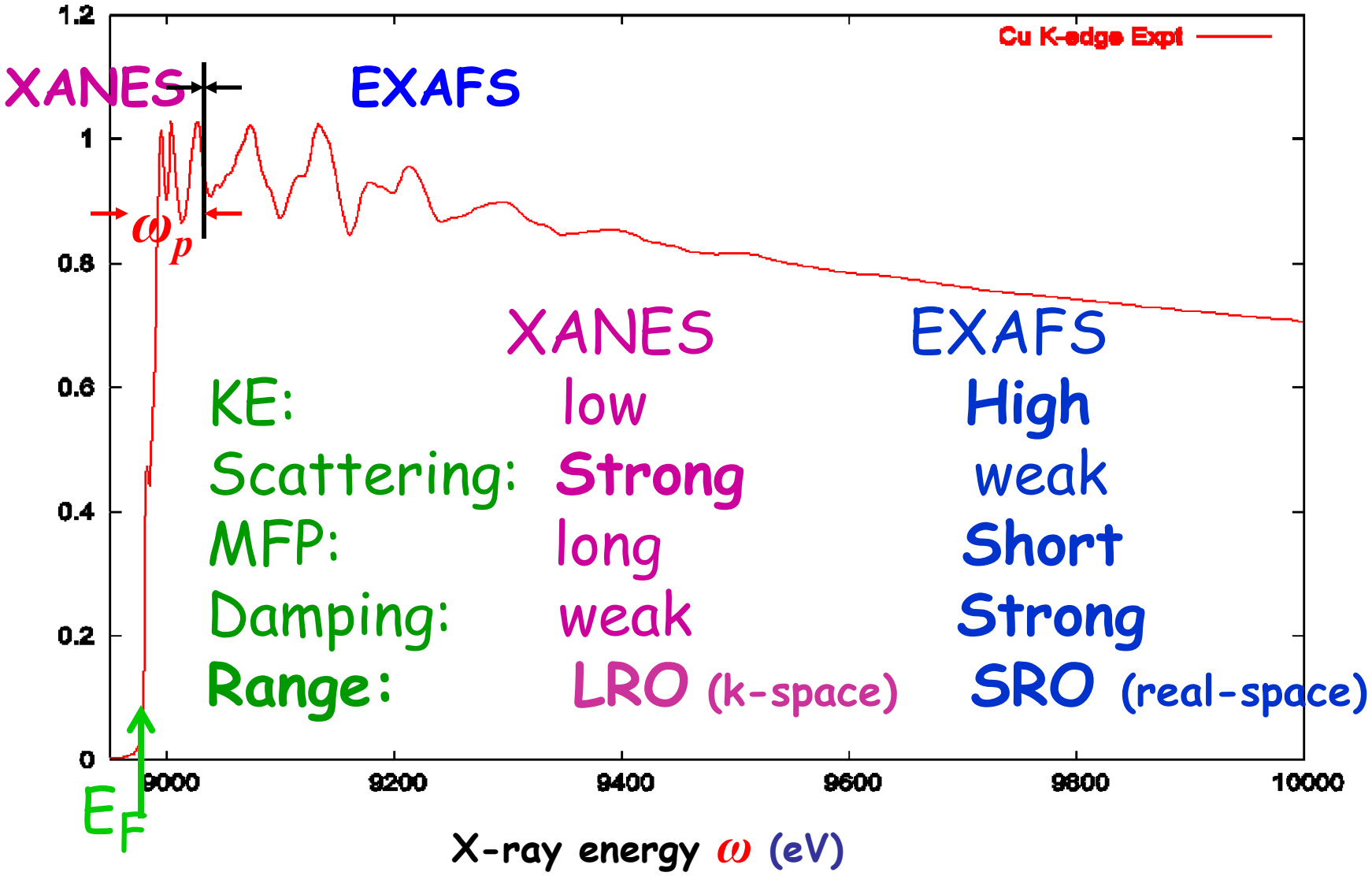
I. RSGF Approach

J. J. Rehr & R.C. Albers

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

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

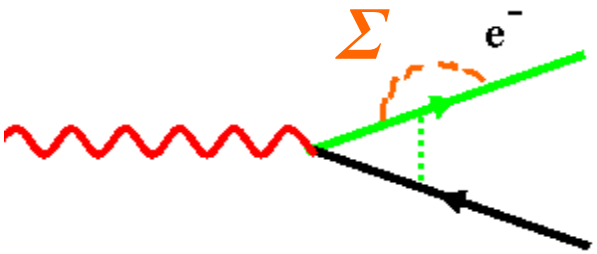
Physical Considerations in XAS



	XANES	EXAFS
KE:	low	**High**
Scattering:	**Strong**	weak
MFP:	long	**Short**
Damping:	weak	**Strong**
Range:	**LRO** (k-space)	**SRO** (real-space)

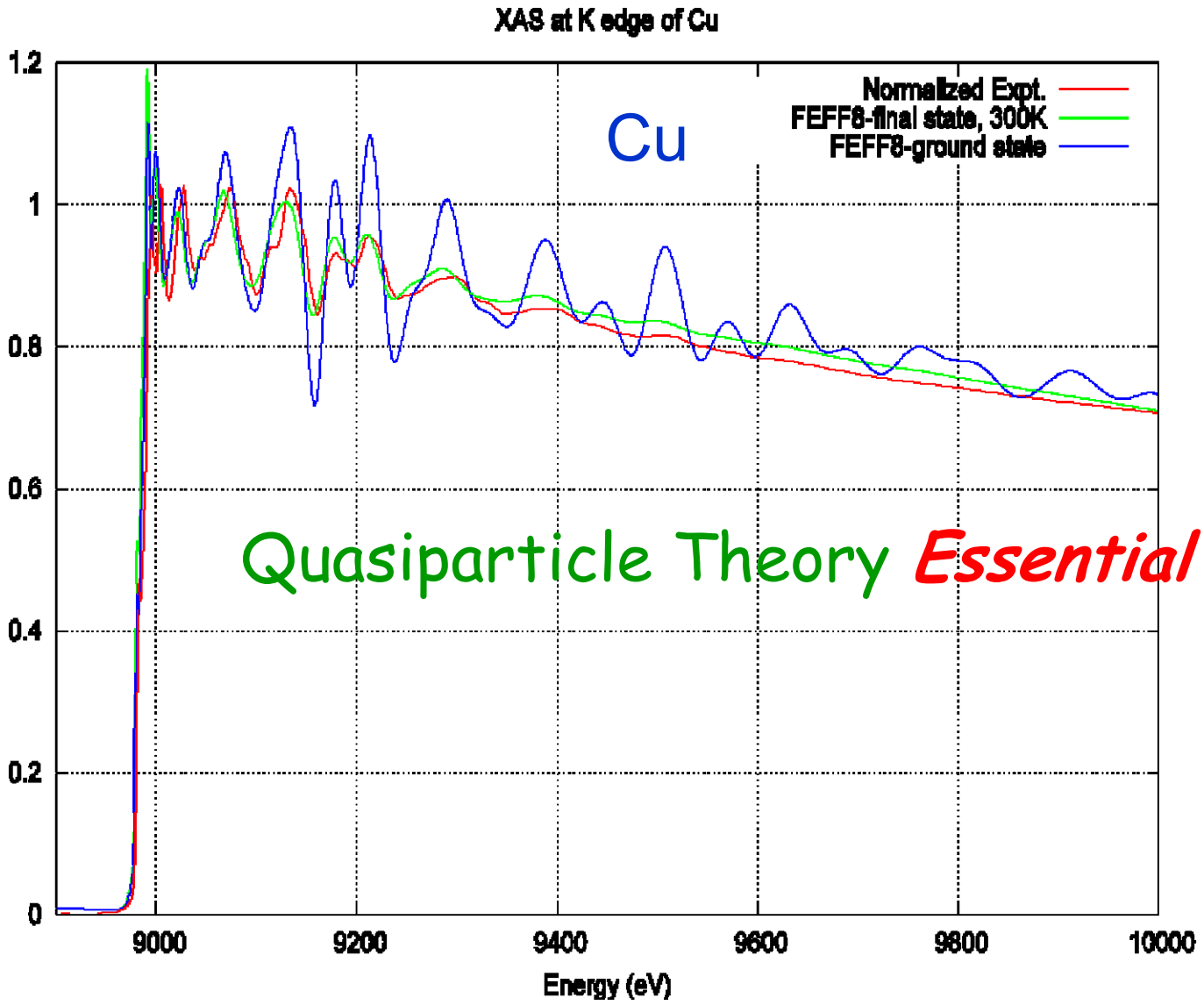
Key Many body effects in XAS

quasi-particle & beyond



- Self-energy $\Sigma(E)$ — *complex*
- Core-hole effects — ? Screening ?
- **Debye-Waller factors** — $e^{-2\sigma^2 k^2}$
- Multi-electron excitations — satellites

Ground-state vs Quasiparticle vs Expt



Conventional Quasi-particle Theory of XAS

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

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

Quasi-particle final states ψ_f with core hole

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

Final state hamiltonian

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

Non-hermitian Self-energy $\Sigma(E)$ (replaces Vxc)

⇨ Inelastic Mean free paths $\lambda = k/|\mathrm{Im}\,\Sigma(E)| \approx 5 - 20$ Å

Green's functions *vs* Wave-functions

Golden rule via Wave Functions

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

Paradigm shift:

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

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

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

Efficient! *No sums over final states*

Connection with Electronic Structure

Density operator $\rho(E) = -\,\mathrm{Im}\, G(E)$

- Spectral function $\rho(E,r,r') = -\,\mathrm{Im} \langle r | G(E)\, r' \rangle$
- Density matrix $\rho(r, r') = \int^{E_F} \rho(E,r,r')\, dE$
- Density $\rho(r) = \int^{E_F} \rho(E,r,r)\, dE$
- *l*DOS $\rho_{R,L}(E) = \langle R,L | \rho(E,r,r) | R,L \rangle$

DFT → **GFT**

Real-space Green's Function Formalism

full-multiple scattering vs MS path expansion

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

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

(MS path expansion - geometric series)

$$= [1 - G^0 t]^{-1} G^0$$ "full MS" **"Real-space KKR"**

Ingredients:

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

Scattering state representation of G

$$G(\vec{r},\vec{r}',E) = -2k\left[\sum_{LL'} R_{Ln}(\vec{r}_n)\bar{G}_{LnL'n'}\bar{R}_{L'n'}(\vec{r}'_{n'}) + \delta_{nn'}\sum_{L} H_{Ln}(\vec{r}_{>})\bar{R}_{Ln}\vec{r}_{<}\right],$$

Angular momentum-site basis $R_L(\mathbf{r},E) = R_l(r;E)\ Y_L(\hat{\mathbf{r}})$

Matrix elements - separable representation*

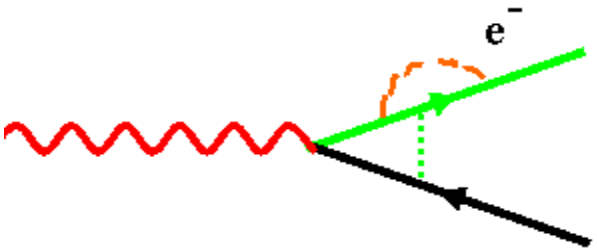
$$G_{Ln,L'n'}(E) = (e^{ik\,Rnn'}/R_{nn'})\Sigma_{ss'}\,\mathbf{Y}_{ls}\,\mathbf{Y}_{l's'}$$

*JJR + R. Albers Phys. Rev. B **41**, 8139 (1990)

Relativistic RSGF

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

2 Steps



1) Production

Dirac-Fock atomic theory $|< f \mid d \mid I >|$

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

Non-relativistic, no spin-flips, …

$$\mu(\omega) = -\frac{4\pi\, e}{\omega} \mathrm{Im} \sum_{I, J_s, J' s'} (I|d^{\dagger}_s|R J_s) G_{J_s, J' s'}(\omega + E_i) (R J' s'|d_s|I).$$

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

A. L. Ankudinov
MST-11, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

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

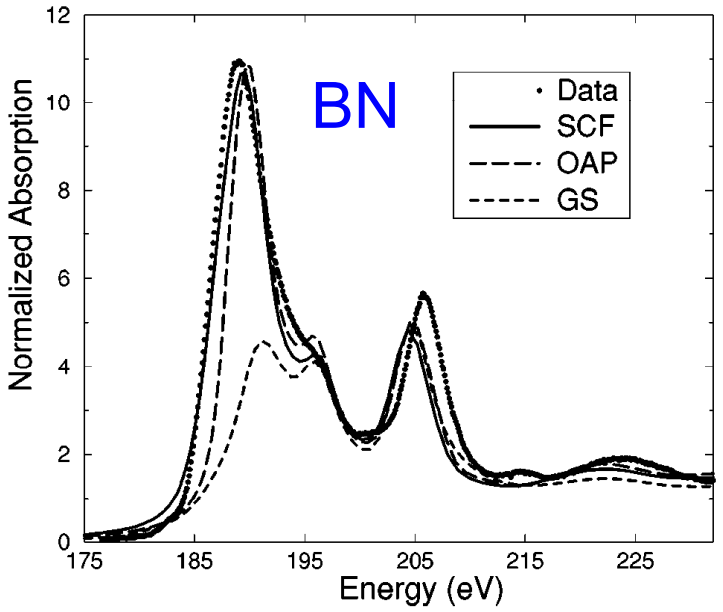
J. J. Rehr
Department of Physics, University of Washington, Seattle, Washington 98195-1560

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

89 atom cluster

Core-hole, SCF potentials

Essential!

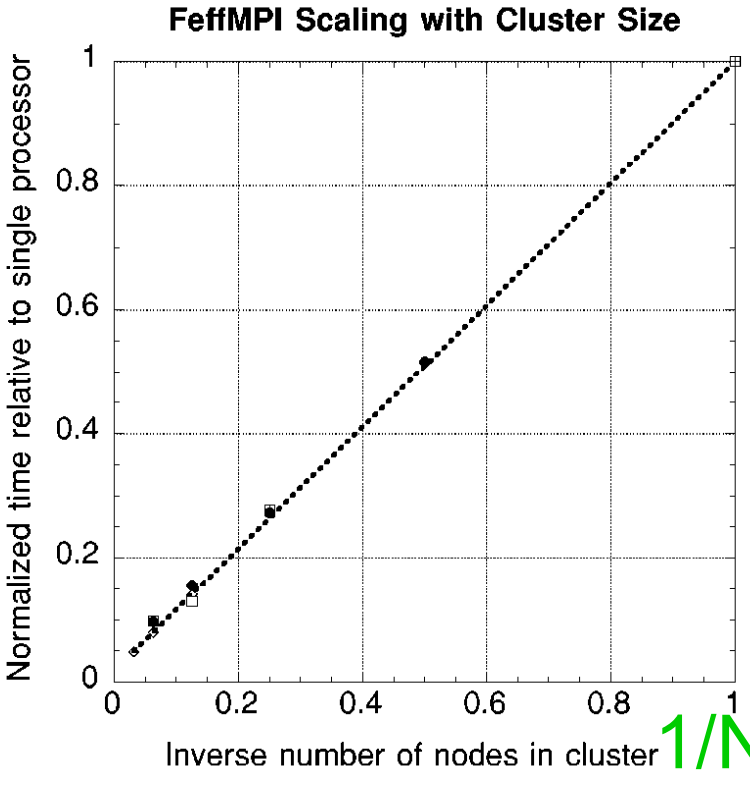


FAST! Parallel Computation FEFFMPI

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*



MPI: "Natural parallelization"

Each CPU does few energies

Lanczos: Iterative matrix inverse

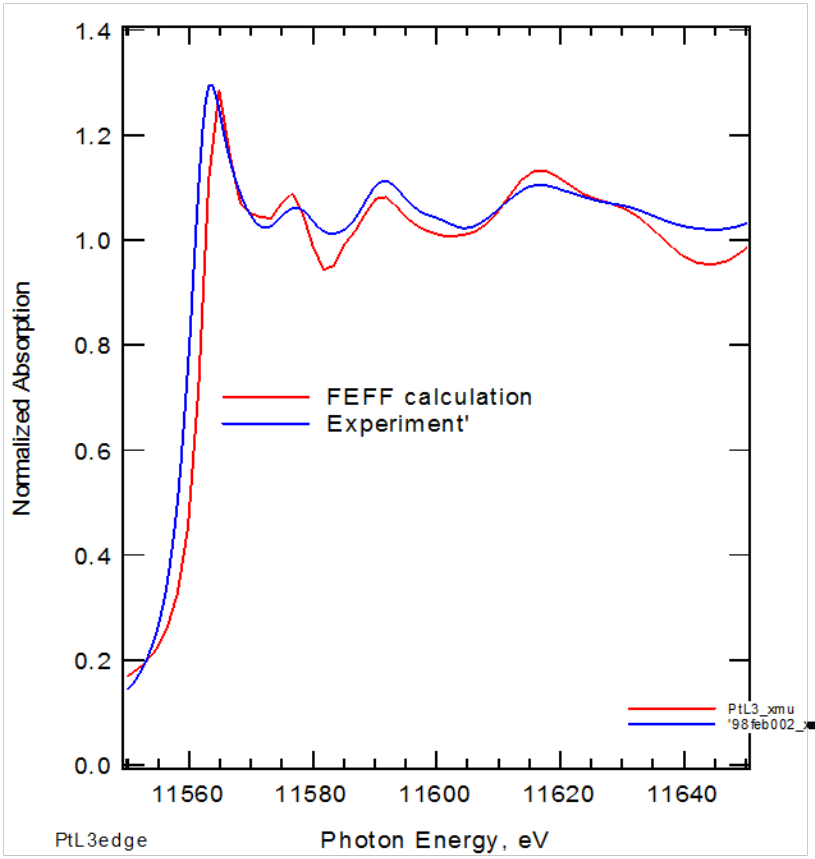
Smooth crossover between

XANES and EXAFS!

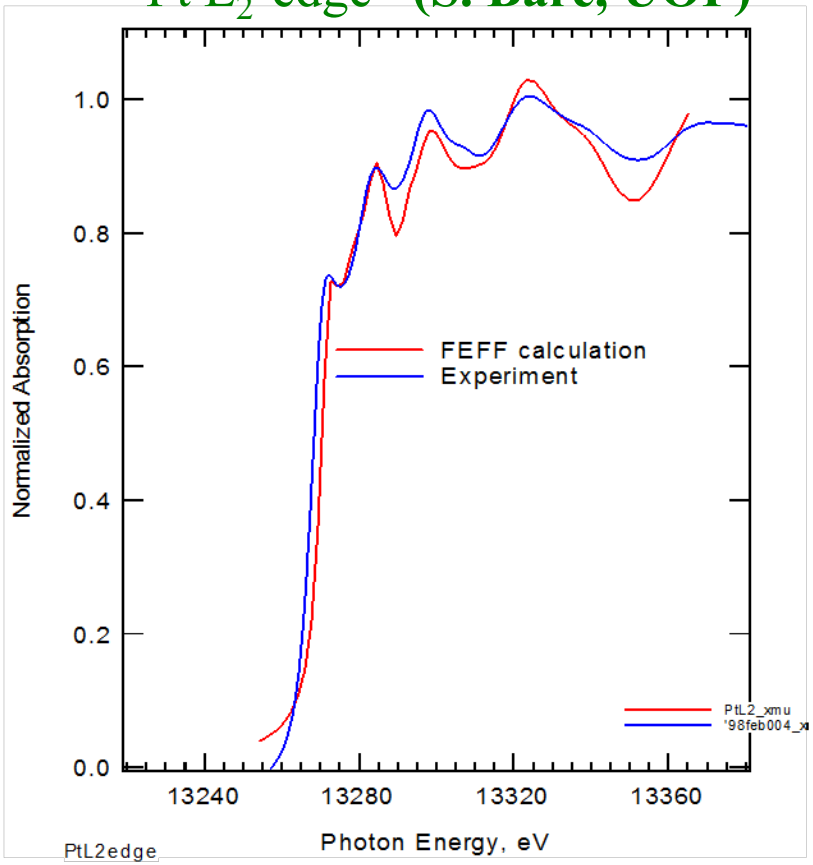
$1/N_{CPU}$

Example 1: XAS of Pt

Pt L_3-edge



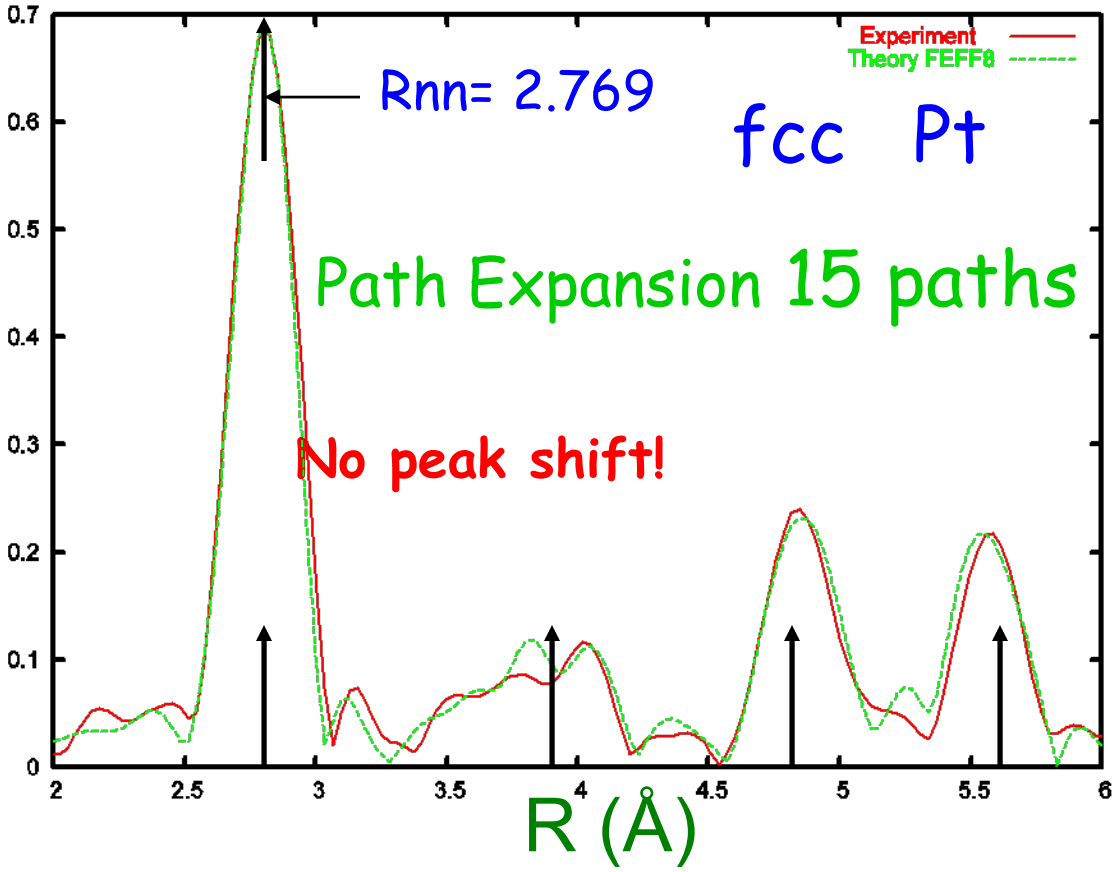
Pt L_2-edge **(S. Bare, UOP)**



- Good agreement: *Relativistic* FEFF8 code reproduces all spectral features, ***including absence of white line at L_2-edge***.
- Self-consistency essential: position of Fermi level strongly affects white line intensity.

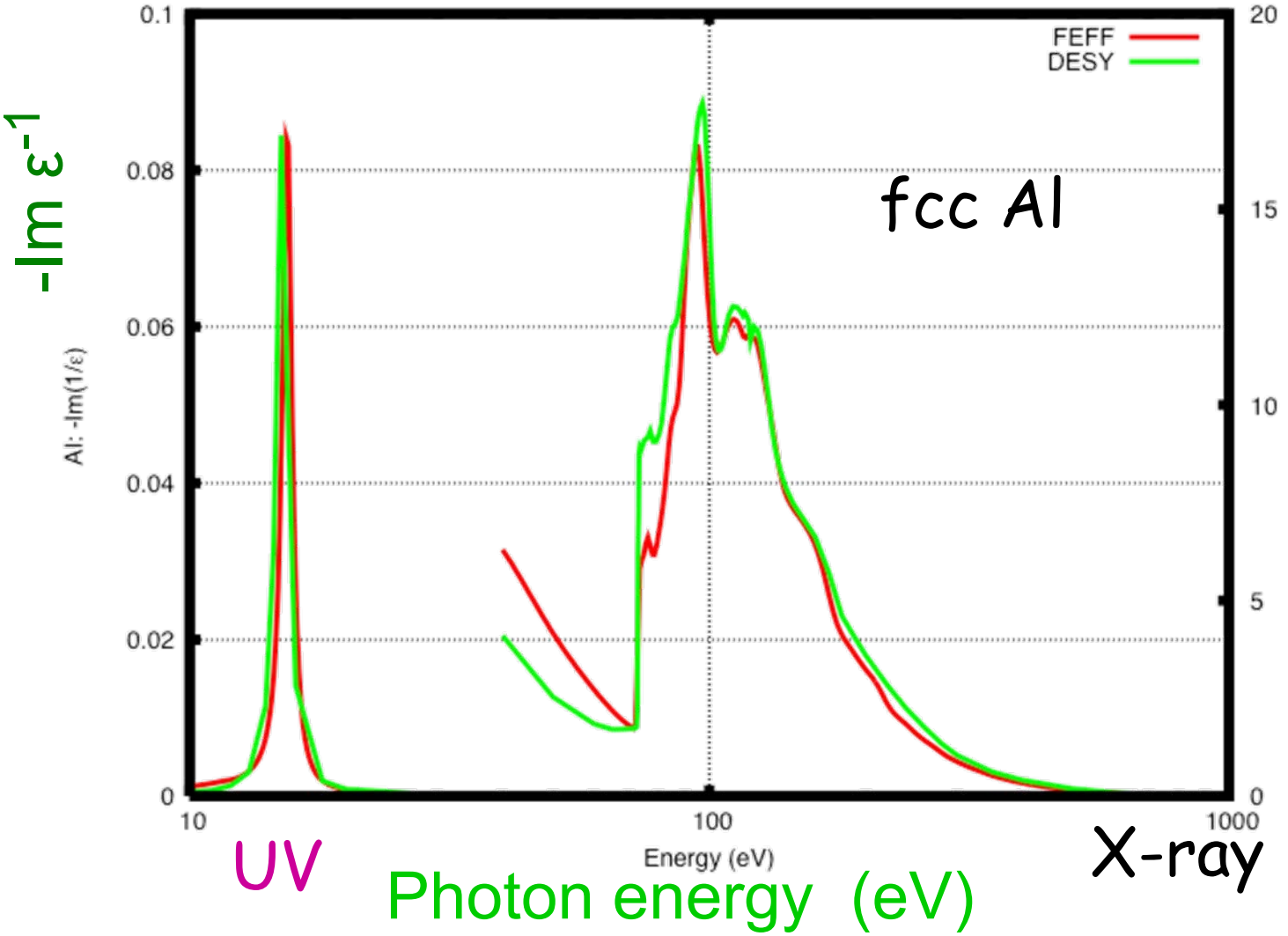
Example 2: Pt EXAFS

Phase Corrected EXAFS Fourier Transform *



Theoretical phases → accurate distances to < 0.01 Å

Example 3: Electron energy Loss spectra (**EELS**)



Example 4: X-ray Raman Spectra (NRIXS) *FEFFq*

UNIVERSITY OF HELSINKI

Finite mom transfer ***q***

RSMS approach to XRS and NRIXS

J.A.Soininen, A.L. Ankudinov, JJR, Phys. Rev. B **72**, 045136 (2005)

Born approximation for the NRIXS double differential cross-section

$$\frac{d^2\sigma}{d\Omega d\omega} = \left(\frac{d\sigma}{d\Omega}\right)_{Th} S(\mathbf{q},\omega) \quad \sim \quad \mathrm{Im}\ \varepsilon^{-1}(\boldsymbol{q},\omega)$$

Fermi's Golden rule:

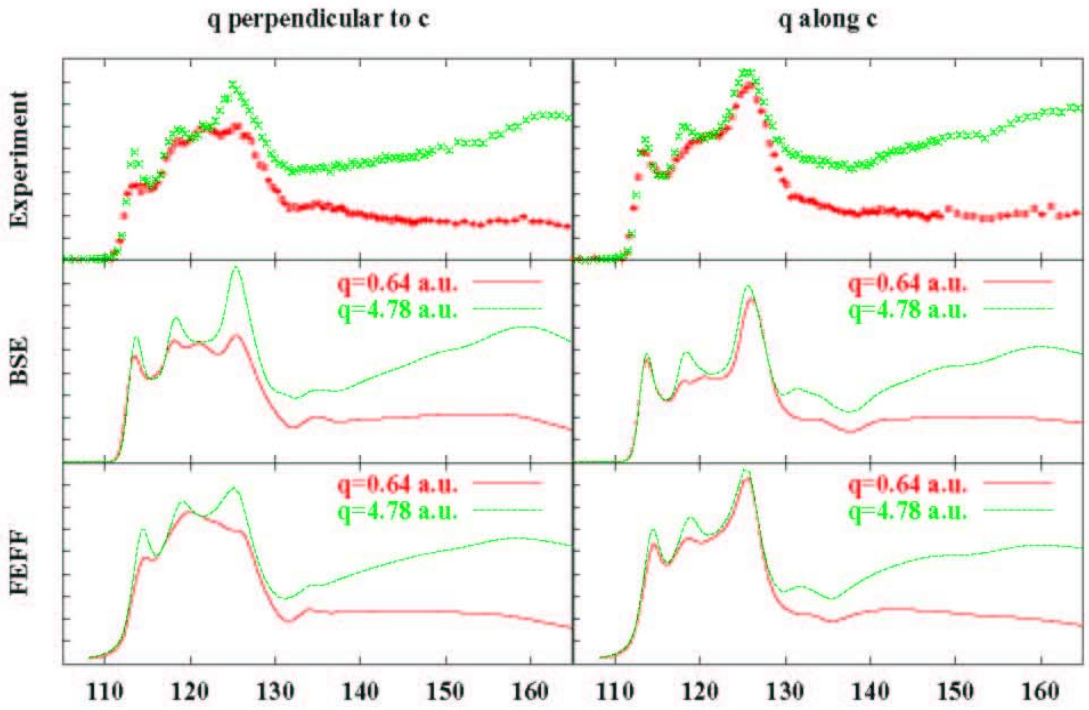
$$S(\mathbf{q},\omega) = \sum_f |\langle f|e^{i\mathbf{q}\cdot\mathbf{r}}|i\rangle|^2 \delta(\hbar\omega + E_i - E_f) \qquad f_{eff}(\boldsymbol{q},k)$$

- E_i (E_f) initial (final) state quasiparticle energy
- Final state rule: "The (photo-electron) states $|f\rangle$ are eigenfunctions of the final state Hamiltonian H' in the presence of a screened core hole."
- $H' = p^2/2m + V'_{\mathrm{coul}} + \Sigma(E)$ includes inelastic losses i.e. lifetime effects using the local density approximation for $\Sigma(E)$ of Hedin and Lundqvist [1]

[1] L. Hedin and S. Lundqvist, J. Phys. C **4**, 2064 (1971).

UNIVERSITY OF HELSINKI

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



Expt

BSE*

$f_{eff}(q)$

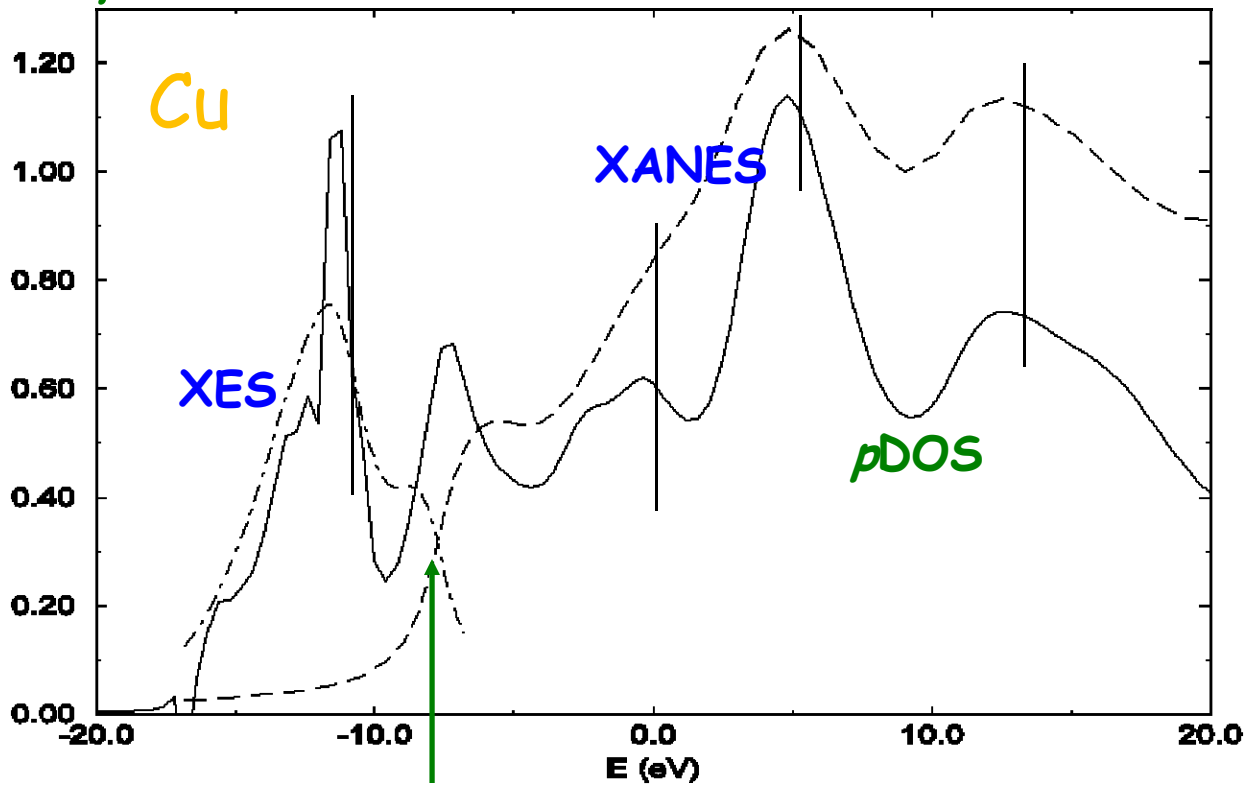
Experiment: C. Sternemann et al., Phys. Rev. B **68**, 035111 (2003).

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

Example 5: *lDOS* and X-ray Spectra

Angular momentum Projected DOS

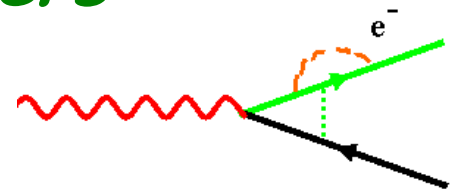
*p*DOS vs XES and XANES



Fermi energy E_F Final state electron energy E

II. Parameter Free RSGF Theory*

GOAL: ***eliminate adjustable parameters***



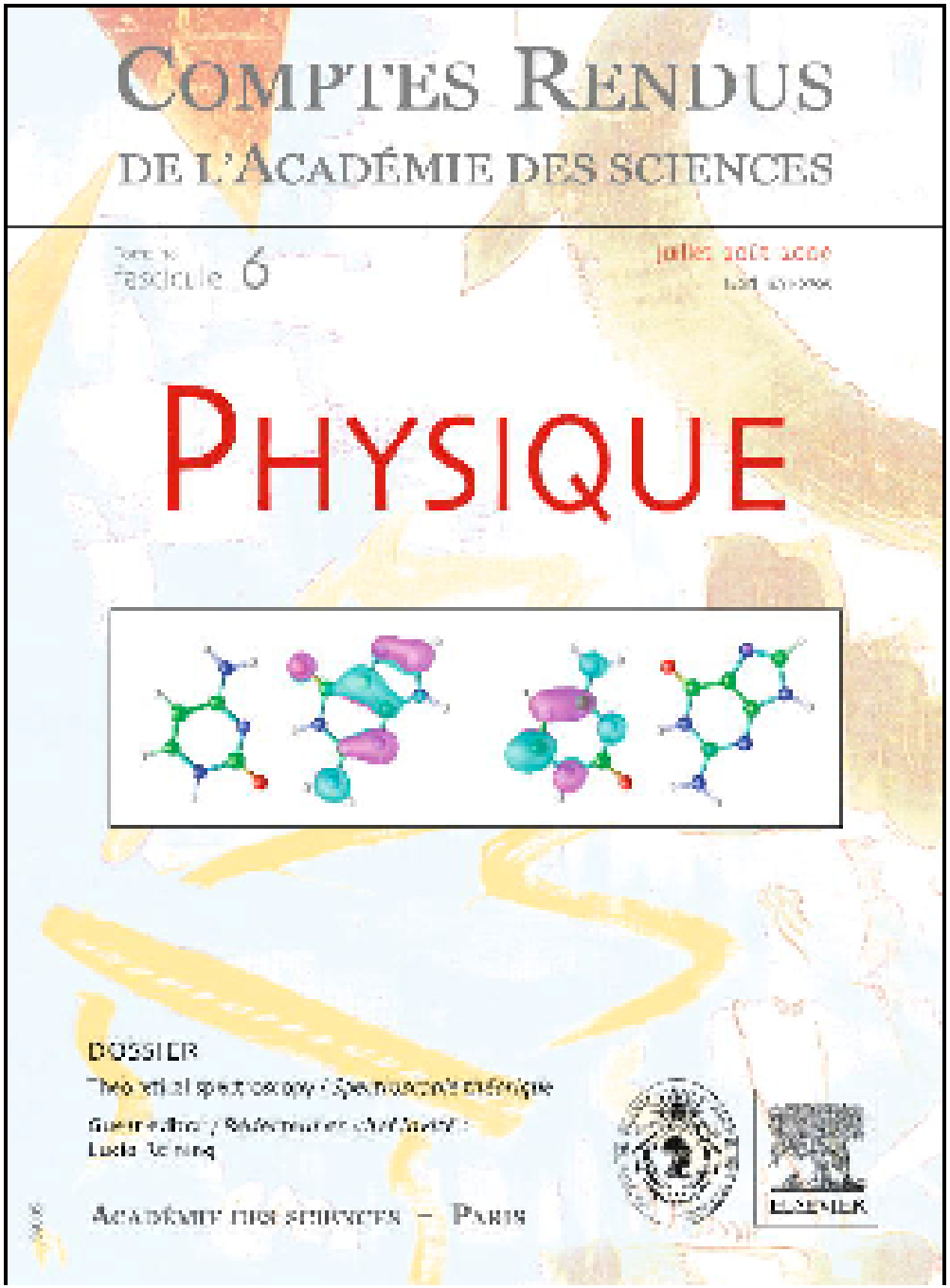
A. Ab initio self-energies and mean free path

B. Multi-electron excitations S_0^2

C. Core-hole and local field effects BSE/TDDFT

D. *Ab initio* Debye Waller factors

E. Full potential corrections



II. Parameter free RSGF theory

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

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

A. Self-energy and Inelastic Losses

Need: complex, energy dependent $\Sigma(E)$

- GW Approximation (Hedin 67)

$$\Sigma(E) = i \int \frac{d\omega}{2\pi} G(E-\omega) W(\omega) e^{-i\delta\omega}$$

- Screened Coulomb Interaction W

$$W = \epsilon^{-1}(\omega) V$$

? How to appproximate $\varepsilon^{-1}(\omega)$?

RSGF approach: *VIS-UV optical constants*

Dielectric function	$\epsilon = \epsilon_1 + i\epsilon_2$
Energy Loss (EELS)	$-\mathrm{Im}\,\epsilon^{-1}$
Absorption coefficient	μ
Refractive index	$n + ik$
Reflectivity	R
X-ray scattering factors	$f = f_0 + f_1 + if_2$
Hamaker constants	$\varepsilon(i\omega)$

Long wavelength limit $q = 0$

+ extrapolation to finite q

FEFF8OP*

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, WA 98195*
[2]*Instituto de Ingeniería y Tecnología, Universidad Autónoma de Ciudad Juárez, Juárez, 32310 Mexico*
[3]*NASA Ames Research Center, Mail Stop 229-1, Moffett Field, California 94035*

(Dated: July 18, 2009)

We present a theory of linear optical constants based on the single-particle density operator and implemented in an extension of the real-space multiple scattering code FEFF. This approach avoids the need to compute wave-functions explicitly, and yields efficient calculations for frequencies ranging from the IR to hard x-rays, which is applicable to arbitrary aperiodic systems. The approach is illustrated with calculations of optical properties and applications for several materials and compared with existing tabulations.

PRB **80**, 155110 (2009)

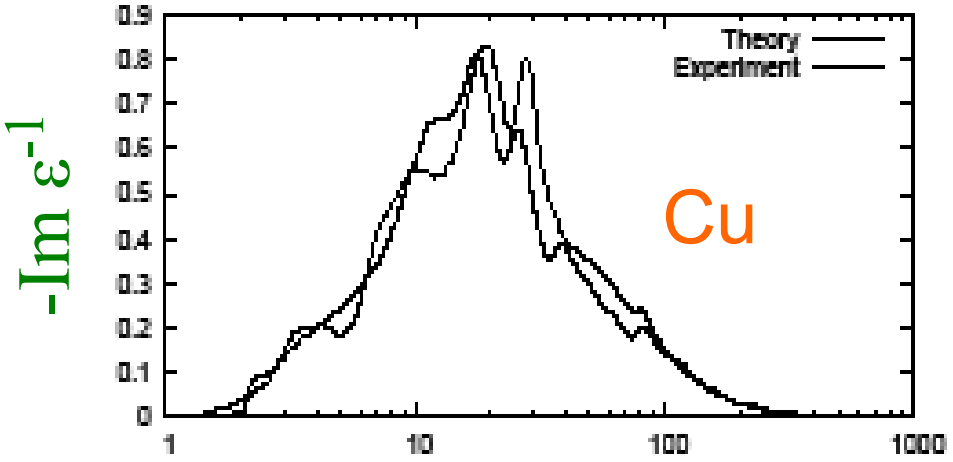


Table 1 – continued fr

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	
.650000E+01	-.582965E+00	.343243E+01	.391885E+00	
.700000E+01	-.510523E+00	.313788E+01	.353755E+00	
.750000E+01	-.431886E+00	.290841E+01	.328818E+00	
.800000E+01	-.358014E+00	.272588E+01	.311956E+00	

*WWW: M. Prange http://leonardo.phys.washington.edu/feff/opcons/

http://www.leonardo.washington.edu/feff/opcons

Optical Constants FEFFOP vs DESY Tables

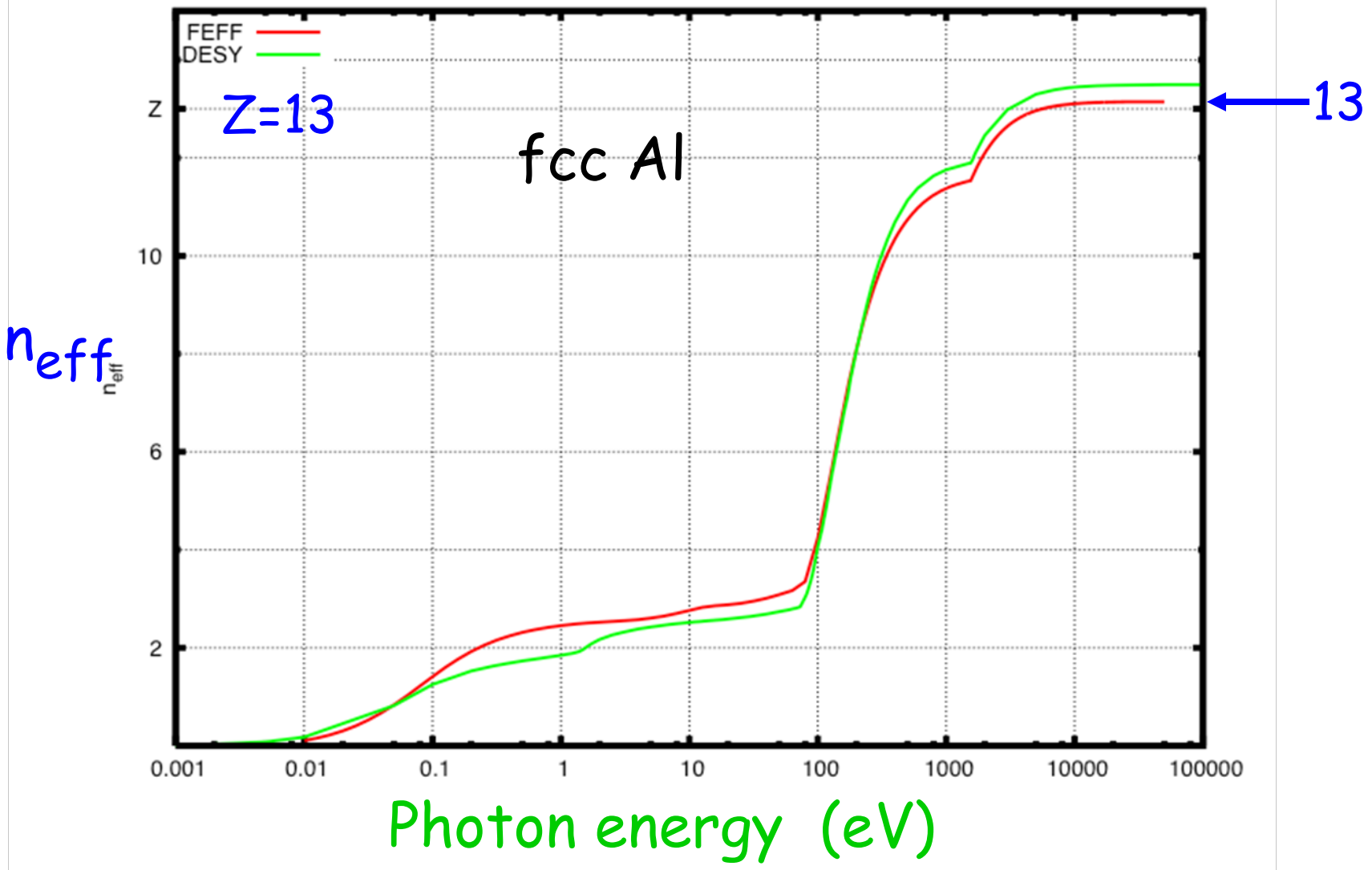
DESY

Energy	epsilon1	epsilon2	n	K	mu	reflect.	Energy loss	n_eff
.200E+02	0.453E+00	0.359E-01	0.673	0.267E-01	0.541E+05	0.38340E-01	0.174E+00	2.586
.300E+02	0.778E+00	0.220E-01	0.882	0.125E-01	0.380E+05	0.39800E-02	0.363E-01	2.638
.400E+02	0.891E+00	0.163E-01	0.944	0.864E-02	0.350E+05	0.86000E-03	0.205E-01	2.688
.500E+02	0.948E+00	0.114E-01	0.974	0.584E-02	0.296E+05	0.19000E-03	0.127E-01	2.736
.600E+02	0.984E+00	0.895E-02	0.992	0.451E-02	0.274E+05	0.20000E-04	0.924E-02	2.778
.650E+02	0.100E+01	0.855E-02	1.001	0.427E-02	0.281E+05	0.40000E-05	0.853E-02	2.799
.670E+02	0.101E+01	0.870E-02	1.005	0.433E-02	0.294E+05	0.10000E-04	0.854E-02	2.807
.690E+02	0.102E+01	0.888E-02	1.009	0.440E-02	0.308E+05	0.20000E-04	0.858E-02	2.817
.700E+02	0.102E+01	0.900E-02	1.012	0.445E-02	0.316E+05	0.40000E-04	0.860E-02	2.821
.710E+02	0.103E+01	0.914E-02	1.015	0.450E-02	0.324E+05	0.60000E-04	0.863E-02	2.826
.720E+02	0.104E+01	0.941E-02	1.021	0.461E-02	0.337E+05	0.11000E-03	0.867E-02	2.832
.725E+02	0.105E+01	0.983E-02	1.026	0.479E-02	0.352E+05	0.17000E-03	0.886E-02	2.834
.727E+02	0.106E+01	0.125E-01	1.031	0.606E-02	0.447E+05	0.24000E-03	0.111E-01	2.835
.729E+02	0.107E+01	0.361E-01	1.036	0.174E-01	0.146E+06	0.39000E-03	0.313E-01	2.838
.731E+02	0.106E+01	0.403E-01	1.030	0.196E-01	0.144E+06	0.31000E-03	0.358E-01	2.843
.733E+02	0.106E+01	0.489E-01	1.028	0.238E-01	0.178E+06	0.33000E-03	0.438E-01	2.848
.735E+02	0.105E+01	0.4[illegible]E-01	1.025	0.240E-01	0.180E+06	0.29000E-03	0.446E-01	2.853
.740E+02	0.104E+01	0.481E-01	1.021	0.236E-01	0.176E+06	0.24000E-03	0.443E-01	2.867
.750E+02	0.103E+01	0.488E-01	1.018	0.240E-01	0.178E+06	0.22000E-03	0.455E-01	2.895
.760E+02	0.103E+01	0.488E-01	1.016	0.240E-01	0.177E+06	0.20000E-03	0.458E-01	2.923
.770E+02	0.103E+01	0.497E-01	1.015	0.245E-01	0.177E+06	0.20000E-03	0.467E-01	2.952
.780E+02	0.103E+01	0.482E-01	1.014	0.238E-01	0.178E+06	0.19000E-03	0.453E-01	2.981
.790E+02	0.103E+01	0.483E-01	1.015	0.238E-01	0.180E+06	0.19000E-03	0.453E-01	3.010
.800E+02	0.103E+01	0.494E-01	1.016	0.243E-01	0.188E+06	0.21000E-03	0.462E-01	3.040

FEFF

Energy	epsilon1	epsilon2	n	K	mu	reflect.	Energy loss	n_eff
.200E+02	0.446E+00	0.331E-01	0.668	0.247E-01	0.502E+05	0.39749E-01	0.165E+00	3.113
.300E+02	0.774E+00	0.293E-01	0.880	0.166E-01	0.506E+05	0.41559E-02	0.488E-01	3.174
.400E+02	0.885E+00	0.247E-01	0.941	0.131E-01	0.532E+05	0.96950E-03	0.315E-01	3.246
.500E+02	0.937E+00	0.183E-01	0.968	0.946E-02	0.480E+05	0.28763E-03	0.209E-01	3.320
.600E+02	0.971E+00	0.128E-01	0.985	0.651E-02	0.396E+05	0.65837E-04	0.136E-01	3.385
.650E+02	0.986E+00	0.107E-01	0.993	0.537E-02	0.353E+05	0.19873E-04	0.110E-01	3.413
.670E+02	0.992E+00	0.995E-02	0.996	0.500E-02	0.339E+05	0.98375E-05	0.101E-01	3.423
.690E+02	0.100E+01	0.937E-02	1.000	0.469E-02	0.328E+05	0.55649E-05	0.937E-02	3.434
.700E+02	0.100E+01	0.912E-02	1.003	0.455E-02	0.323E+05	0.64646E-05	0.904E-02	3.438
.710E+02	0.101E+01	0.892E-02	1.005	0.444E-02	0.320E+05	0.11291E-04	0.875E-02	3.443
.720E+02	0.102E+01	0.926E-02	1.009	0.459E-02	0.335E+05	0.26609E-04	0.893E-02	3.448
.725E+02	0.103E+01	0.154E-01	1.014	0.760E-02	0.559E+05	0.65406E-04	0.145E-01	3.452
.727E+02	0.103E+01	0.186E-01	1.016	0.913E-02	0.673E+05	0.84189E-04	0.174E-01	3.454
.729E+02	0.103E+01	0.217E-01	1.016	0.107E-01	0.790E+05	0.91235E-04	0.204E-01	3.456
.731E+02	0.103E+01	0.249E-01	1.015	0.123E-01	0.909E+05	0.90650E-04	0.235E-01	3.459
.733E+02	0.103E+01	0.280E-01	1.013	0.138E-01	0.103E+06	0.90065E-04	0.267E-01	3.462
.735E+02	0.102E+01	0.305E-01	1.012	0.151E-01	0.112E+06	0.89303E-04	0.291E-01	3.465
.740E+02	0.102E+01	0.312E-01	1.010	0.154E-01	0.116E+06	0.85985E-04	0.299E-01	3.473
.750E+02	0.102E+01	0.325E-01	1.010	0.161E-01	0.122E+06	0.86931E-04	0.313E-01	3.492
.760E+02	0.102E+01	0.340E-01	1.008	0.169E-01	0.130E+06	0.89557E-04	0.328E-01	3.511
.770E+02	0.102E+01	0.330E-01	1.008	0.164E-01	0.128E+06	0.82878E-04	0.320E-01	3.531
.780E+02	0.102E+01	0.321E-01	1.010	0.159E-01	0.126E+06	0.84146E-04	0.309E-01	3.550
.790E+02	0.102E+01	0.332E-01	1.011	0.164E-01	0.131E+06	0.95876E-04	0.317E-01	3.569
.800E+02	0.102E+01	0.354E-01	1.012	0.175E-01	0.142E+06	0.11137E-03	0.337E-01	3.590

Theoretical check: ε_2 Sumrule



Many-pole Self-energy Algorithm*

Plasmon-pole model ⟶ many-pole model

$-\mathrm{Im}\,\varepsilon^{-1}(\omega)$ ⟶ *Many-pole* Dielectric Function

$$\sim \sum_i g_i\,\delta(\omega - \omega_i)$$

⟶ *Many-pole* GW self-energy $\Sigma(E)$

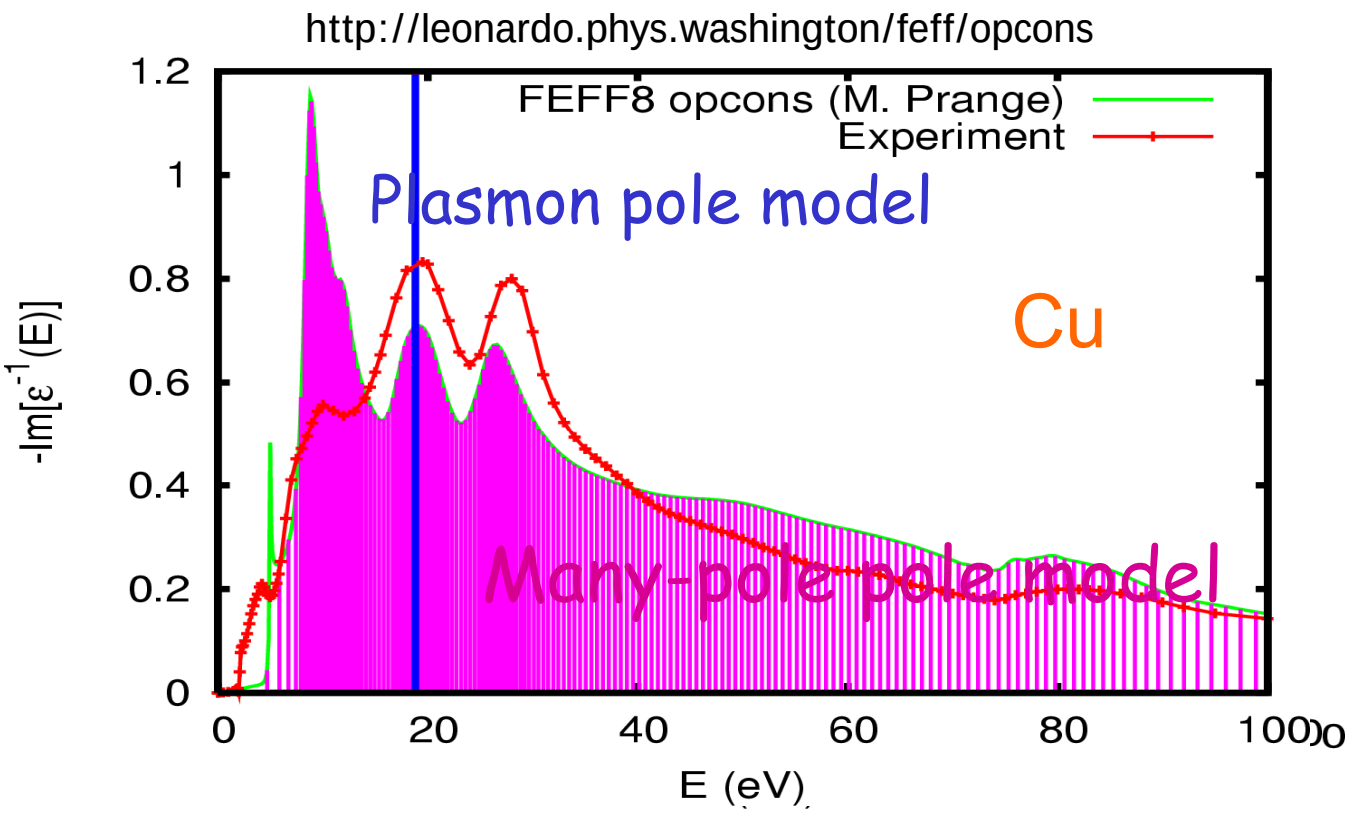
* J. Kas et al. PRB **76**, 195116(2008)

Example: Many-pole model for Cu*

- *ab initio* **q**=0 loss function

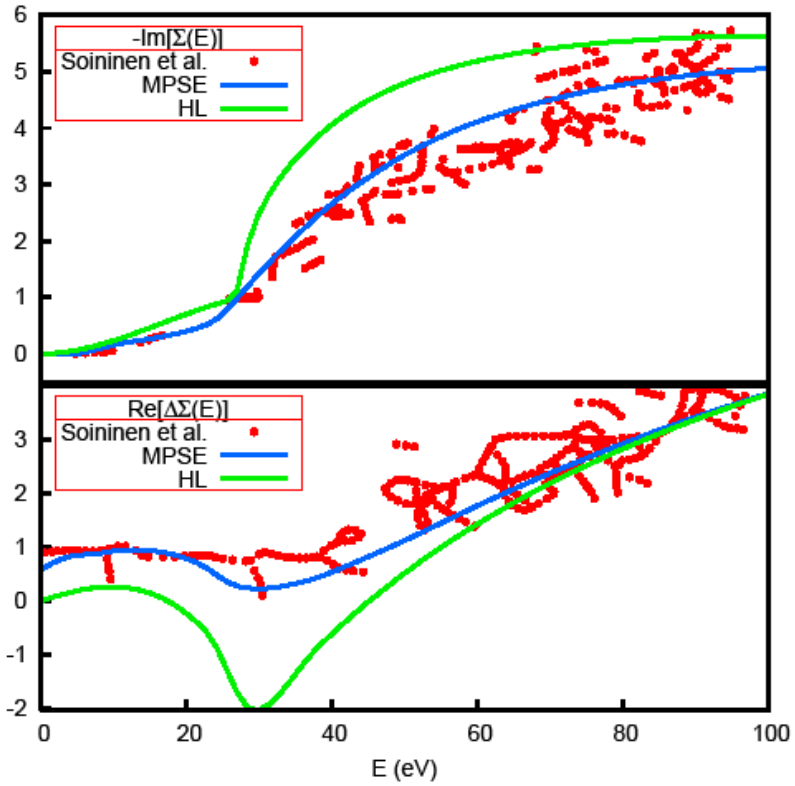
  $-\mathrm{Im}\ \varepsilon^{-1}(\omega)$

- Sum of single pole self-energies



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

Many-pole vs Single Plasmon Pole Self-energy Models



PHYSICAL REVIEW B 76, 195116 (2007)

Many-pole model of inelastic losses in x-ray absorption spectra

J. J. Kas,[1] A. P. Sorini,[1] M. P. Prange,[1] L. W. Cambell,[2] J. A. Soininen,[3] and J. J. Rehr[1]
[1]*Department of Physics, University of Washington, Seattle, Washington 98195, USA*
[2]*Pacific Northwest National Laboratory, Richland, Washington 99352, USA*
[3]*Division of X-ray Physics, Department of Physical Sciences, University of Helsinki, Helsinki FI-00014, Finland*

$\Sigma = \Sigma(E)$ *indep of r*

INSTITUTE OF PHYSICS PUBLISHING — JOURNAL OF PHYSICS: CONDENSED MATTER
J. Phys.: Condens. Matter 15 (2003) 2573–2586 — PII: S0953-8984(03)59657-6

• • • •

Electron self-energy calculation using a general multi-pole approximation

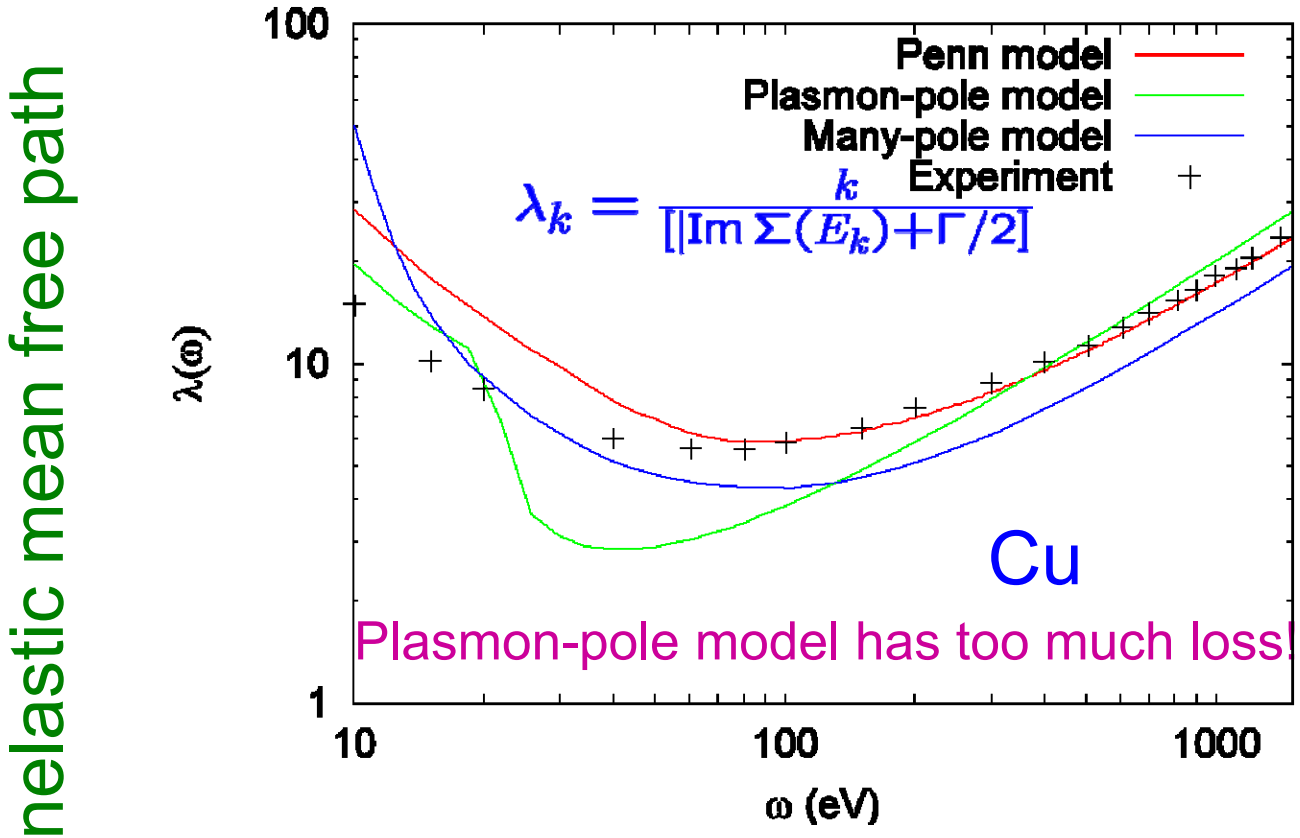
J A Soininen[1], J J Rehr[1] and Eric L Shirley[2]

[1] Department of Physics, University of Washington, Seattle, WA 98195, USA
[2] Optical Technology Division, Physics Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

$\Sigma = \Sigma(E,k)$ **Full GW** (Lanczos)

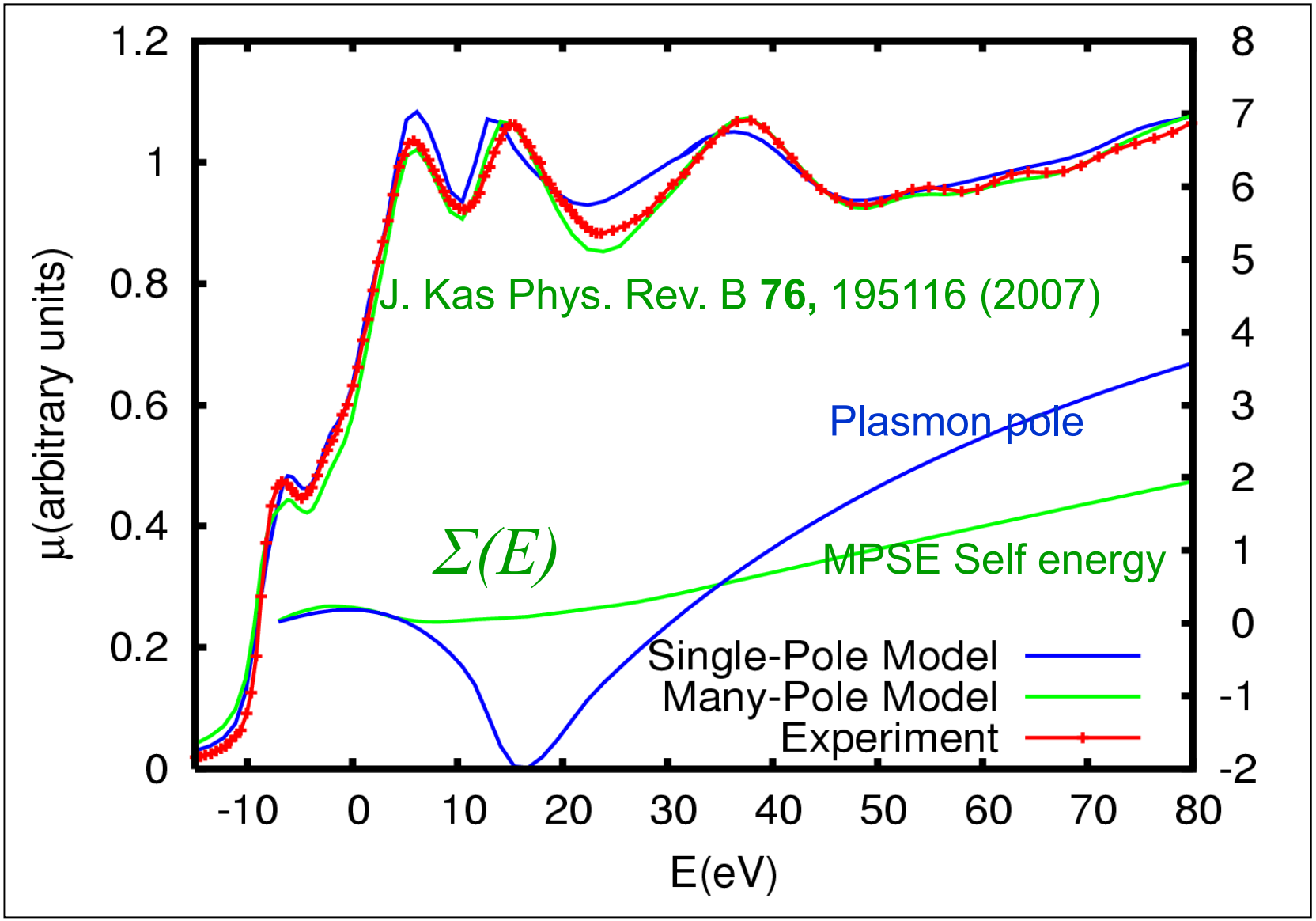
ab initio Inelastic Mean Free Paths

Plasmon-pole model → ***many-pole*** model

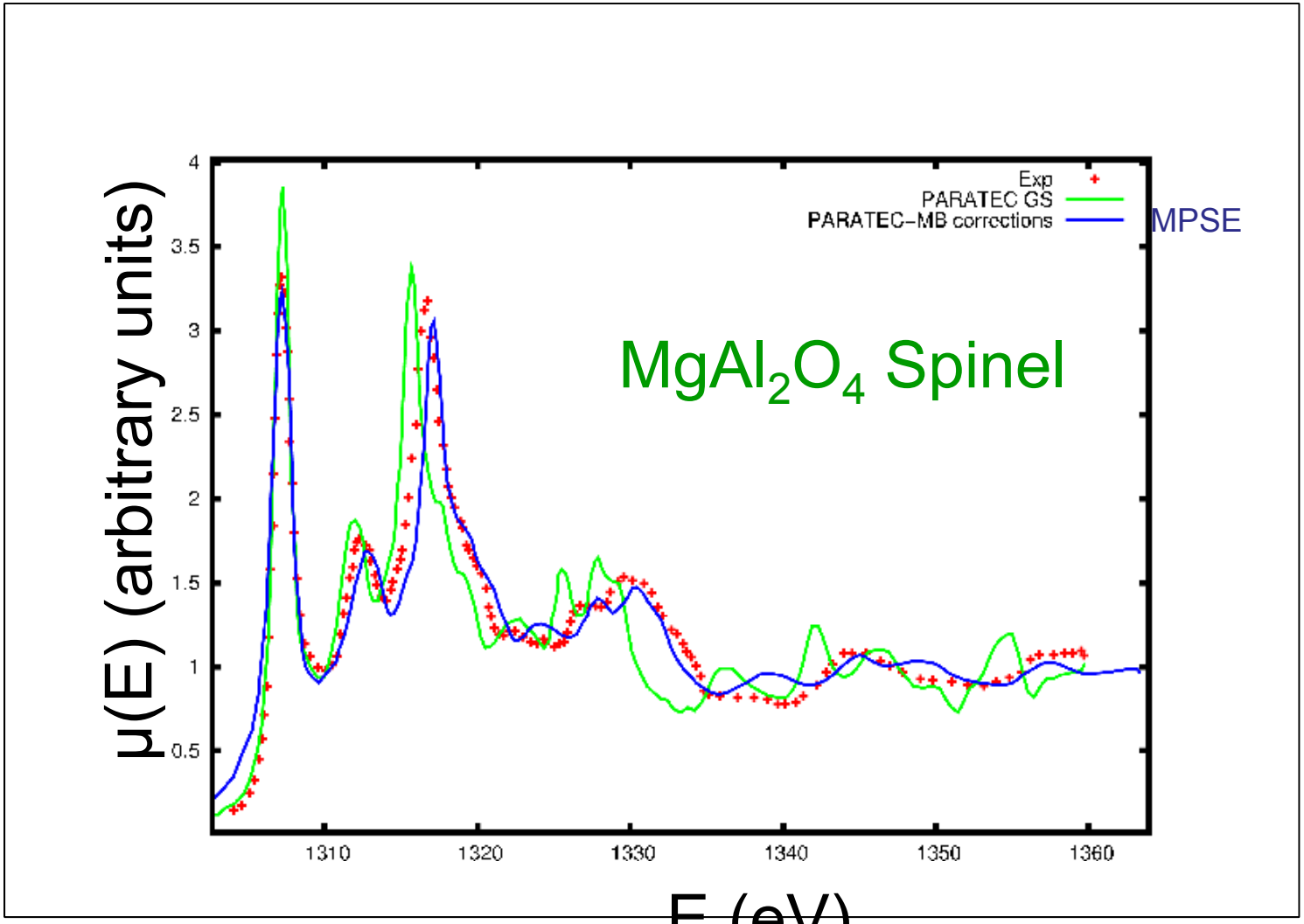


J. Kas et al. **76**, 195116 (2008)

Self-energy Effects in Cu K-edge XAS



Aposteriori Self-energy corrections to DFT and GW codes



PARATEC: D. Cabaret et al. (2008)

B. Intrinsic losses: Multi-electron Excitations

Quasi-boson Model

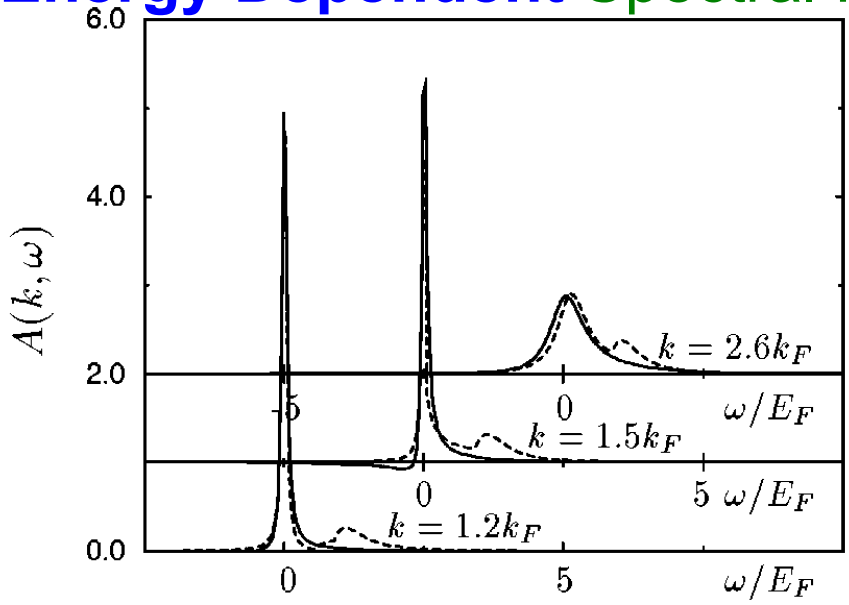
PHYSICAL REVIEW B, VOLUME 65, 064107

Beyond quasiparticles!

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 $A(k,\omega)$

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

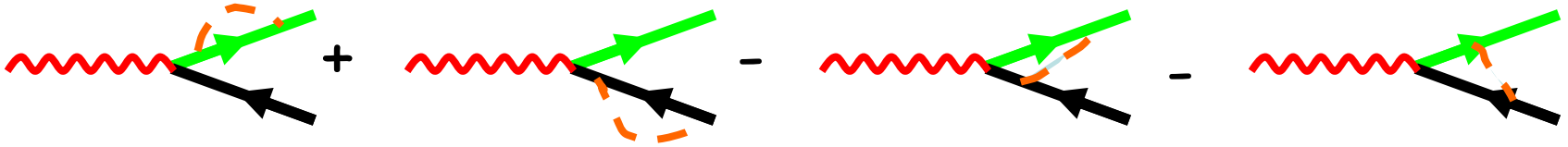
$V^n \rightarrow -\mathrm{Im}\, \varepsilon^{-1}(\omega_n, q_n)$ fluctuation potentials

*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: $A(\omega) = -(1/\pi)\ \mathbf{Im}\ g_{eff}(\omega)$

Effect on Spectra: Amplitude reduction

- XAS = Convolution with **spectral function** $A(\omega, \omega')$

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

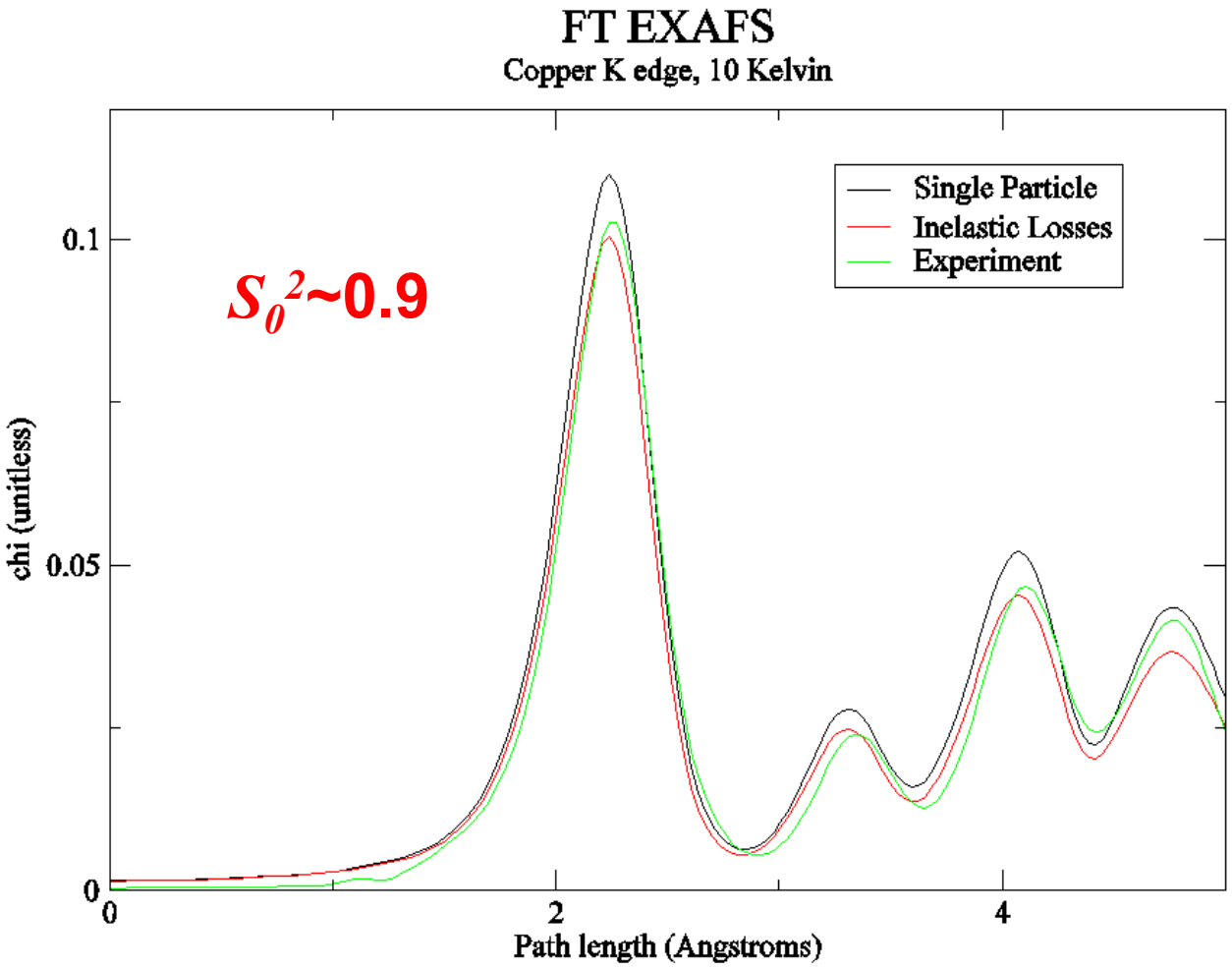
$$\equiv \langle \mu_{qp}(\omega) \rangle \approx \mu_{qp}(\omega) \, S_0^2$$

- Explains crossover: **adiabatic**

to sudden approximation

Many-body amplitude reduction in EXAFS

Quantitative *R*-space EXAFS



C. Core-hole and local field effects

PHYSICAL REVIEW B 71, 165110 (2005)

Combined Bethe-Saltpeter equations and time-dependent density-functional theory approach for x-ray absorption calculations

A. L. Ankudinov, Y. Takimoto, and J. J. Rehr
Department of Physics, University of Washington, Seattle, Washington 98195-1560, USA
(Received 23 December 2004; published 14 April 2005)

Two step approach to TDDFT/BSE

$$\chi = (1 - K\chi_0)^{-1}\chi_0 \qquad K = V + W$$

1) $\chi' = (1 - V\chi_0)^{-1}\chi_0$ χ ~ RPA response

2) $\chi = (1 - W\chi')^{-1}\chi'$ W ~ RPA core hole

Step 1: Local Field Effects

- Transition operator ***not*** *external x-ray field* φ^{ext}
  Must include polarization $\varphi = \varphi^{ext} + \varphi^{induced}$
  $= \varepsilon^{-1} \varphi^{ext}$

$\varepsilon = 1 - K\chi^0$ Dielectric matrix

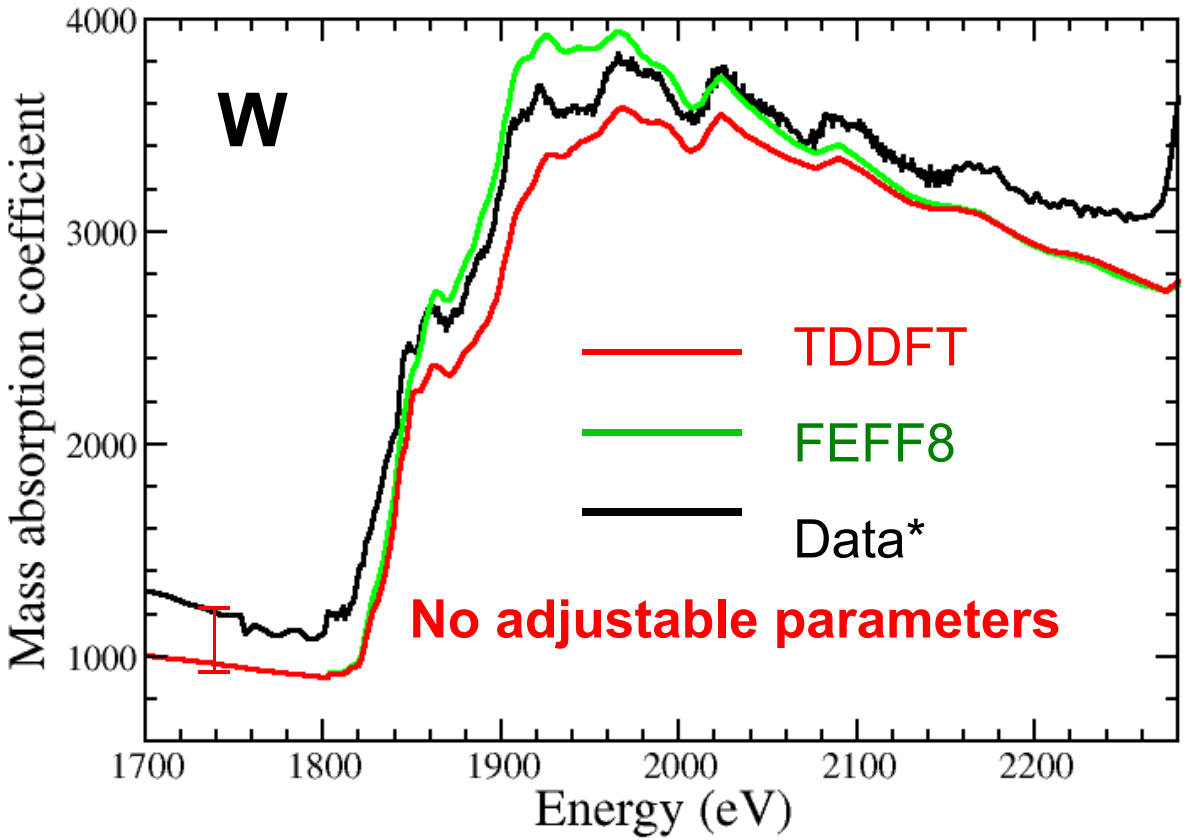
$K = V$ *RPA* *(or* $V + f_{xc}$ *for TDDFT)*

⟶ Golden rule with *screened matrix elements** $\tilde{M}$

$$\sigma(\omega) = \frac{4\pi\omega}{c} \sum_{i,LL'} f_i \tilde{M}^*_{iL}(\omega) \rho_{LL'}(E) \tilde{M}_{iL'}(\omega),$$

*A. Zangwill + P Soven, Phys Rev A **21**, 1561 (1980)

Example: local field effects in XAS TDDFT



*Data: Z. Levine et al. J. Research. NIST 108, 1 (2003)

Step 2. Screened Core Hole

Corrections to *ad hoc* core-hole approx

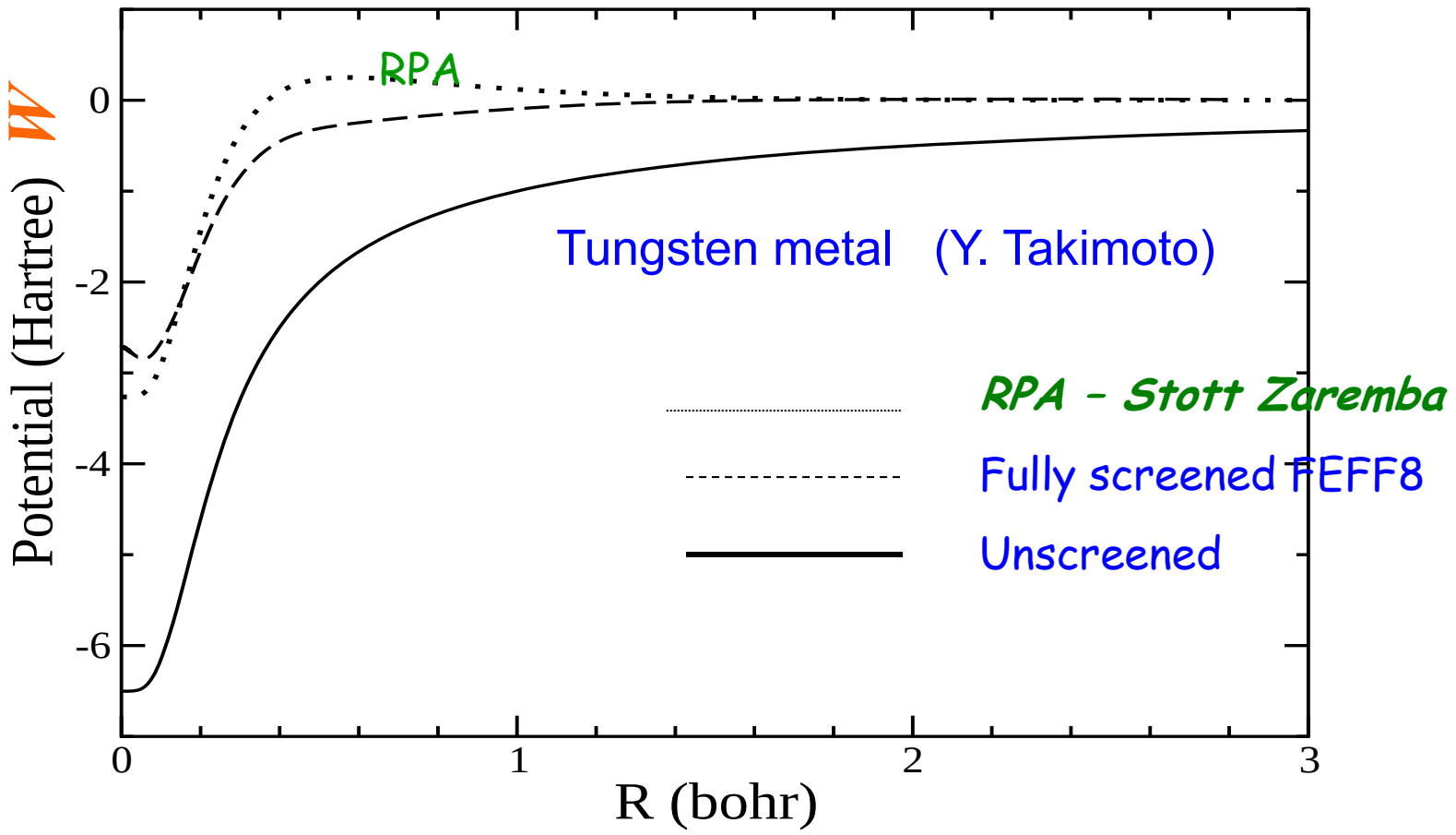
final state rule, Z+1, half-core hole …

Stott-Zaremba algorithm (= static RPA)

$$W = \varepsilon^{-1} V_{ch}$$

Approx: Include W in $g' = 1/(E - h' - \Sigma)$

as in quasi-boson model


RPA
W
Potential (Hartree)
0
-2
-4
-6
0
1
2
3
R (bohr)
Tungsten metal (Y. Takimoto)
RPA - Stott Zaremba
Fully screened FEFF8
Unscreened

D. *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)

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

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

$$\rho(\omega^2) = \langle Q_i | \delta(\omega^2 - D) | Q_i \rangle \quad = \text{ VDOS}$$

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

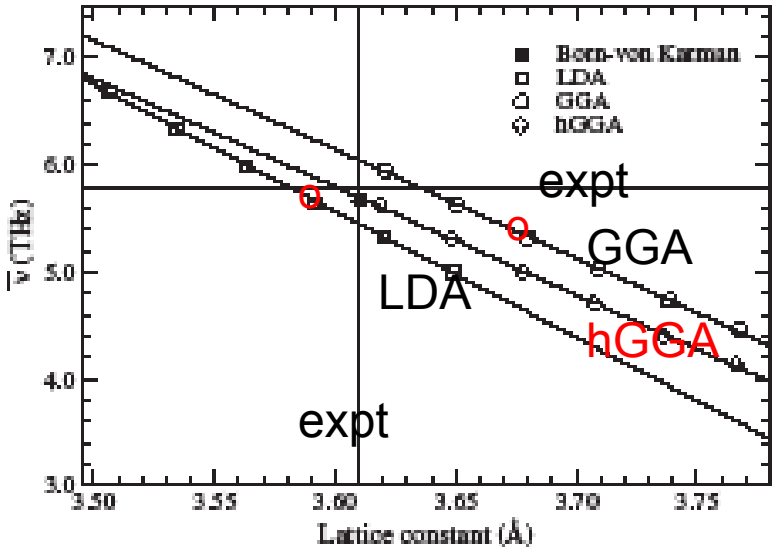
D = Dynamical matrix

Replaces correlated Debye and Einstein Models !

***Ab initio* DFT** Phonon Green's function

$$\mathbf{G} = (\omega^2 - \boldsymbol{D})^{-1}$$

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

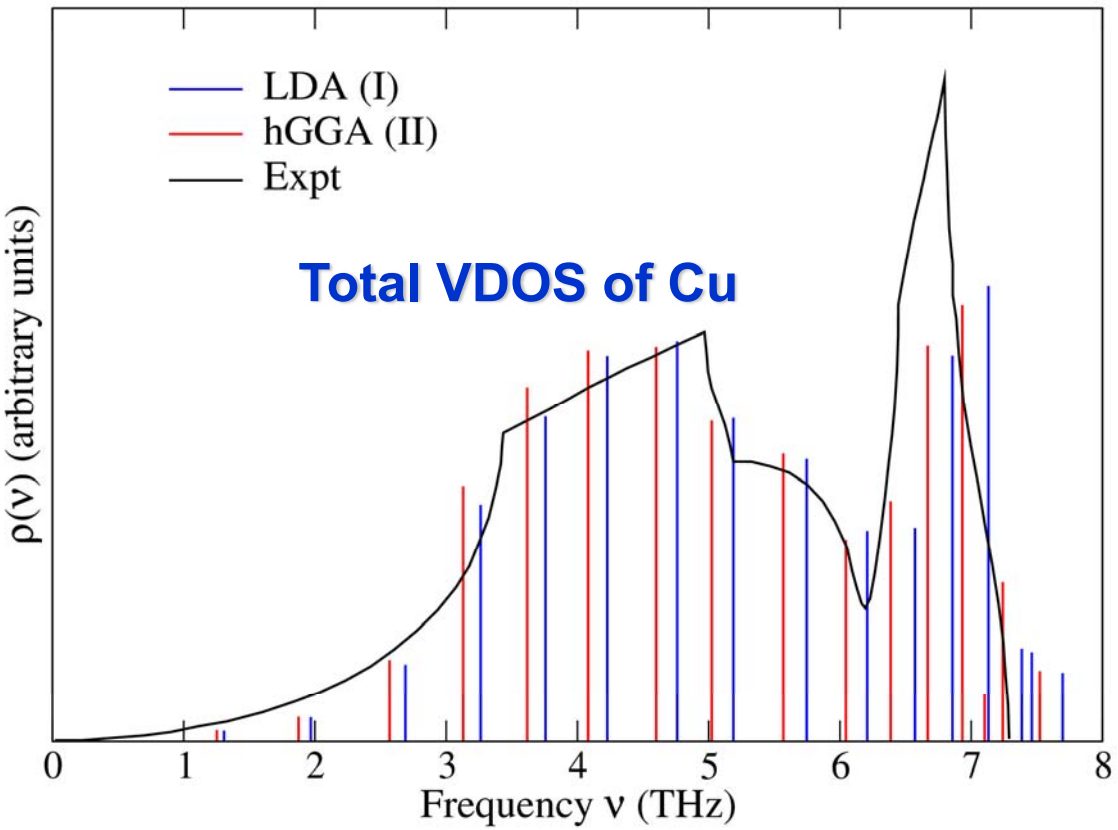


NB: ***Need functional for both bond lengths and phonons:***

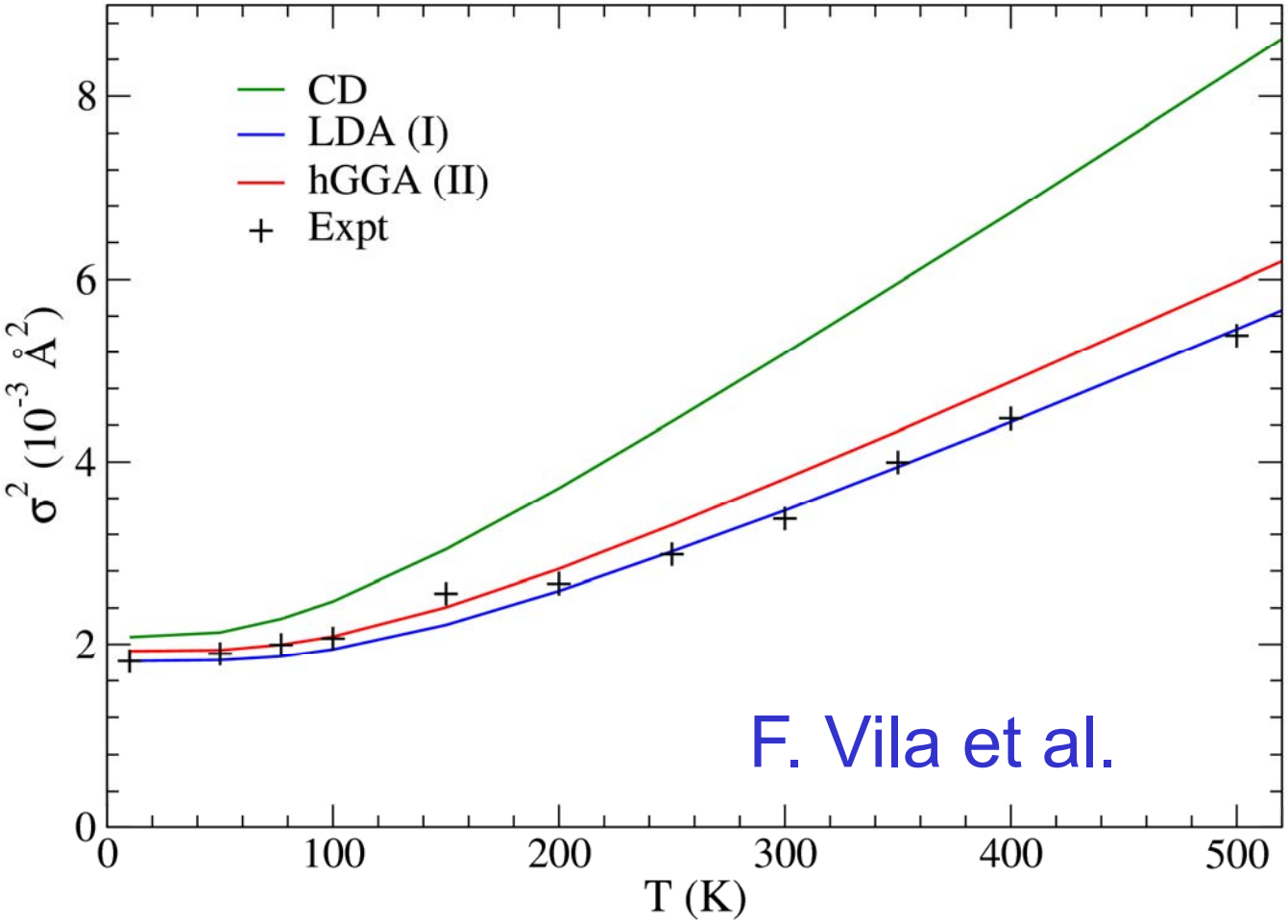
"hGGA" = **"half and half PBE"**

Strong correlation between lengths a and $\langle\omega\rangle$

Lanczos Recursion (Many-pole)

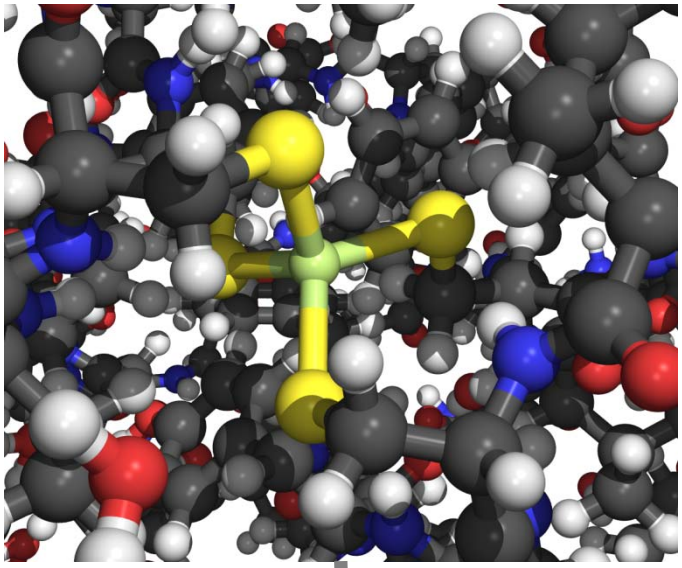


XAFS Debye-Waller Factor of Ge



Expt: Dalba *et al.* (1999)

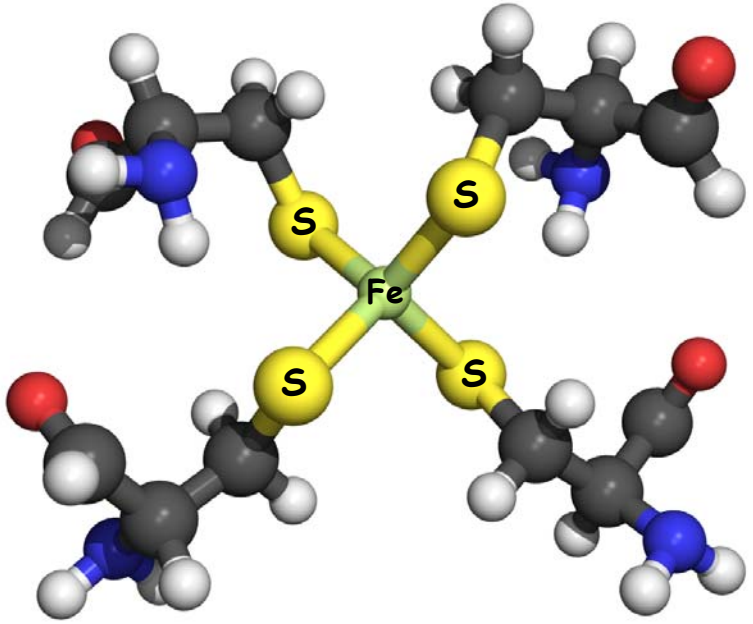
Ab Initio Debye-Waller Factors in Rubredoxin



σ^2 (in 10^{-3} Å^2)

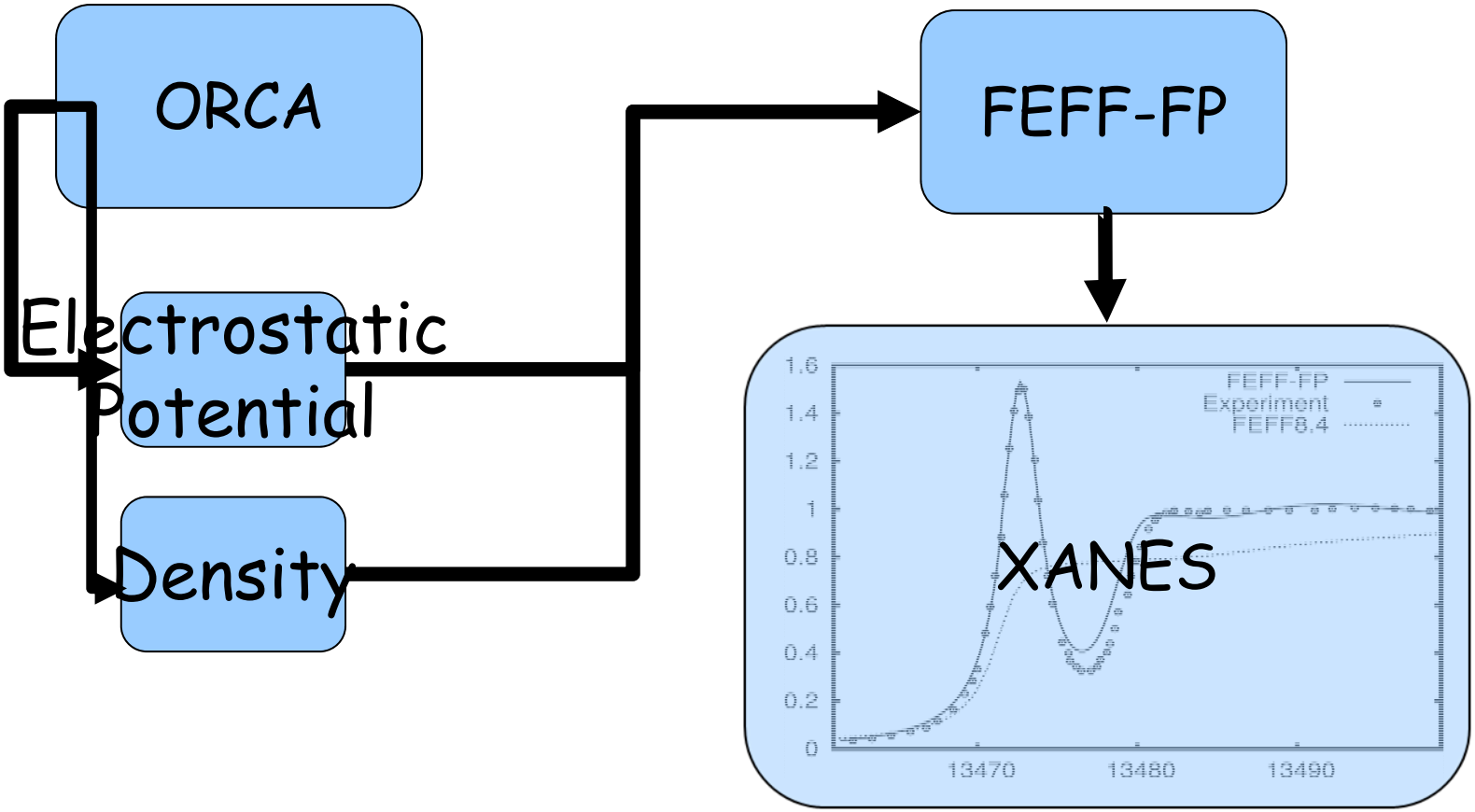
Path	Theory	Exp.
Fe-S_1	2.9	2.8±0.5
Fe-S_2	2.9	2.8±0.5
Fe-S_3	3.3	2.8±0.5
Fe-S_4	3.5	2.8±0.5

Convert Full System into Smaller Model



F. Full Potential Multiple Scattering* *In progress*

Interface with ORCA FP-SCF code (J. Kas)



*A. L. Ankudinov and J. J. Rehr, *Physica Scripta,* **T115,** 24 (2005)

CONCLUSIONS

- Parameter free *ab initio* RSGF approach for electronic & vibrational structure & spectra: VIS - X-ray, EELS, NRIXS, …

- Attractive alternative to k-space approach

- Efficient relativistic all electron code **FEFF9**

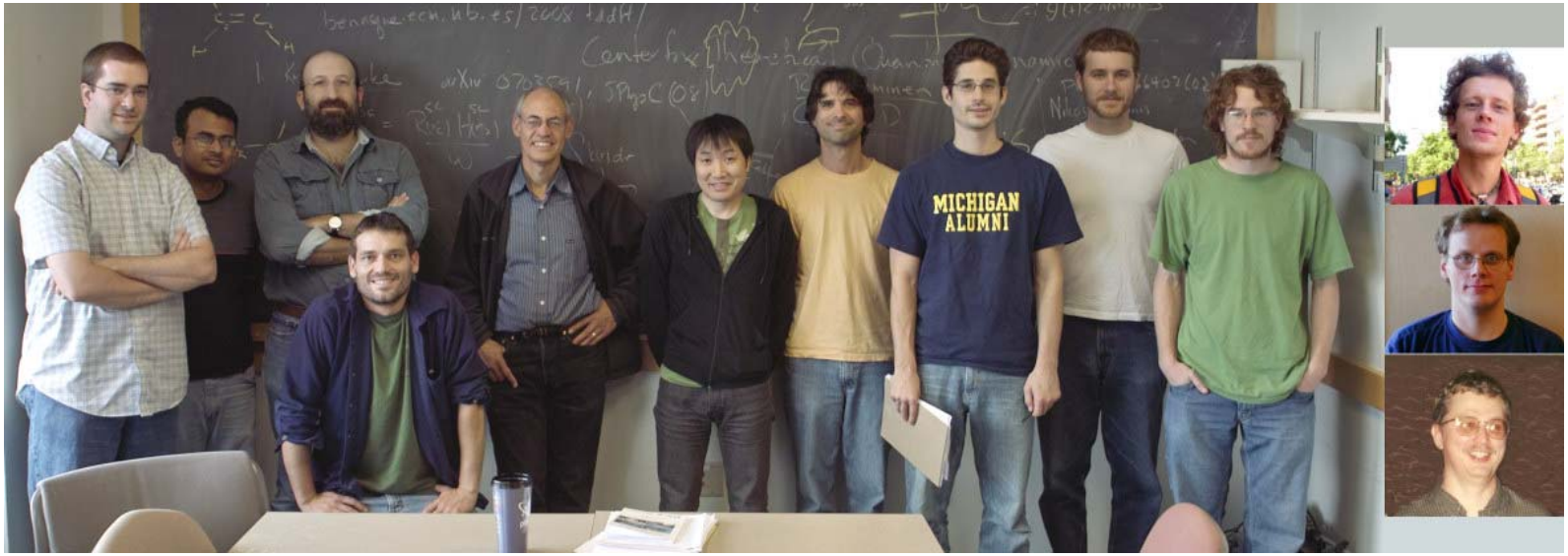
Acknowledgments

Rehr Group

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

Collaborators

A.L. Ankudinov (APD)
R.C. Albers (Los Alamos))
Z. Levine (NIST)
E. Shirley (NIST)
A. Soininen (U. Helsinki)
H. Krappe (HZB)
H. Rossner (HZB)



Supported by DOE BES & NIST

That's all folks