

# Theory and Calculation of X-ray spectra

J. J. Kas



# Theoretical Spectroscopy Calculations

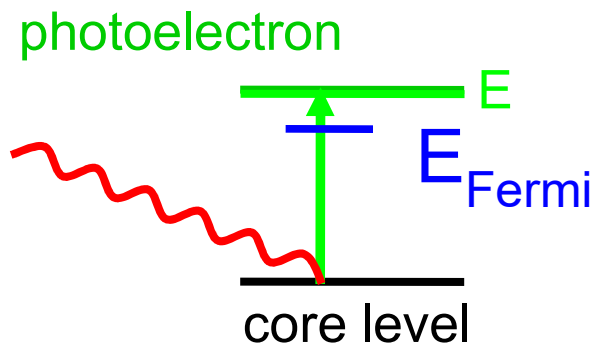
- **GOAL:** Next Generation Theory  
for Next Generation X-ray Sources

- **TALK**

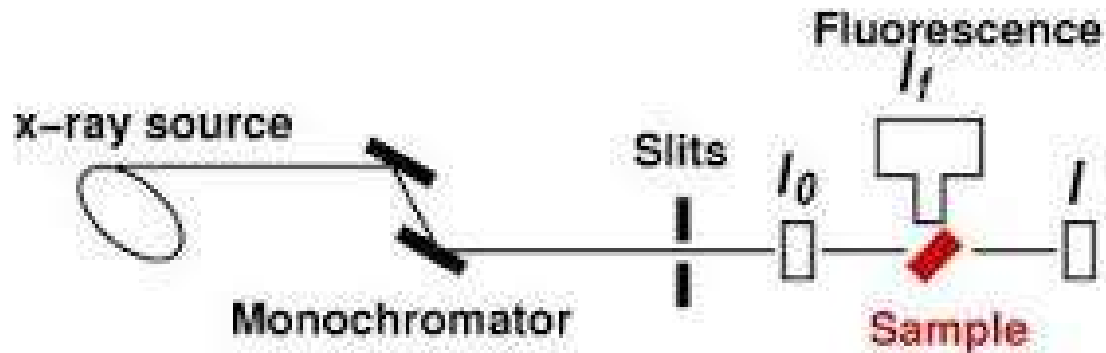
- I Introduction
- II State-of-the-art
- III Next generation

Current approximations  
Ab initio calculations  
Multi-electron excitations  
& strong correlations

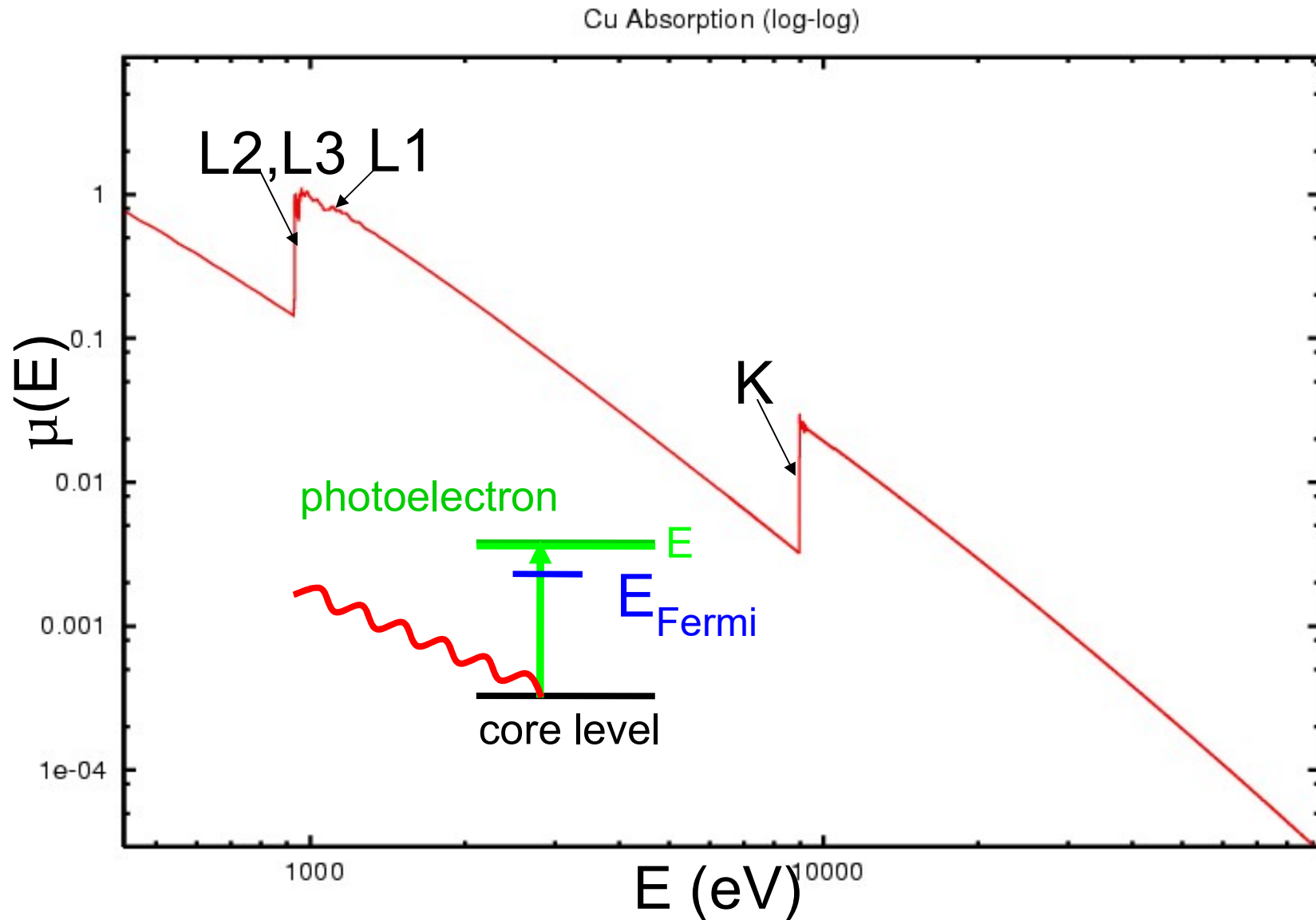
# What is x-ray absorption?



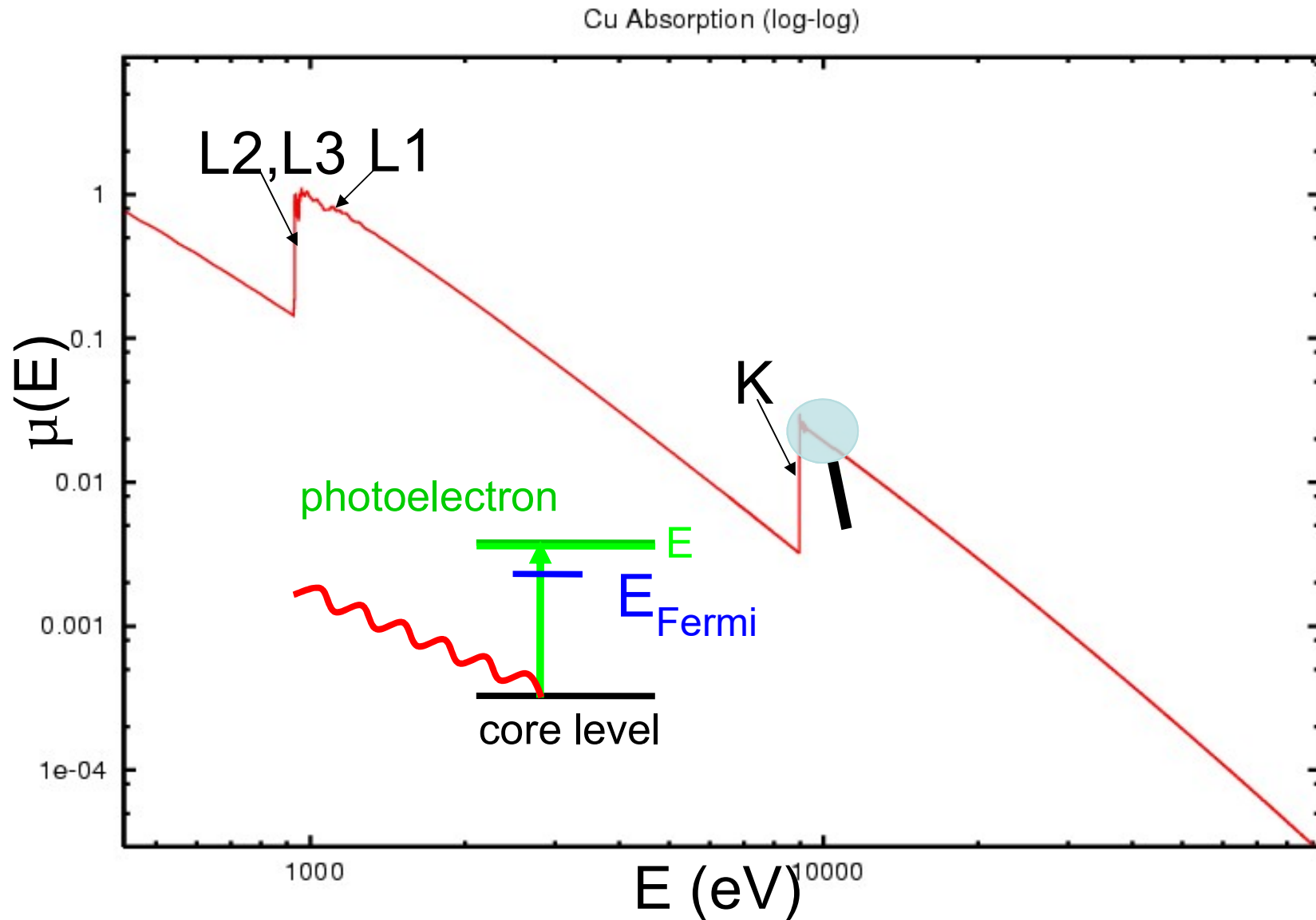
$$I = I_0 e^{-\mu(\omega)x} \Rightarrow \mu(\omega) \propto \text{Log}[I_0 / I]$$



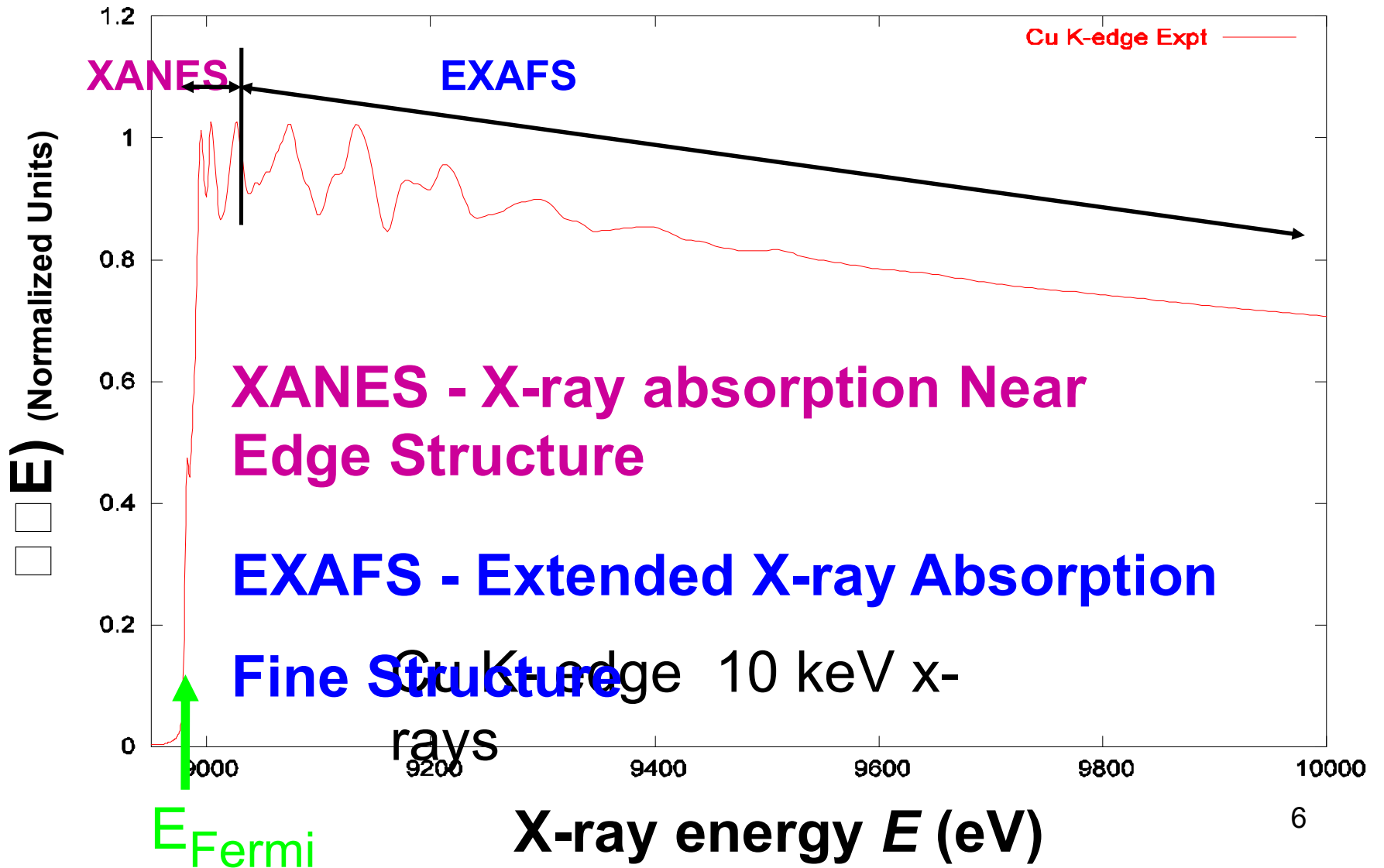
# What is x-ray absorption?



# What is x-ray absorption?

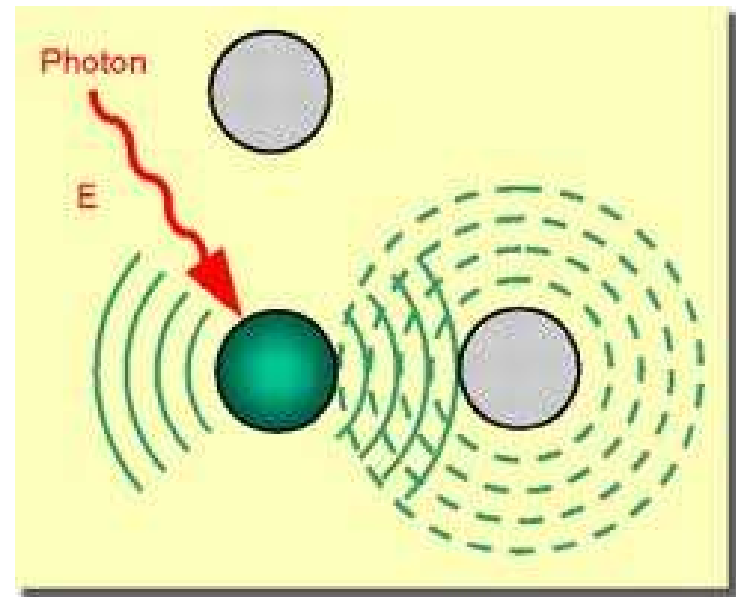


# What is EXAFS?



# What is EXAFS?

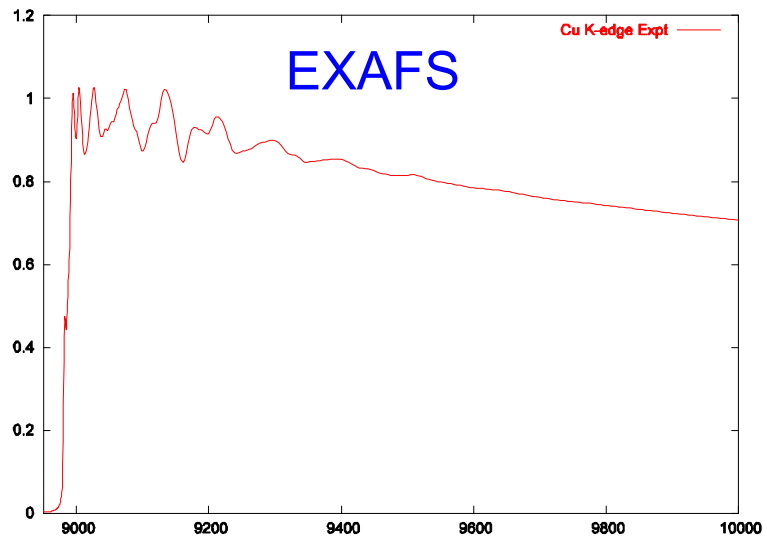
- Quantum interference



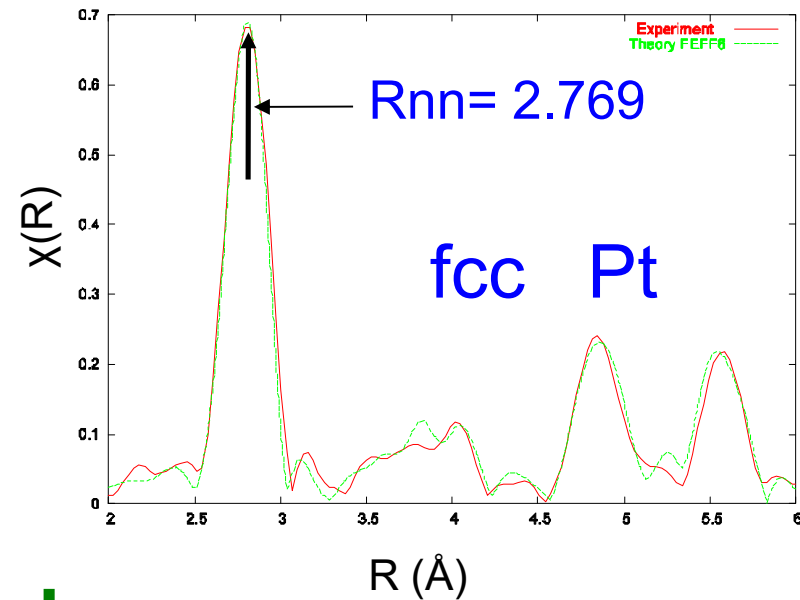
# Qualitative Interpretation

**D.Sayers** Stern & Lytle 1970

Short range order theory



EXAFS Fourier transform –  
radial distribution function



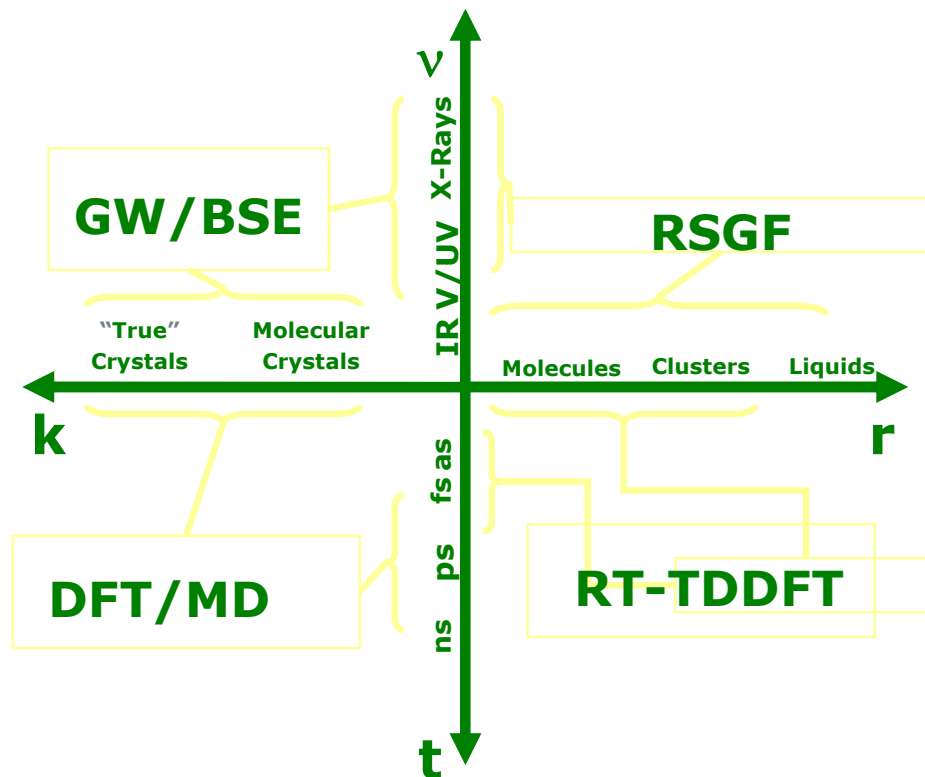
→ **X-ray Microscope!**



# Introduction

Promise of Next generation Light sources: NSLSII, LCLS ...

Powerful probes of multiple length and time scales  
Partial solution to DOE 5 Grand Challenges, etc.

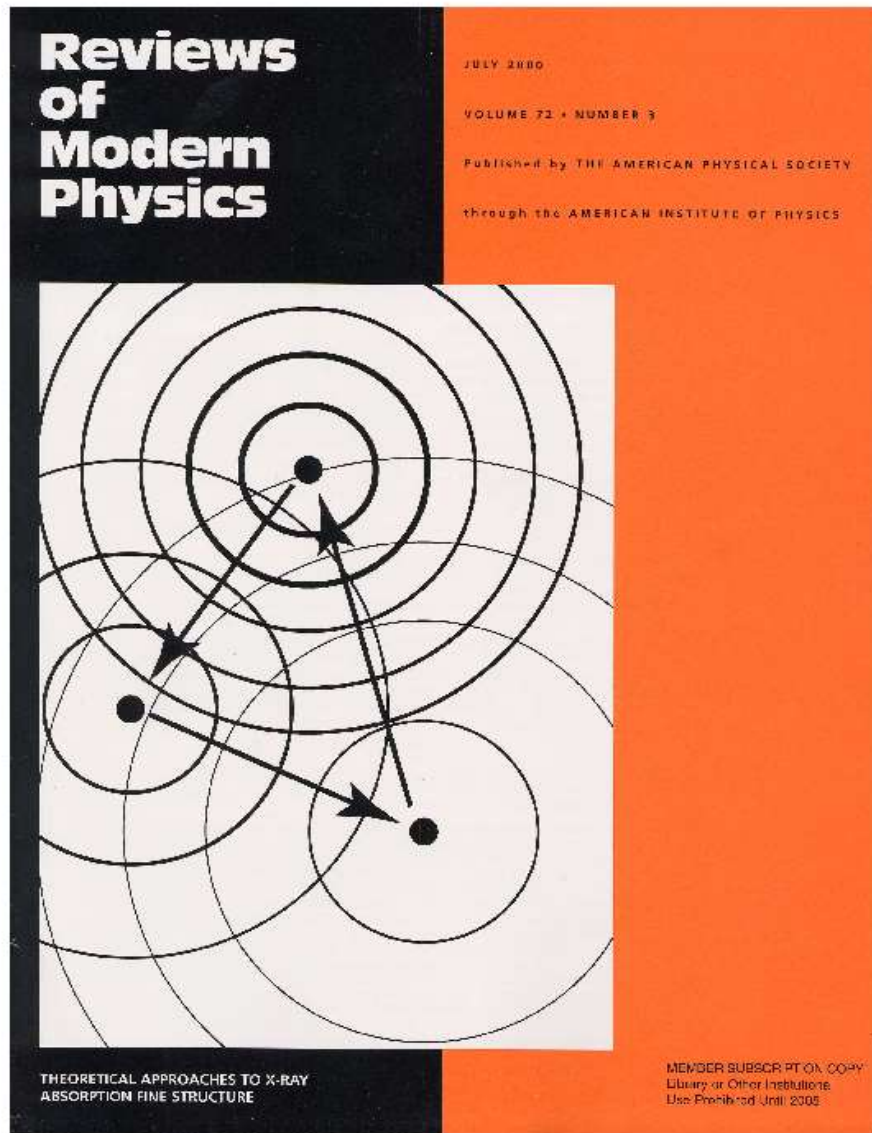


**BUT**

**Promise cannot be fully  
exploited without**

Next generation theory  
& software

# I Current methods



## EXAFS & XANES

Automated & Integrated  
XAS codes

FEFF

> 20 yrs development

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

# Real-space Green's Function (RSGF) Theory VIS – X-ray

~~Fermi golden rule via Wave Functions~~

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



Paradigm shift:

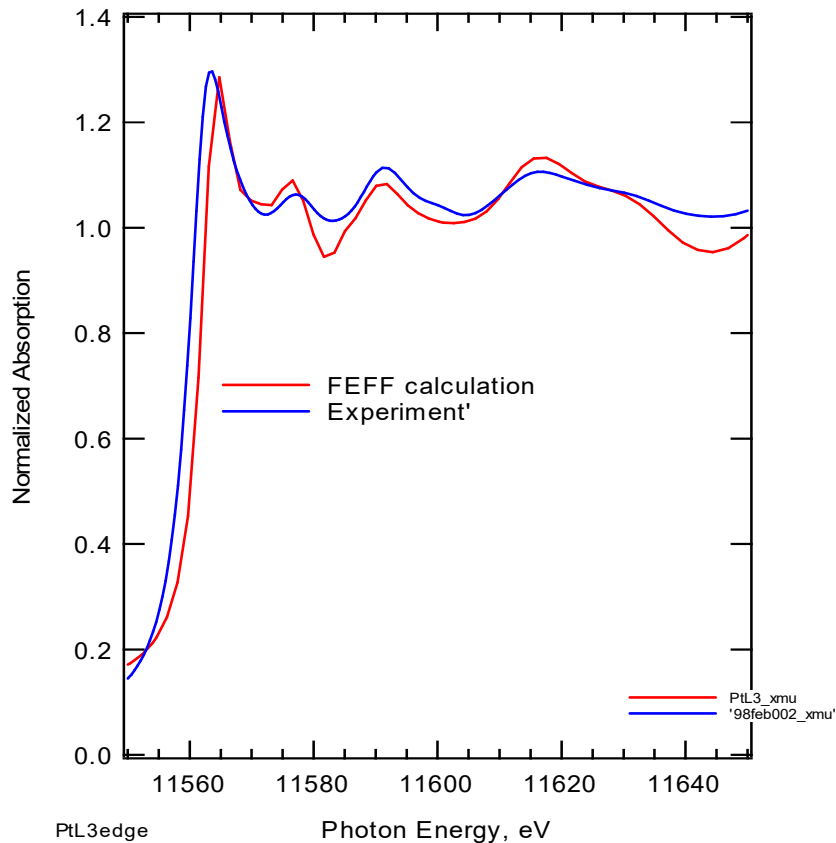
Golden rule via Green's Functions  $\mathbf{G} = 1/(E - h - \Sigma)$

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

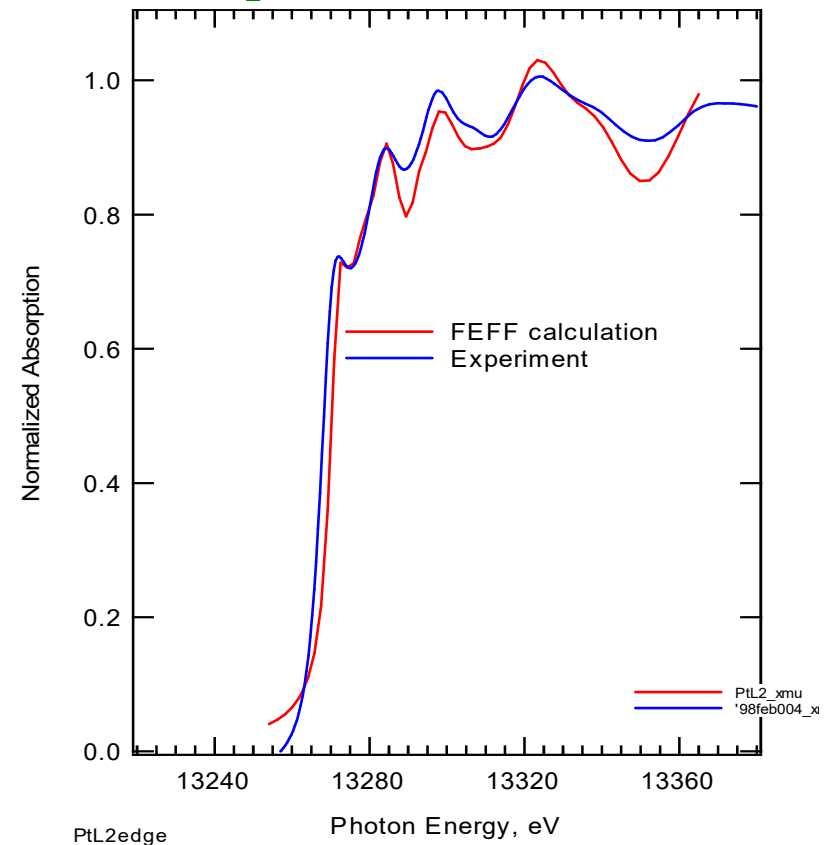
**EFFICIENT: No sums over final states !**

# Example: Pt XANES full multiple-scattering

Pt L<sub>3</sub>-edge



Pt L<sub>2</sub>-edge (S. Bare, UOP)



- Good agreement: *Relativistic* FEFF8 code reproduces all spectral features, *including absence of white line at L<sub>2</sub>-edge*.
- *Self-consistency essential*: position of Fermi level strongly affects white line intensity.

# Spectra: RIXS, XES, Compton, ...

PHYSICAL REVIEW B 83, 235114 (2011)

## Real-space Green's function approach to resonant inelastic x-ray scattering

J. J. Kas,<sup>1</sup> J. J. Rehr,<sup>1,\*</sup> J. A. Soininen,<sup>2</sup> and P. Glatzel<sup>3</sup>

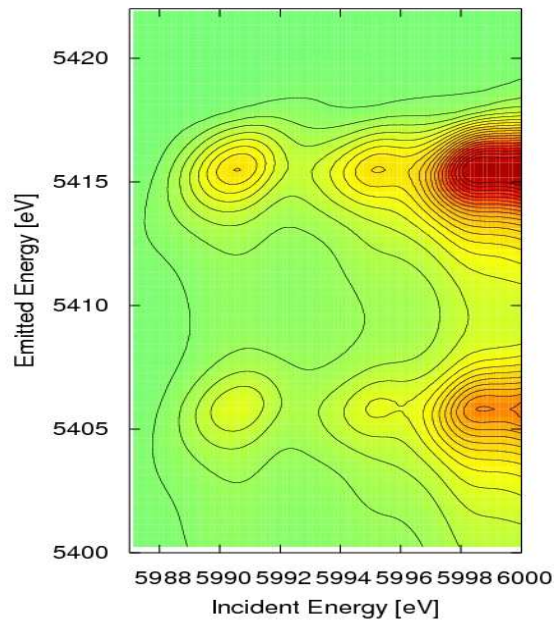
<sup>1</sup>Department of Physics, Box 351560, University of Washington, Seattle, Washington 98195-1560, USA

<sup>2</sup>Department of Physics, P.O. Box 64, University of Helsinki, FI-00014 Helsinki, Finland

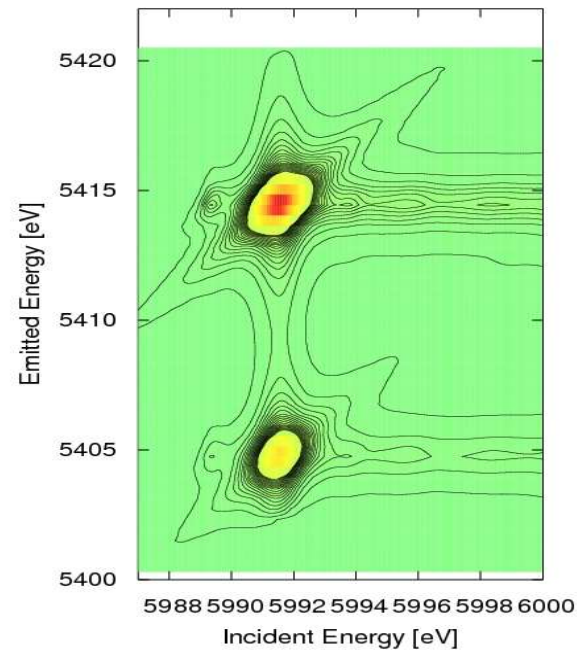
<sup>3</sup>European Synchrotron Radiation Facility, B.P. 220, F-38043 Grenoble, France

$$\frac{d^2\sigma}{d\Omega d\omega} \propto \frac{\omega}{\Omega} \int d\omega_1 \frac{\mu_e(\omega_1)\mu(\Omega - \omega - \omega_1 + E_b)}{|\omega - \omega_1 - i\Gamma_b|^2}$$

Cr<sub>2</sub>O<sub>3</sub> K alpha RIXS



K<sub>2</sub>CrO<sub>4</sub> K alpha RIXS

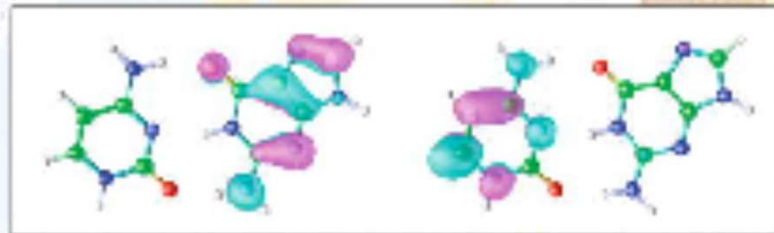


# COMPTES RENDUS DE L'ACADÉMIE DES SCIENCES

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ISSN 0764-4467

## PHYSIQUE



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

DOSSIER

Theoretical spectroscopy / Spectroscopie théorique

Guest editors / Rédacteurs en chef invités :  
Lucia Reining

ACADÉMIE DES SCIENCES - PARIS



## II. State of the art theory

### FEFF9

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

# State of the art theory

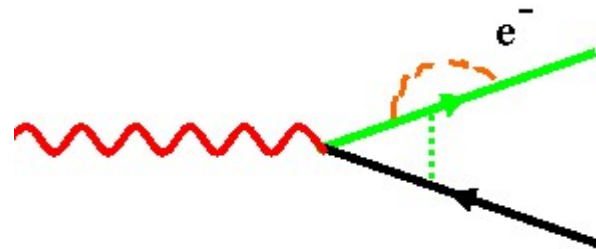
**GOAL: ab initio many-body effects**

***no adjustable parameters***

GW Self-energy

Debye Waller factors

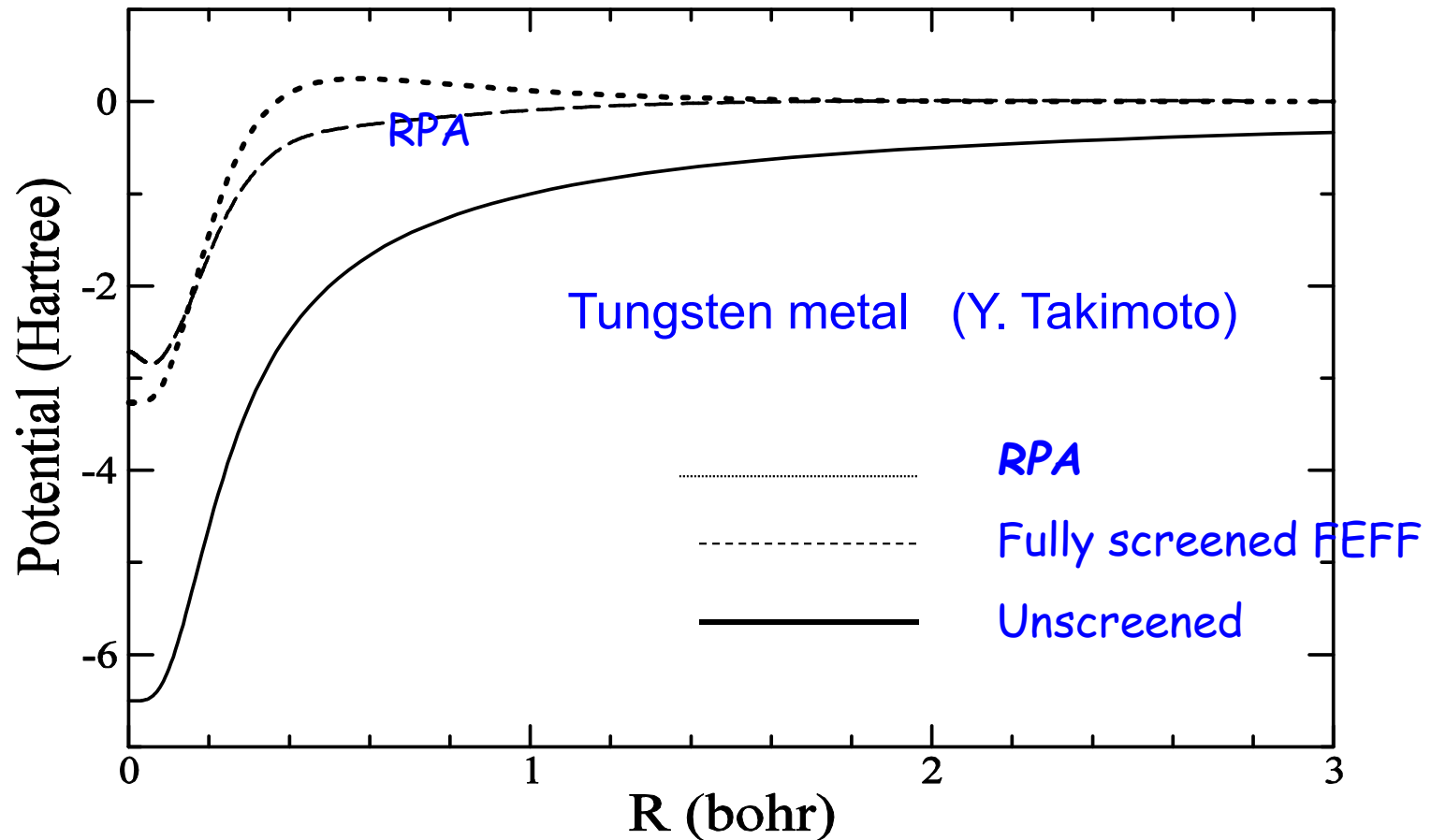
RPA core-hole



Need: **multiple codes**: DFT, self-energy, Phonons

No one group or code can do it all

# RPA Core-hole potential



\* Also used in BSE

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

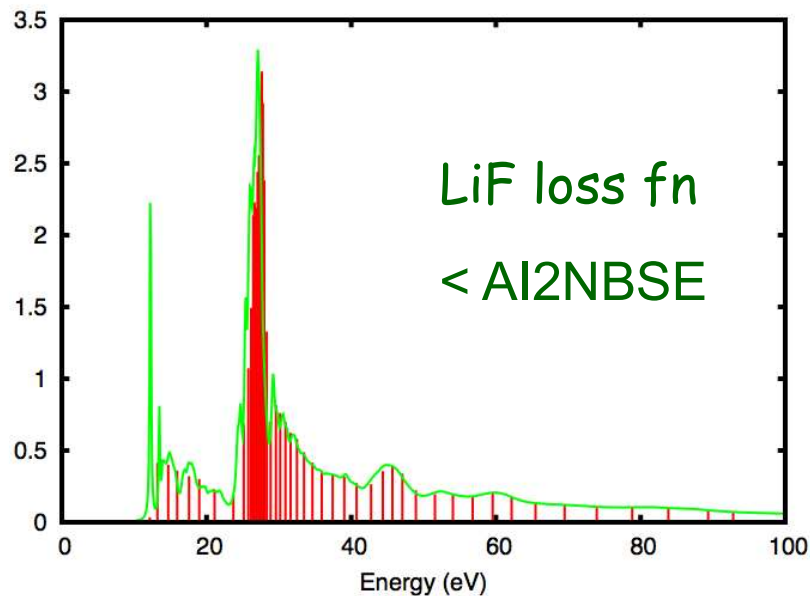


# Many-pole GW Self-energy

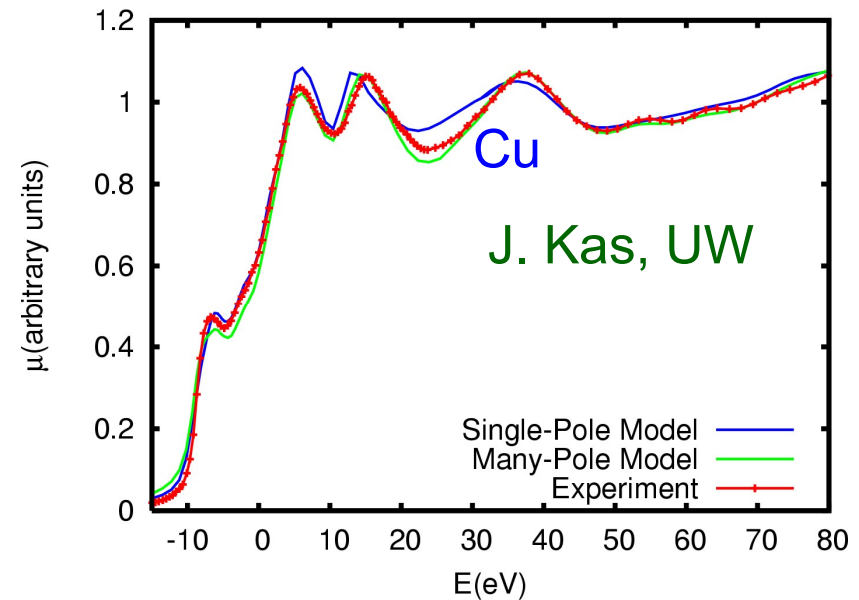
Energy dependent  $\Sigma(E)=iGW$  – replaces  $V_{xc}$

*MFP, energy shifts*

cf. Hedin-Lundqvist plasmon-pole



## Improved XANES



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

# 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*

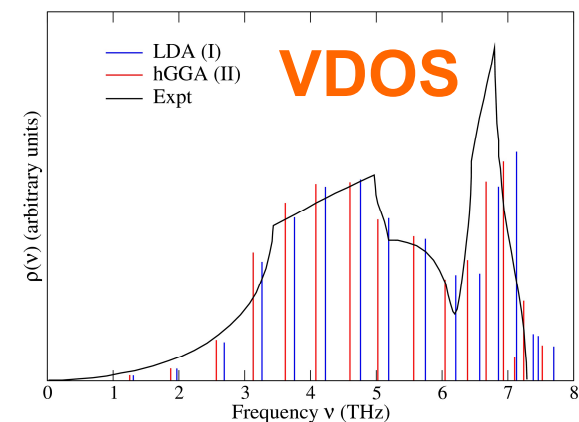
H. H. Rossner and H. J. Krappe  
*Hahn-Meitner-Institut Berlin, Glienicker Strasse 100, D-14109 Berlin, Germany*  
(Dated: August 23, 2005)



Many Pole model  
for phonons

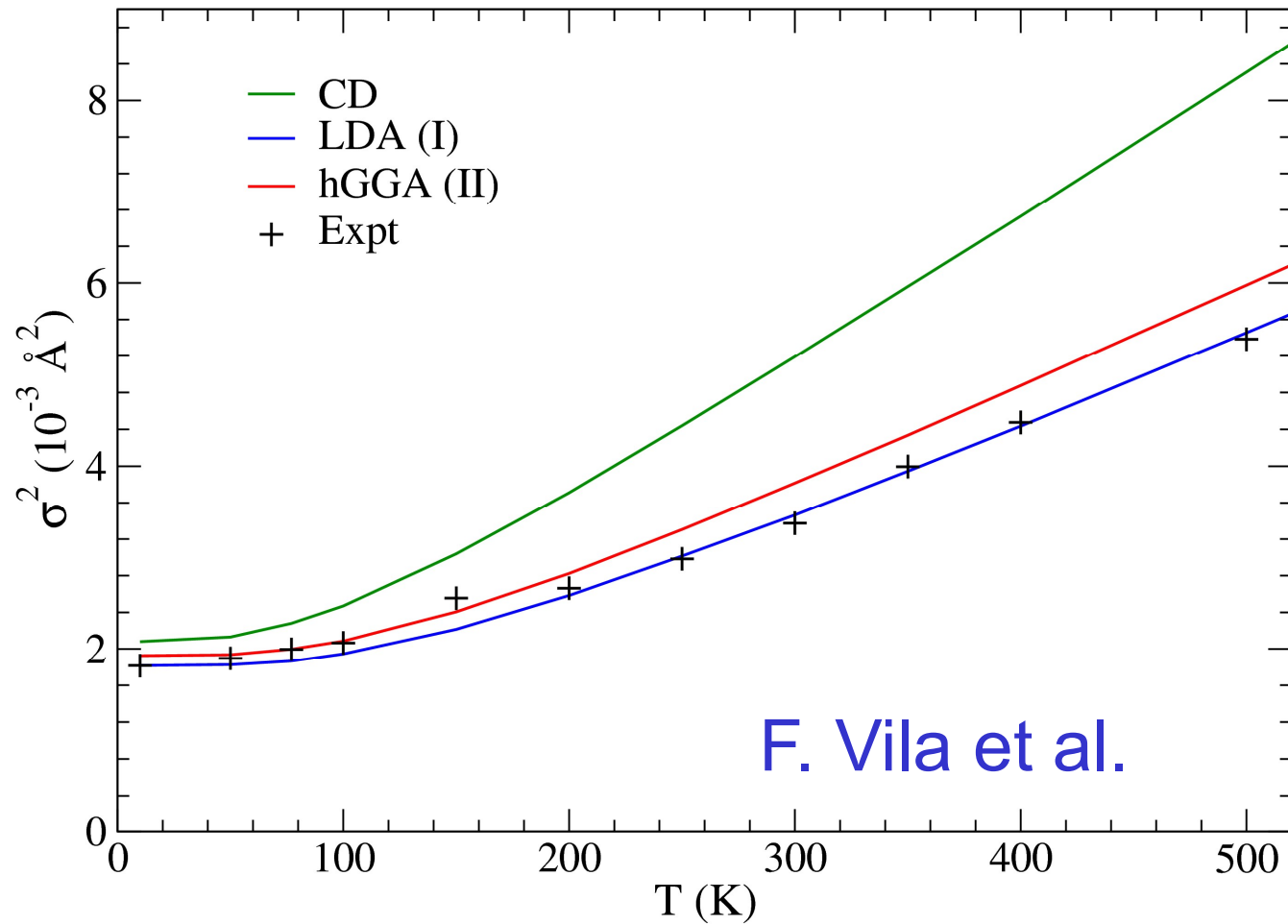
$$\sigma^2 = \frac{\hbar}{\mu_i} \int_0^\infty \rho(\omega^2) \coth \frac{\beta \hbar \omega}{2} d\omega$$

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



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

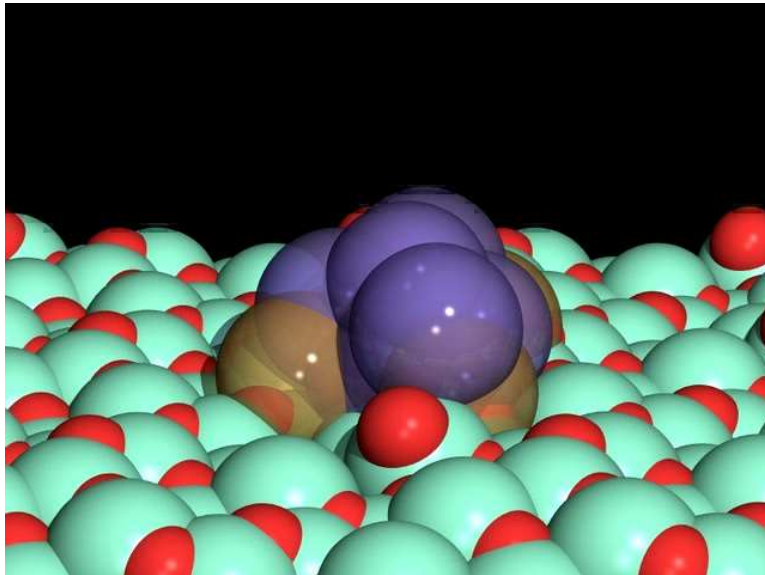
# Example: XAFS Debye-Waller Factor of Ge



Expt: Dalba *et al.* (1999)

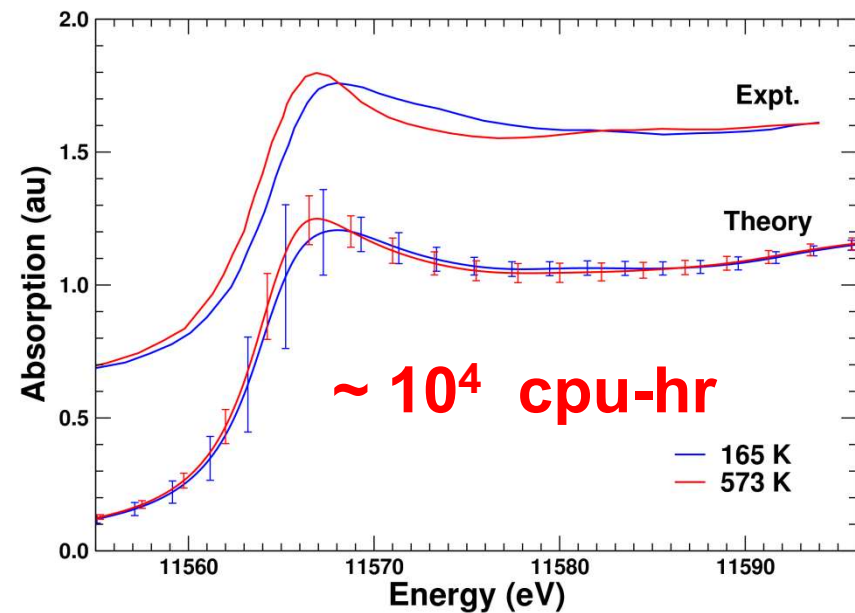
# Real-time Finite $T$ DFT-MD / XAS

## Nanoscale Pt catalysts\*



metallic Pt     Al  
oxidized Pt    O

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



\*F. Vila, J.J. Rehr, J. Kas, R.G. Nuzzo, A.I. Frenkel, Phys. Rev. B **78**, 121404(R) (2008)

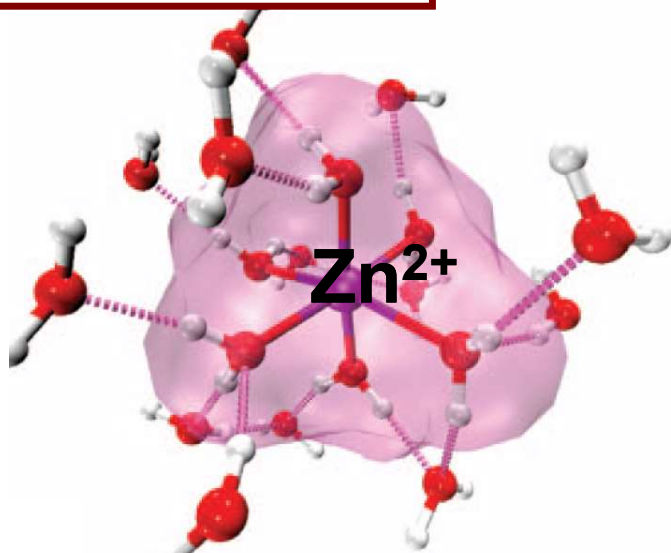
# EXAFS and DFT-MD

## Aqueous ions

### Transition metals, $Me^{2+}$

Exceptional agreement for:

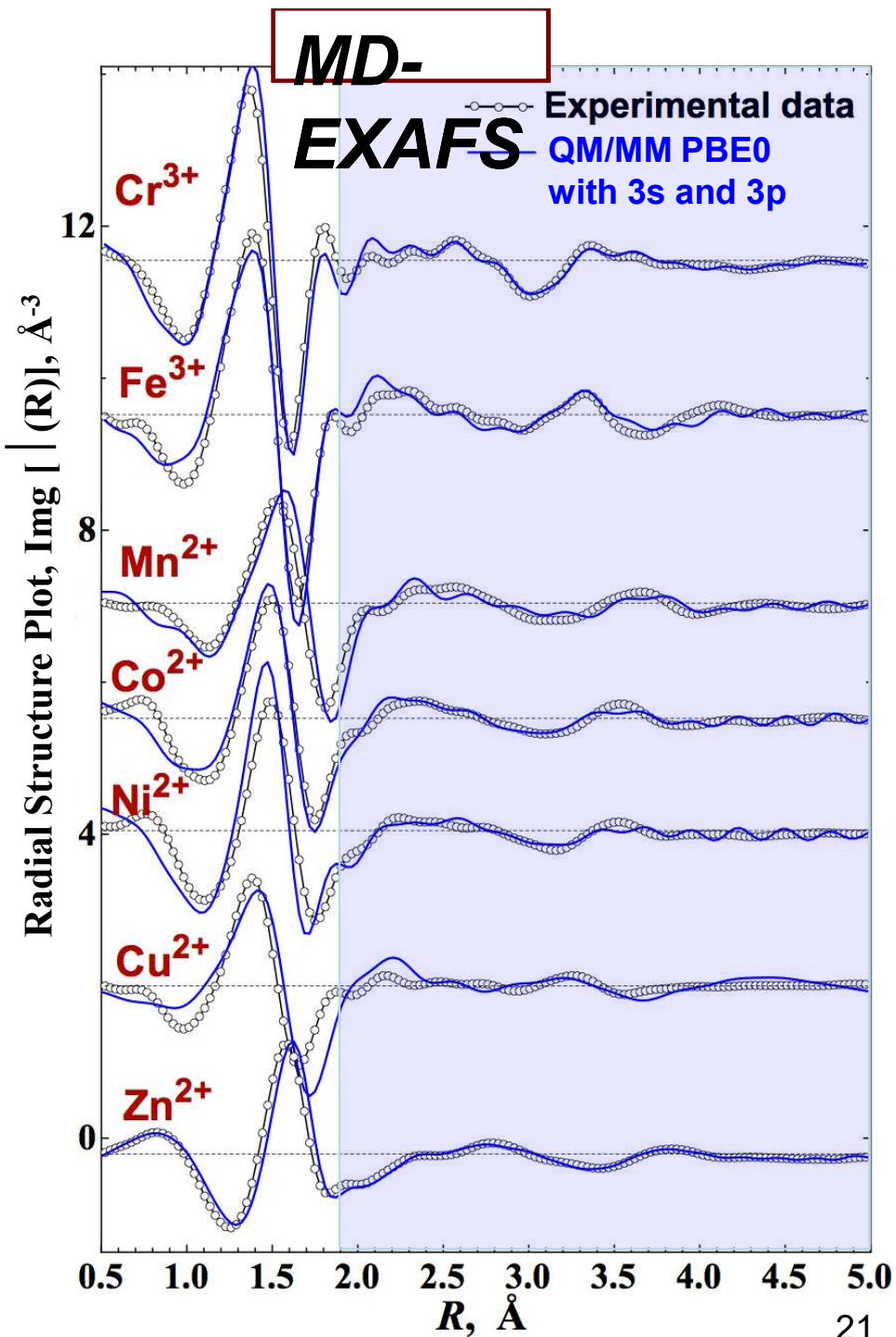
- 1<sup>st</sup> shell distance and disorder
- Octahedral symmetry
- Angular distribution functions
- Vibrational motions of first shell
- 2<sup>nd</sup> shell distance and disorder



• QM/MM  $Cr^{3+} + 6H_2O / 58 H_2O$   
 DFT PBE0/CPMD MM "SPC/E"  
 300K

Fulton, Bylaska, Schenter, et al *JPC Lett.*, 3, 2588 (2012)

24	51.996	25	54.938	26	55.845	27	58.933	28	58.693	29	63.546	30	65.39
<b>Cr</b>	<b>Mn</b>	<b>Fe</b>	<b>Co</b>	<b>Ni</b>	<b>Cu</b>	<b>Zn</b>							
CHROMIUM	MANGANESE	IRON	COBALT	NICKEL	COPPER	ZINC							



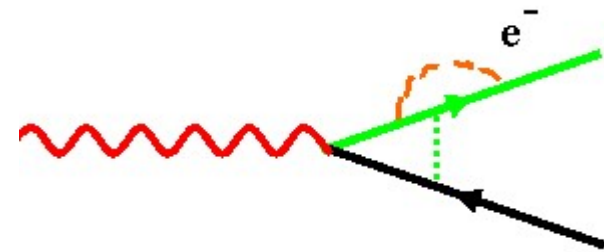
# III. Next generation XAS Calculations

## - beyond-quasiparticles

Excitonic effects BSE

Multi-electron excitations

Strong correlations



**Plus integrated Codes: DFT, GW/BSE, Real-time  
etc.**

# GW Bethe-Salpeter Equation

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

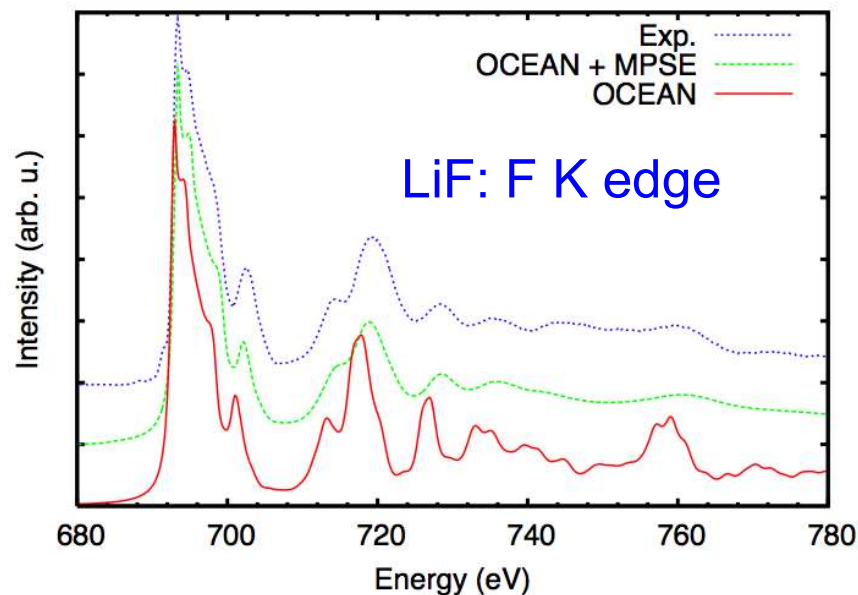
E. L. Shirley

National Institute of Standards and Technology (NIST), Gaithersburg, Maryland 20899, USA

(Received 29 September 2010; published 4 March 2011)

We present a hybrid approach for Bethe-Salpeter equation (BSE) calculations of core excitation spectra including x-ray absorption (XAS), electron energy loss spectra (EELS), and nonresonant inelastic x-ray scattering (NRIXS). The method is based on *ab initio* wave functions 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 self-energy model to account for final-state broadening and self-energy shifts. Multiplet effects are also approximately 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<sub>2,3</sub> edge in SrTiO<sub>3</sub> as probed by XAS, and the Mg L<sub>2,3</sub> edge in MgO as probed by XAS. These results are compared with experiment and with other theoretical approaches.

**BSE**  
**OCEAN\***



**Phys. Rev. B83, 115106 (2011)**

**\*Obtaining Core Excitations  
from *ab initio* NBSE**

**Plane-wave, pseudo-potential  
+ PAW + MPSE**

***cf.* EXC, EXC!TING,  
BerkeleyGW**

# Many-body Amplitudes in XAS $S_0^2$

- Many-body X\*S  $\approx$  Convolution

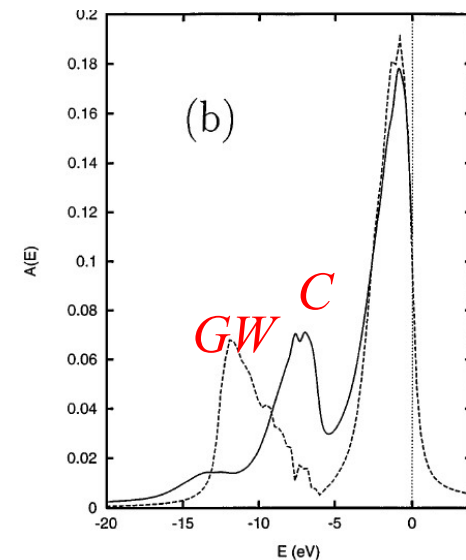
$$\mu(\omega) = \int_0^\infty d\omega' \tilde{A}(\omega, \omega') \mu_{qp}(\omega - \omega')$$
$$\equiv \langle \mu_{qp}(\omega) \rangle$$

- Source: multi-electron excitations

- Spectral function  $\sim$  XPS

$$A = -\text{Im } G$$

Na XPS





# Which Green's function ? $GW$ vs Cumulant

J. Phys.: Condens. Matter 11 (1999) R489–R528

On correlation effects in electron spectroscopies and the  $GW$  approximation

Lars Hedin

Department of Theoretical Physics, Lund University, Sölvegatan 14A, 223 62 Lund, Sweden

$$\Sigma = i GW$$

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

$GW$

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

$$\Gamma = 1 \quad \Sigma^{GW} = iGW$$

Cumulant

$$G(t) = G_0(t) e^{C(t)}$$

$$C \sim \text{Im} \Sigma^{GW}$$

Similar ingredients; all many-body effects in  $\Sigma^{GW}$

# Test: Satellites in XPS of simple metals\*

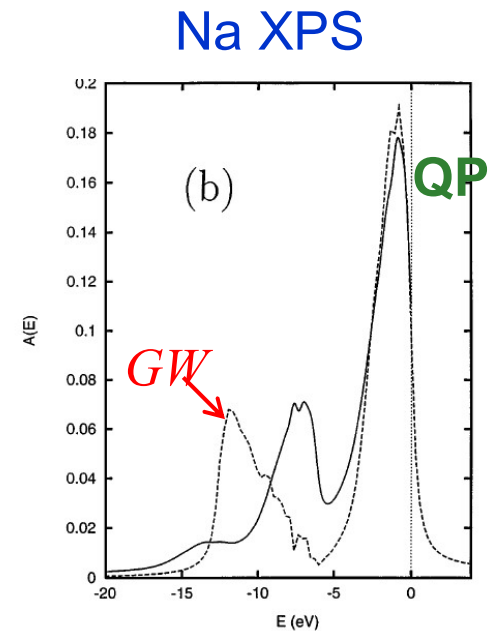
Multiple Plasmon Satellites in Na and Al Spectral Functions  
from *Ab Initio* Cumulant Expansion

F. Aryasetiawan,<sup>1,2</sup> L. Hedin,<sup>1</sup> and K. Karlsson<sup>3</sup>  
Phys Rev Lett **77**, 2268 (1996)

Good news: *GW* quasi-particle peak agrees with XPS

Bad news: *GW* has *one* satellite  
@ wrong energy

XPS has multiple satellites



# Test 2: Multiple Satellites in XPS of Si

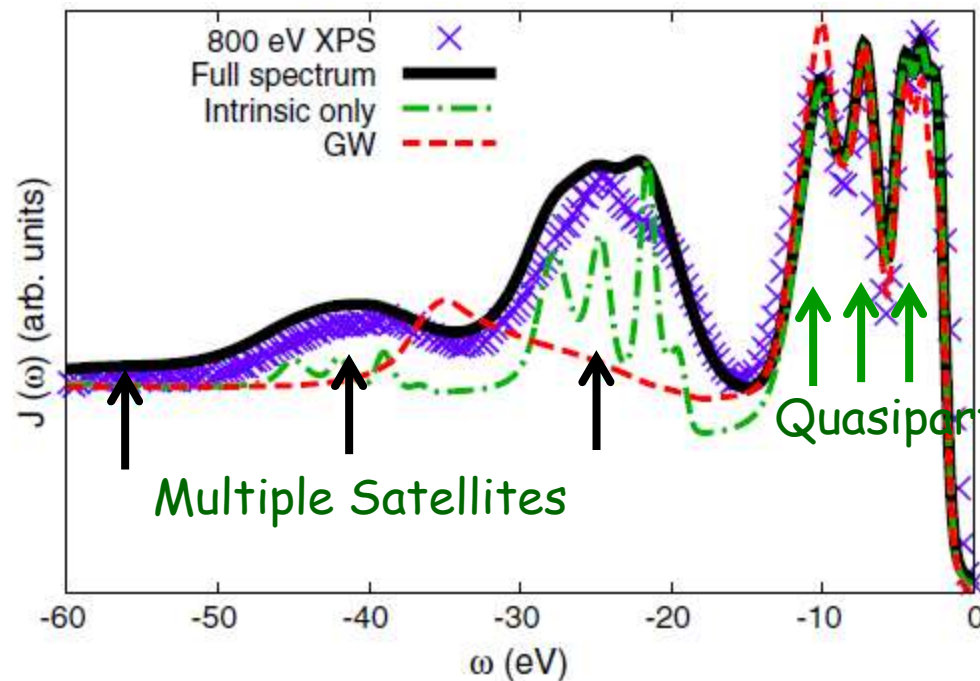
PRL 107, 166401 (2011)

PHYSICAL REVIEW LETTERS

week ending  
14 OCTOBER 2011

## Valence Electron Photoemission Spectrum of Semiconductors: *Ab Initio* Description of Multiple Satellites

Matteo Guzzo,<sup>1,2,\*</sup> Giovanna Lani,<sup>1,2</sup> Francesco Sottile,<sup>1,2</sup> Pina Romaniello,<sup>3,2</sup> Matteo Gatti,<sup>4,2</sup> Joshua J. Kas,<sup>5</sup> John J. Rehr,<sup>5,2</sup> Mathieu G. Silly,<sup>6</sup> Fausto Sirotti,<sup>6</sup> and Lucia Reining<sup>1,2,†</sup>



Lucia Reining

# XPS Intensity Ratios in Molecules

PRL 108, 193005 (2012)

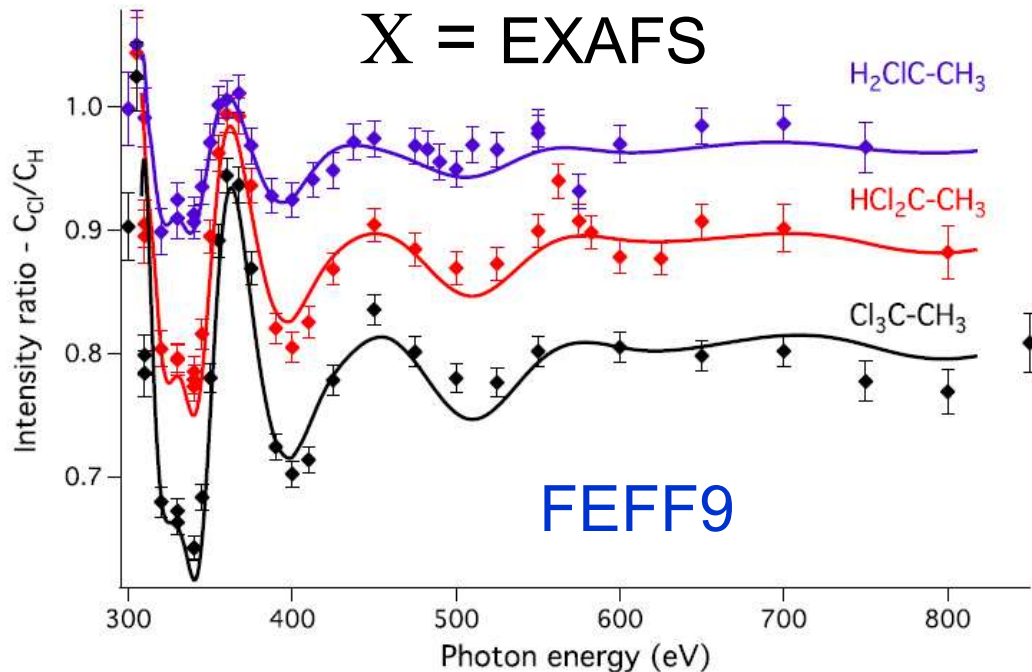
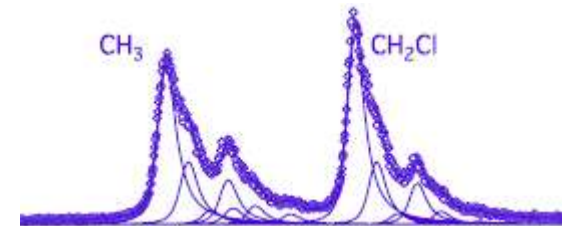
PHYSICAL REVIEW LETTERS

week ending  
11 MAY 2012

## Nonstoichiometric Intensities in Core Photoelectron Spectroscopy

J. Söderström,<sup>1</sup> N. Mårtensson,<sup>1</sup> O. Travnikova,<sup>2</sup> M. Patanen,<sup>2</sup> C. Miron,<sup>2</sup> L. J. Sæthre,<sup>3</sup> K. J. Børve,<sup>3</sup>  
J. J. Rehr,<sup>4</sup> J. J. Kas,<sup>4</sup> F. D. Vila,<sup>4</sup> T. D. Thomas,<sup>5</sup> and S. Svensson<sup>1</sup>

$$R = \frac{\mu_{C\alpha}}{\mu_{C_H}} = \frac{\mu_{0C\alpha} Z_{C\alpha} (1 + X_{C\alpha})}{\mu_{0C_H} Z_{C_H} (1 + X_{C_H})} \approx R_0 (1 + X_R)$$



**<XPS> = XAS**

Intensity ratio  $\sim Z$

*including all losses  
explains non-  
stoichiometric ratios*

**Question: Can the cumulant method work  
for CT satellites in correlated systems ?**

**Hedin's answer \* **MAYBE****

“Calculation similar to core case ... but with more  
complicated fluctuation potentials ...

... not question of principle, but of computational work...”

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

# Approach: Cumulant expansion in real-time

Real time cumulant approach for charge transfer satellites in x-ray photoemission spectra

J. J. Kas,<sup>1</sup> F. D. Vila,<sup>1</sup> J. J. Rehr,<sup>1</sup> and S. Chambers<sup>2</sup>

[arXiv:1408.2508](https://arxiv.org/abs/1408.2508)

<sup>1</sup>Dept. of Physics, Univ. of Washington, Seattle, WA 98195-1560

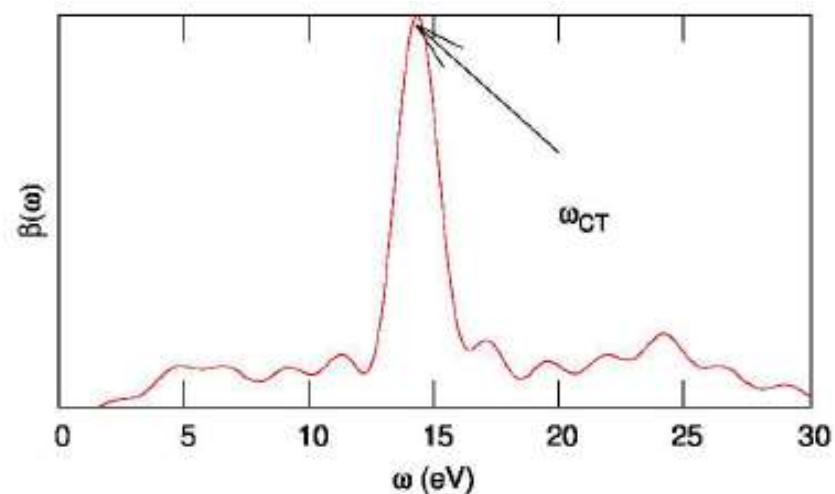
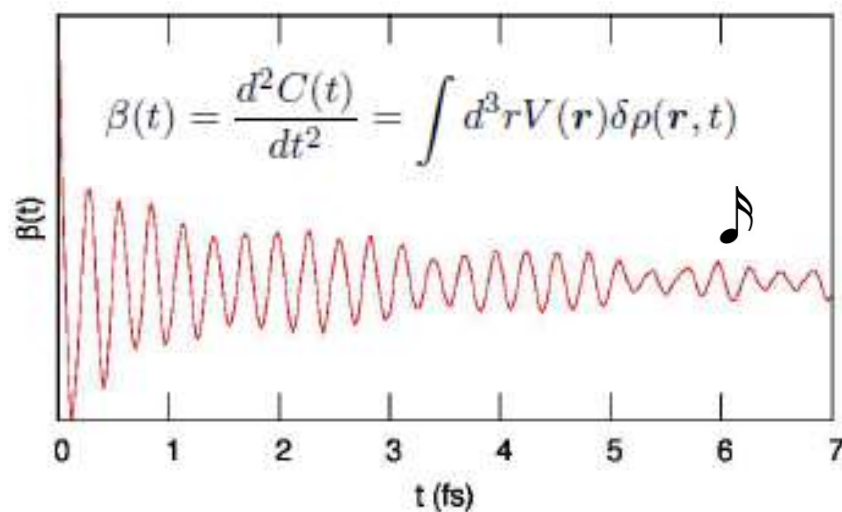
<sup>2</sup>Physical Sciences Division, Pacific Northwest National Laboratory, Richland, WA 99352

(Dated: August 7, 2014)

Langreth 
$$C(t) = \sum_{\mathbf{q}, \mathbf{q}'} V_{\mathbf{q}}^* V_{\mathbf{q}'} \int d\omega S(\mathbf{q}, \mathbf{q}', \omega) \frac{e^{i\omega t} - i\omega t - 1}{\omega^2} = \int d\omega \beta(\omega) \frac{e^{i\omega t} - i\omega t - 1}{\omega^2}$$

RT Cumulant: RT-TDDFT

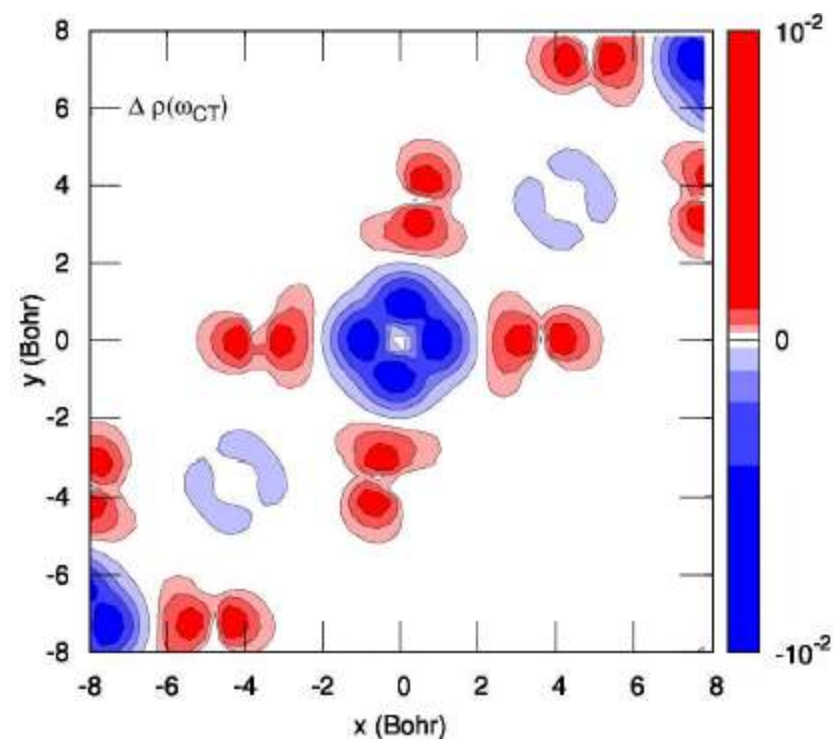
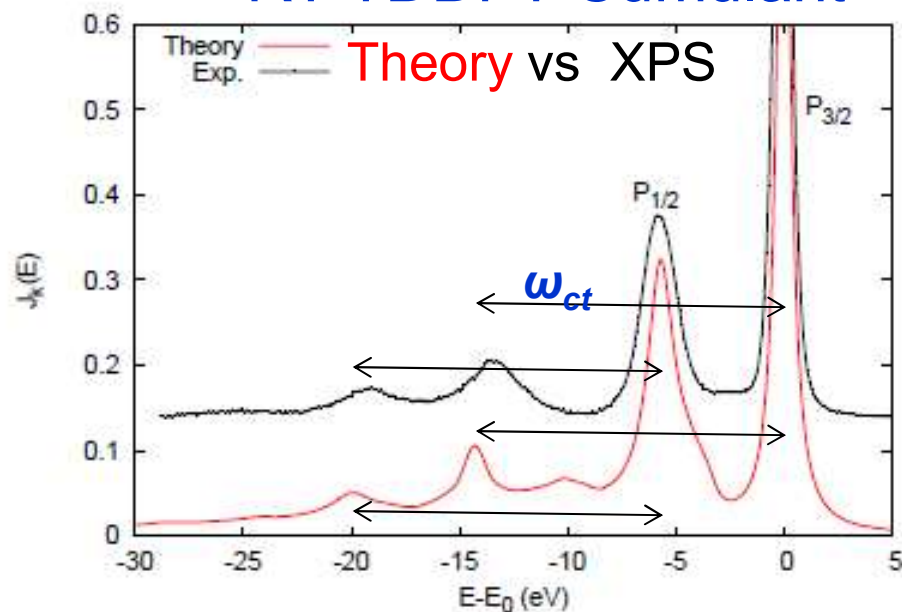
$$S(\mathbf{q}, \mathbf{q}', \omega) = \int \frac{dt}{2\pi} e^{i\omega t} \langle \rho_{\mathbf{q}}(t) \rho_{\mathbf{q}'}(0) \rangle$$



# XPS & Real-space Interpretation

## Charge Fluctuations

### RT TDDFT Cumulant



**Interpretation:** satellites due to local ligand-metal charge fluctuations at frequency  $\sim \omega_{ct}$  in response to transient core-hole potential

JJ Kas, FD Vila, JJR & S.Chambers arXiv:1408.2508

# Conclusions and Outlook

EXAFS - well understood with current methods

RSGF + DFT/MD

XANES – semi-quantitative state of the art theory

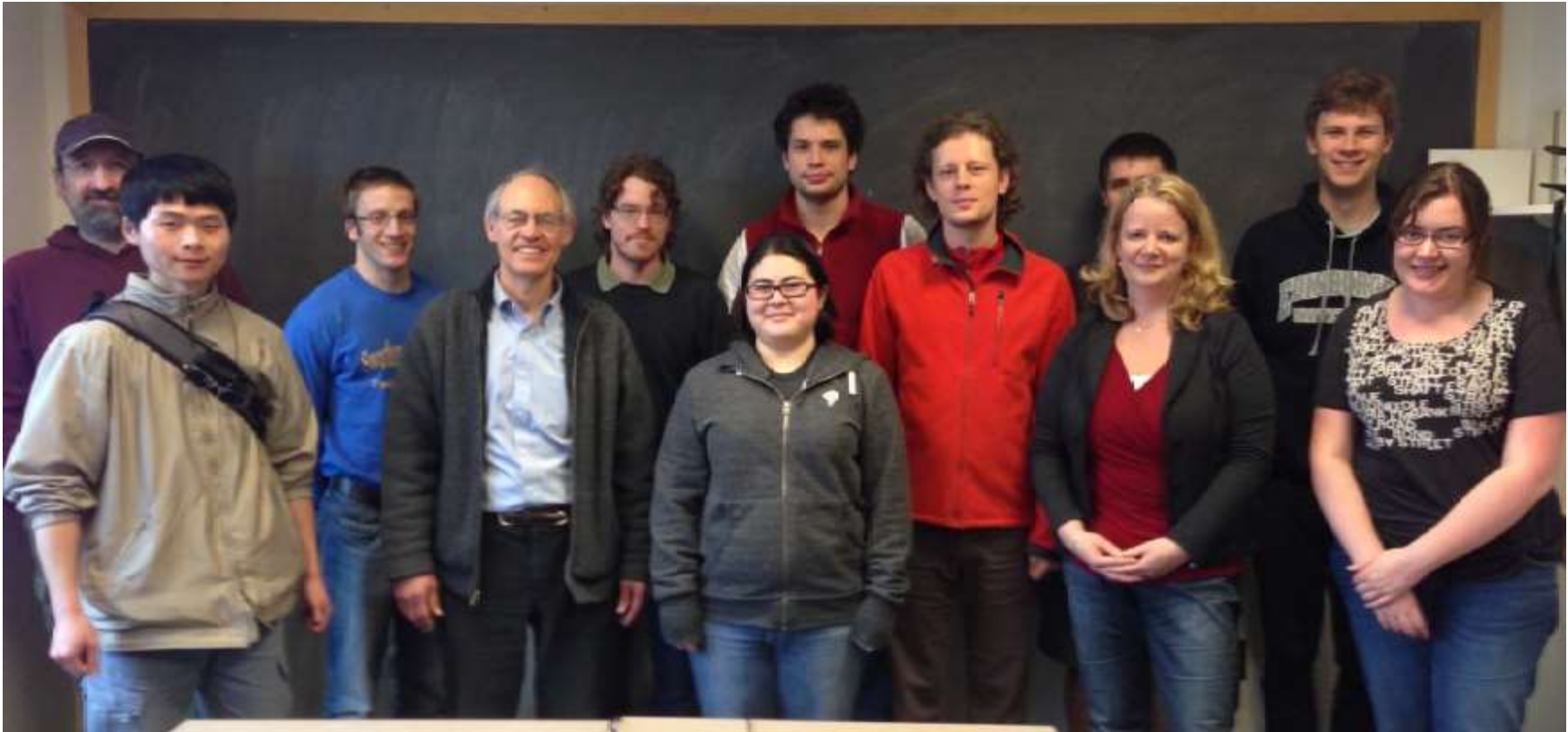
GW, GW/BSE, DW factors, ...

XAS, XPS - Multi-electron excitations & correlations  
via *quasi-boson/cumulant theory*

**Full spectrum calculations possible in arbitrary  
materials with NG theory and codes.**



## Rehr group & collaborators



Thanks for Listening!

# Many Success Stories

## XAS of doped SiC

M Ohkubo et al., Sci. Rep., 2, 831 (2012)



X-ray absorption near edge spectroscopy  
with a superconducting detector for  
nitrogen dopants in SiC

SUBJECT AREAS:  
PHYSICS  
MATERIALS SCIENCE  
SPECTROSCOPY  
ANALYTICAL CHEMISTRY

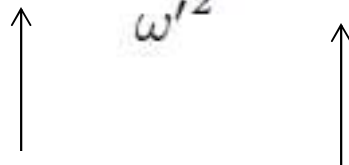
M. Ohkubo<sup>1</sup>, S. Shiki<sup>1</sup>, M. Ukibe<sup>1</sup>, N. Matsubayashi<sup>1</sup>, Y. Kitajima<sup>2</sup> & S. Nagamachi<sup>3</sup>

“FEFF8.4 played an important role in analysis of XANES spectra of N-doped SiC. I appreciate your effort for developing this fantastic software ...”

Masataka Ohkubo

# Cumulant Expansion & Spectral Function

$$G_k(t) = e^{i\epsilon_k^0 t} e^{C(t)}$$

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


## Spectral Function

$$A_k(\omega) = \int \frac{dt}{2\pi} e^{i(\omega - \epsilon_k)t} \exp \left\{ \int d\omega' \beta(\omega') \frac{e^{i\omega' t} - i\omega' t - 1}{\omega'^2} \right\}$$

\*see L. Hedin, J. Phys.: Condens. Matter **11**, R489 (1999)  
cf. D.C. Langreth *Phys. Rev. B* **1**, 471 (1970) (Linked cluster theorem)

## Other properties

Kernel:  $\beta(\omega) = |\text{Im } \Sigma_k(\omega)| \sim \text{Im } \varepsilon^{-1} \sim \text{loss function}$

Peaks in  $A(\omega) \sim \text{Peaks in loss function}$

$$Z = e^{-\bar{n}} \quad \bar{n} = \sum_q g_q^2 / \omega_q^2 = \int \beta(\omega) / \omega^2 d\omega.$$

$\bar{n} = 0.201 r_s^{3/4}$  mean number of shake-up bosons  
Dimensionless measure of correlation strength

**$n \sim 0.3 \text{ to } 0.4$  even in s-p systems !**

# IV. Problems with Cumulant Expansion\*

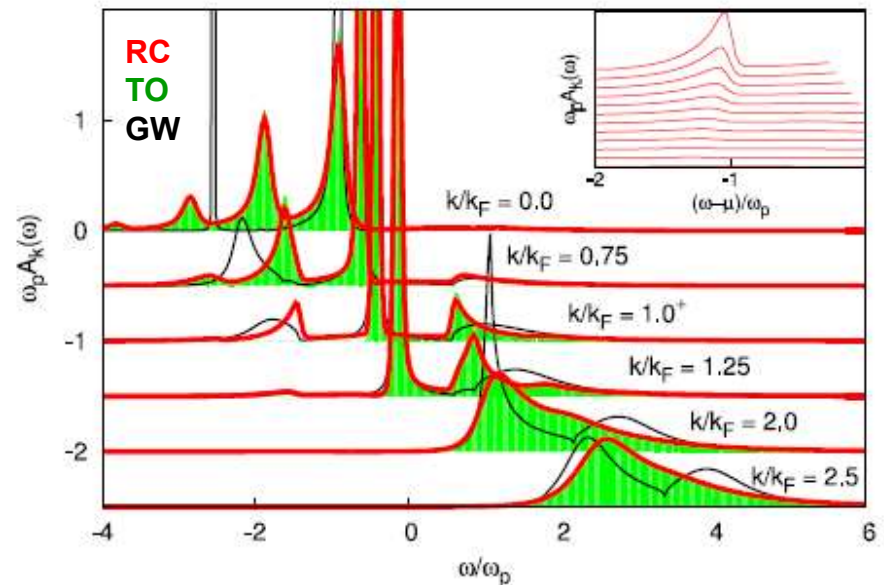
## BAD: Pathologies at Fermi energy\*

Time-ordered GF (TO) lacks satellites on both sides of QP peak near Fermi energy

GW lacks multiple satellites

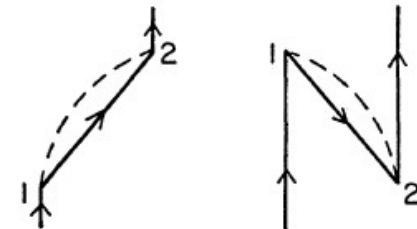
Source: recoil approximation: neglect of “exchange diagrams” in time-ordered cumulant

Electron spectral function



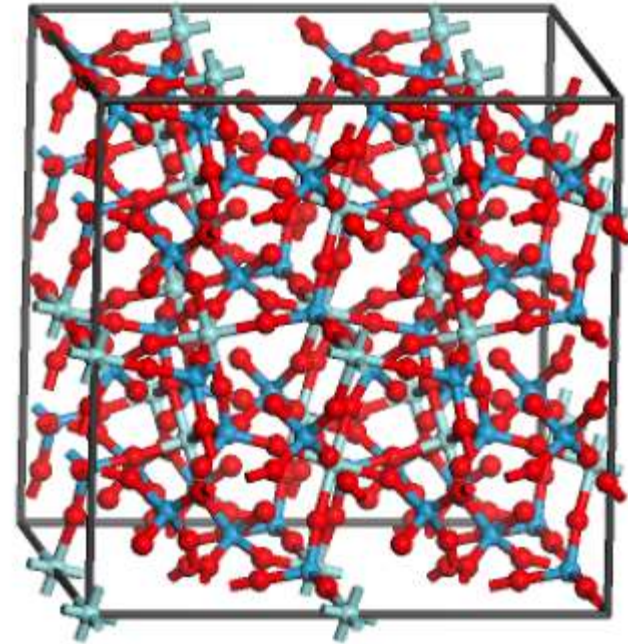
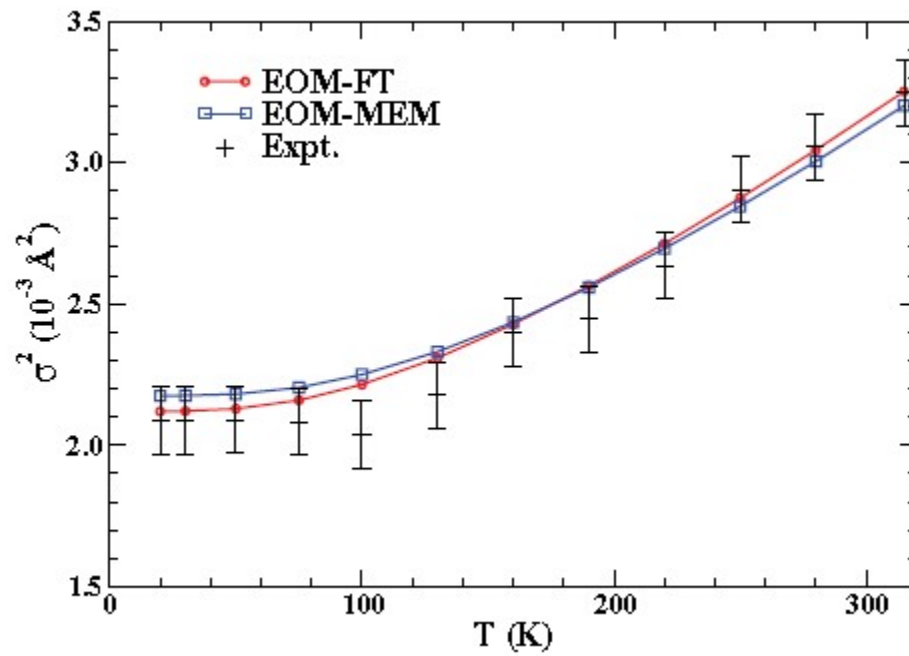
direct

exchange



\*arXiv:1402.0022

# Debye-Waller factors $\sigma^2$ in Zr tungstate



# FIX: Retarded Cumulant expansion\*

PHYSICAL REVIEW B 00, 005100 (2014)

## Cumulant expansion of the retarded one-electron Green function

J. J. Kas,<sup>1,\*</sup> J. J. Rehr,<sup>1,2,†</sup> and L. Reining<sup>3,2,‡</sup>

<sup>1</sup>Department of Physics, University of Washington, Seattle, Washington 98195, USA

<sup>2</sup>European Theoretical Spectroscopy Facility (ETSF)

<sup>3</sup>Laboratoire des Solides Irradiés, École Polytechnique, CNRS, CEA-DSM, F-91128 Palaiseau, France

(Received 31 January 2014; revised manuscript received 28 July 2014; published xxxxxx)

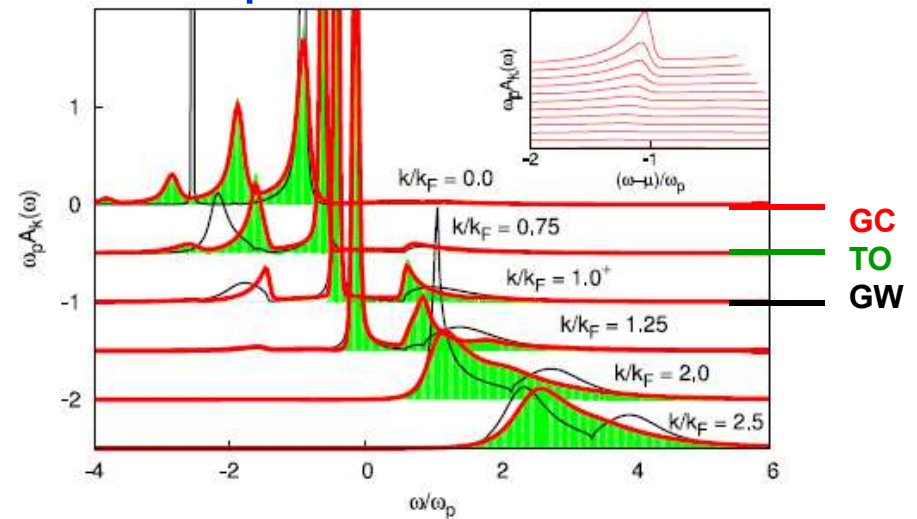
## Retarded formalism

$$G_k^R(t) = -i\theta(t)e^{-i\epsilon_k^{HF}t}e^{\tilde{C}_k^R(t)},$$

$$\tilde{C}_k^R(t) = \int d\omega \frac{\beta_k(\omega)}{\omega^2} (e^{-i\omega t} + i\omega t - 1),$$

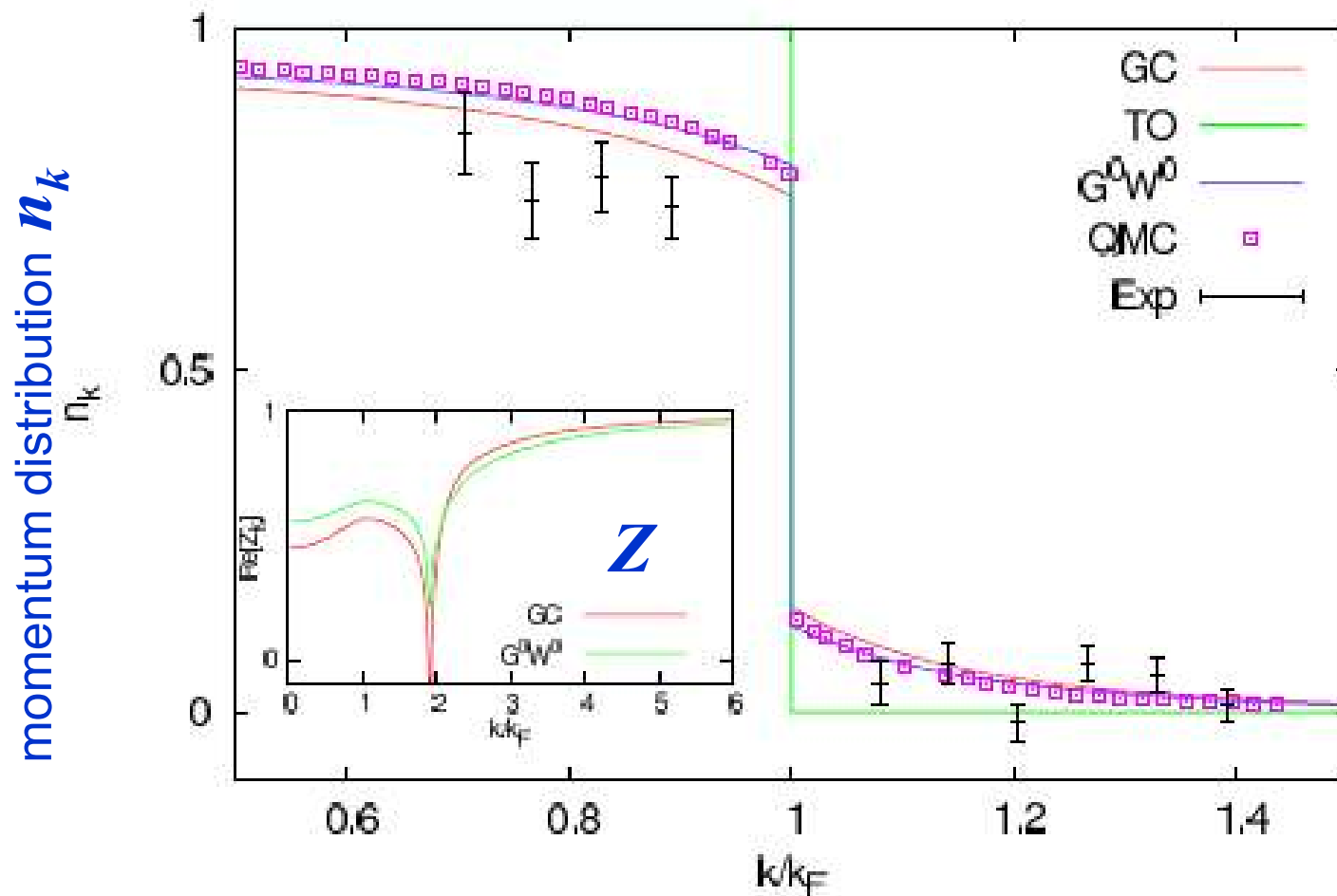
$$\beta_k(\omega) = \frac{1}{\pi} |\text{Im} \Sigma_k^R(\omega + \epsilon_k)|,$$

## Spectral function



\*Phys. Rev. B. (in press, Aug. 2014); arXiv:1402.0022

# Retarded Cumulant (GC) gives **GOOD** quasi-particle properties





# Many-body Amplitudes in X-ray Spectra

- Many-body X\*S  $\approx$  Convolution

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

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

$$|g_q|^2 = |g_q^{ext}|^2 + |g_q^{intrin}|^2 - 2 g_q^{ext} g_q^{intrin}$$

Interference reduces loss!

# Strong correlation effects: 1. Hubbard 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

### cRPA calculated $U$

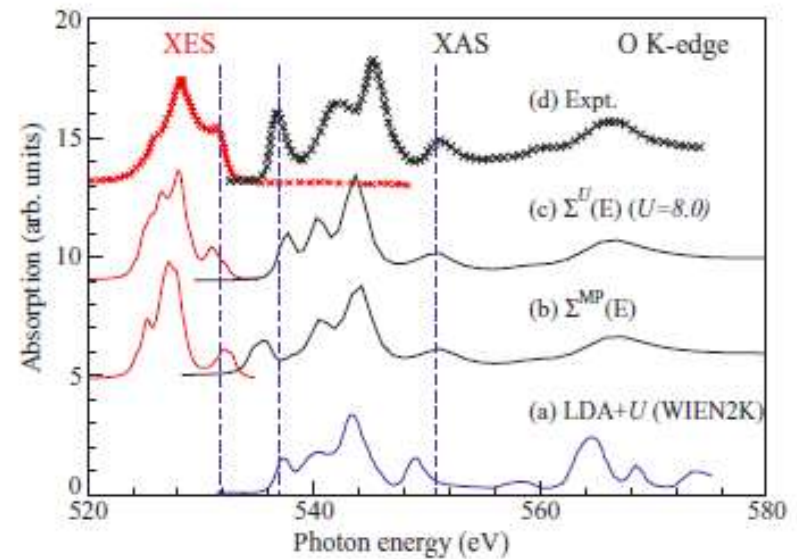
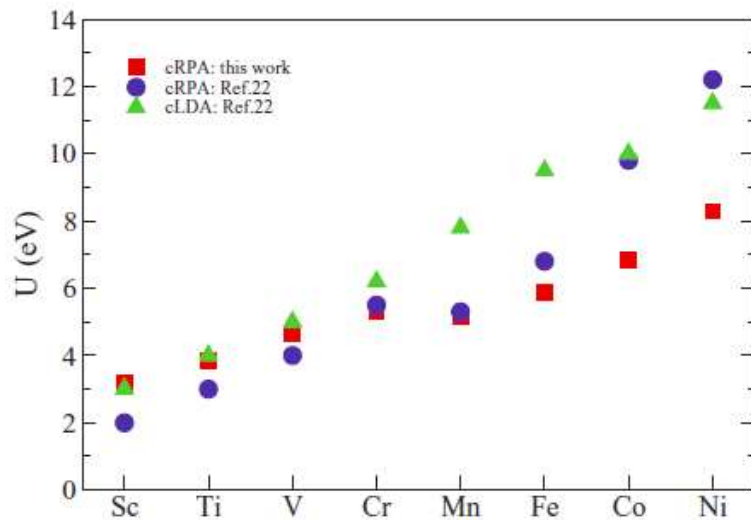


FIG. 1. (Color online) Results of our cRPA calculations of  $U$  (re

# FIX: Next generation approach

## Quasi-Boson Approximation

IDEA: Neutral Excitations\* - plasmons, phonons, electron-hole pairs, magnons are **bosons**  $\gamma$

Many-body Model:  $|N\rangle = |e^-, h, \gamma\rangle$

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

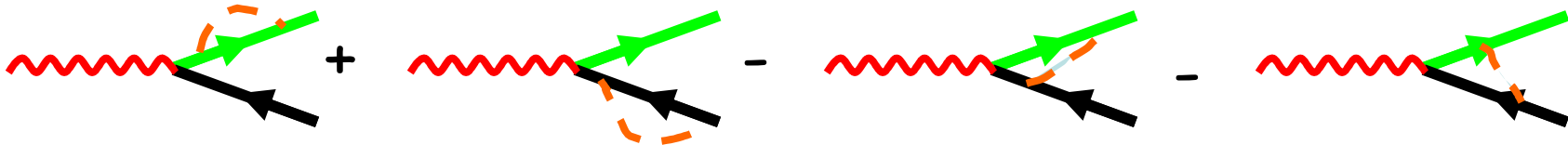
$V^n \rightarrow -\text{Im } \epsilon^{-1}(\omega_n, q_n)$  “fluctuation potentials”

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

# GW++: Effective Green's Function - perturbation theory\*

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

Extrinsic + Intrinsic - 2 x Interference



Leading term:  $g'(\omega)$  damped Green's function in presence of core-hole ( $\sim$  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)

# 2. Multiplets a la GW/BSE

Phys. Rev. B **86**, 195135 (2012)

## BSE calculations of transition metal L-shell spectra

J. Vinson and J. J. Rehr

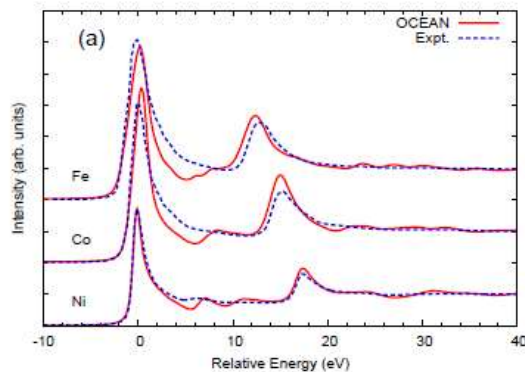
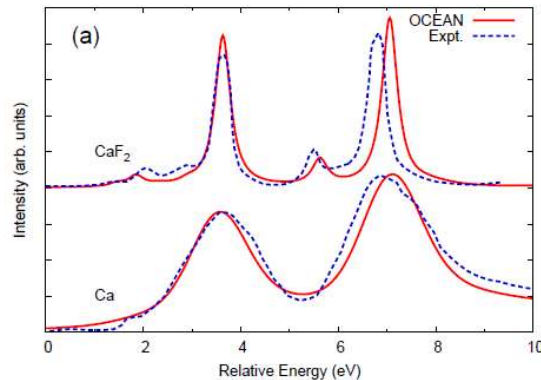
Dept. of Physics, Univ. of Washington Seattle, WA 98195

(Dated: July 3, 2012)

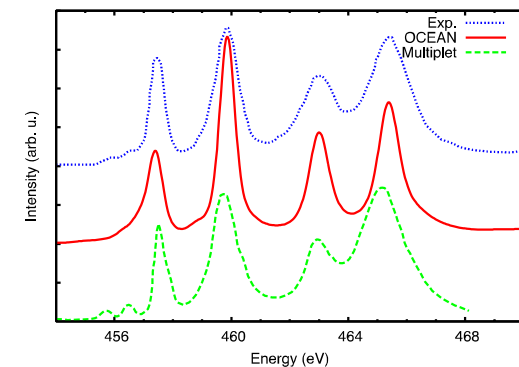
We present *ab initio* Bethe-Salpeter equation (BSE) calculations of the  $L_{2,3}$  edges of several insulating and metallic compounds containing Ca, V, Fe, Co, Ni, and Cu, spanning a range of  $3d$ -electron occupations. Our approach includes the key ingredients of a unified treatment of both extended states and atomic multiplet effects, i.e., self-consistent crystal potentials, ground-state magnetism, *GW* self-energy corrections, spin-orbit terms, and Coulomb interactions between the  $L_2$  and  $L_3$  states. The method is implemented in the OCEAN package, which uses plane-wave pseudopotential wave functions from ABINIT as a basis, a PAW construction for transition matrix elements, and a resolvent formalism for the BSE calculation. The results are in near quantitative agreement with experiment, including both fine-structure at the edges and the non-statistical  $L_3/L_2$  ratios observed in these systems.

GW/BSE  
+ Spin & SO  
+ MPSE  
+ Slater  $F, G$

## Transition metal oxides



## Multiplets in SrTiO3



# 3. Charge Transfer Satellites

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

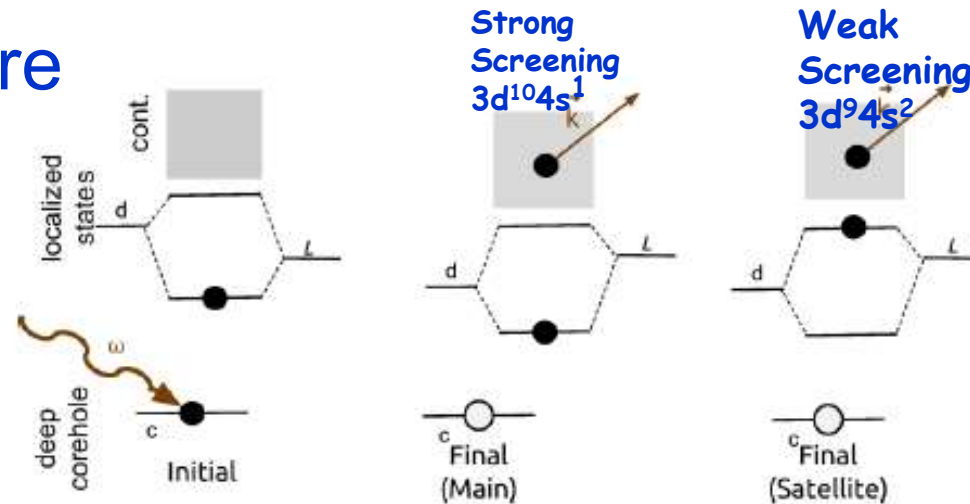
J. D. Lee and O. Gunnarsson

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 14 A, S-223 62 Lund, Sweden

## 2-state picture



Approaches: Anderson impurity, DMFT, multiplets, ....  
+ Lots of **Sound & Fury** + millions of cpu hrs  
**BUT** still no satisfactory 1<sup>st</sup> principles theory ...

# Simple picture: 2-state model of LGH\*

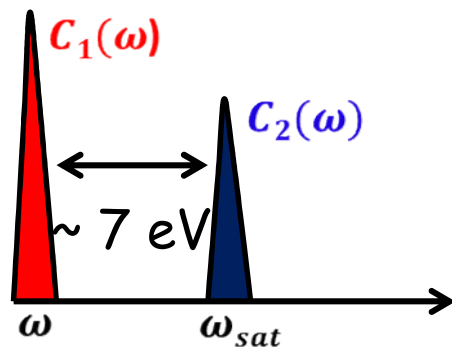
PHYSICAL REVIEW B 89, 085123 (2014)

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

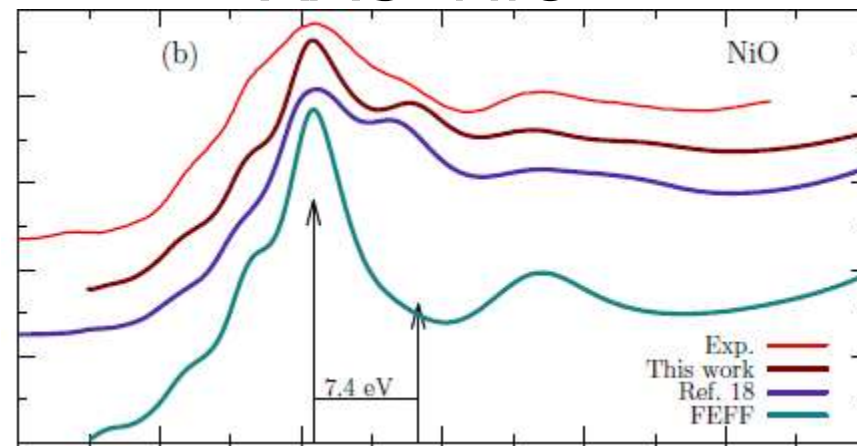
E. Klevak, J. J. Kas, and J. J. Rehr

Department of Physics, University of Washington, Seattle, Washington 98195, USA

$$H = \sum_{i\sigma} \varepsilon_{i\sigma}^{DFT} n_{i\sigma} + \sum_{ij} U_{ij} n_{i\uparrow} n_{j\downarrow} + t(c_{3d}^\dagger c_{4s} + c_{4s}^\dagger c_{3d})$$

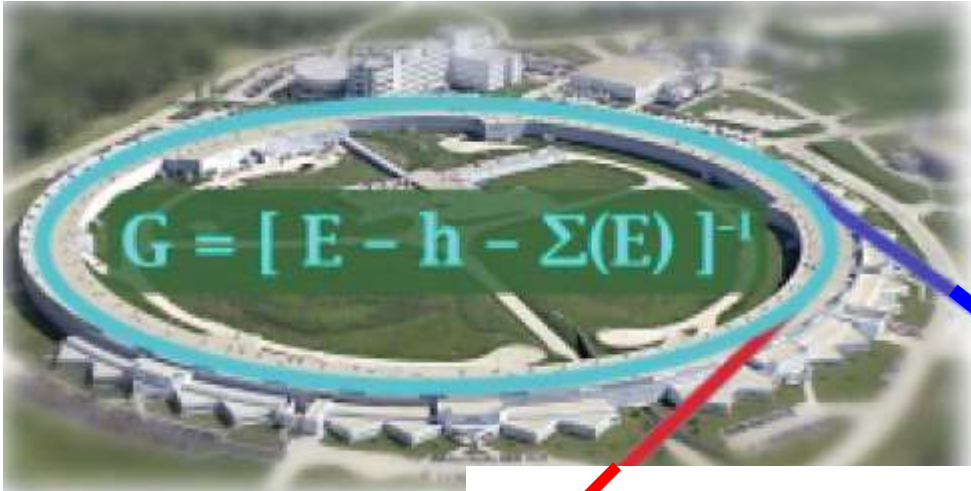


## XAS NiO



\*Lee, Gunnarsson & Hedin, Phys Rev B 60, 8034 (1999)

# Goal: X-ray Spectroscopy Beamline



XAS  
XES  
XMCD  
NRIXS  
RIXS  
etc.

Full spectrum  
theoretical tools





# EU Model

## European Theoretical Spectroscopy Facility

[www.etsf.eu](http://www.etsf.eu)



European Theoretical Spectroscopy Facility



**A new facility for research!**

**Nanoquanta builds the ETSF** European Theoretical Spectroscopy Facility  
Network of Excellence

### An innovative project...

The Nanoquanta Network of Excellence, partially financed by the European Union under the Sixth Framework Programme, is building up a new type of facility called European Theoretical Spectroscopy Facility (ETSF). On the lines of the synchrotron facilities successfully shared by researchers across Europe, the ETSF will offer users the opportunity to benefit from the latest developments in the field of Electronic excited states in matter.

### To burst the secrets of matter

What happens in matter when it is exposed to radiation? What does the response of the material to the radiation – that is, the spectra we measure – teach us? That is what the researchers of the ETSF want to know.



In matter, the electrons occupy energy levels. When absorbing radiation, they can be promoted to a higher level, depending on the characteristics of the system. These transitions must then be calculated taking into account the fact that the electron is moving.

An example of  $^{12}\text{C}$  of a diamond, which contains  $8 \times 10^{23}$  electrons, shows that the task is huge! Mathematica expressions must then be derived, taking into account the "many-body" physics in an approximate way.

Nevertheless, much computer power is necessary to obtain a reliable result for a "real" material. To do that, researchers develop software, which translates the expressions into the language of computers.

### Our work then includes:

- to derive modified and reliable mathematical expressions
- to build up efficient, associated software
- to create user-friendly software and manuals and to organize training events.



### 1-The core of the ETSF

A network of prominent European Condensed Matter theory groups, which will take responsibility for management of the ETSF and reach out

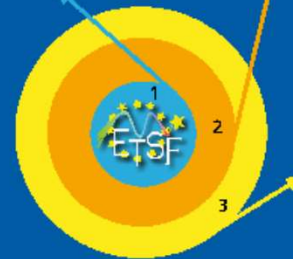
- They developed, thanks to a 15 years collaboration, many of the theoretical approaches and computational solutions which are commonly used in the framework of calculations of electronic excitations from first principles.

### 2-Associate theory groups

A broad and federal community of research groups working on similar topics

- They fully benefit from the scientific exchange enabled and stimulated by the ETSF and will be able to advertise on the ETSF website and call for proposals just like members of the Core.

The ETSF will bridge the gap between fundamental research and technological applications



### 3-Users

A large and varied group of researchers from the public or private sector

Demand for collaboration using the developed software and support for these calculations is growing rapidly amongst theoreticians and experimentalists, some working at large institutions such as synchrotrons, others in individual laboratories and others in private companies.

- They benefit from the ETSF in different ways, depending on the proximity of the user to the field:

### Theoretical spectroscopy and fight against cancer, an example

Theory and software help not only to show the properties of matter, but also to understand how it works and therefore to envisage important innovations.

For example, the Green Fluorescent Protein (GFP), which gives the Aquorea victoria jellyfish its "green" appearance, is large and used in molecular biology. But now does the GFP absorb light? Why and how does it change structure to become fluorescent and after a while, return to its initial state?

A deeper understanding of the fluorescent (GFP, porphyrin, etc.) behaviour enables to improve its use as a biological marker. In the fight against cancer, it will become possible to destroy "cell markers" cells without touching the healthy ones around them.

- download software and use it with the help of publications, manuals and tutorials provided by the ETSF;
  - participate in training events;
  - require ongoing consultancy for a project;
  - demand pieces of theory or software that do not yet exist but are sufficiently relevant to be devised by a member of the ETSF. In collaboration with the proposer if appropriate;
  - propose a relevant project that requires full-time work of a member of the ETSF.
- Users of the ETSF may already propose pilot projects on different levels, according to their expertise. The first open call for user projects will start in 2005.



- ▶ About the ETSF
- ▼ **Beamlines**
  - Energy Loss Spectroscopy
  - Optics
  - ▶ Photo-emission Spectroscopy
  - Quantum Transport
  - Time-resolved Spectroscopy
  - Vibrational Spectroscopy
  - X-Rays Spectroscopy
- ▶ Services
- ▶ Resources
- Funding
- ▶ Press
- Impressum

Home

## Beamlines

The ETSF is divided into 7 beamlines, each of which is concerned with a specific scientific topic. A beamline coordinator is responsible for the contact with the users of each line. He/She also serves as the contact person for users who want to submit a proposal to the ETSF.

Further details are available on the beamlines' description.

## Beamlines and Coordinators

### Optics

**Dr. Olivia Pulci**

University of Rome Tor Vergata, Rome, Italy  
Olivia.Pulci@roma2.infn.it

### Energy Loss Spectroscopy

**Dr. Francesco Sottile**

Ecole Polytechnique, Palaiseau, France  
francesco.sottile@polytechnique.edu

### Quantum Transport

**Dr. Peter Bokes**

Slovak University of Technology, Bratislava, Slovakia  
peter.bokes@stuba.sk

### Time-resolved Spectroscopy

**Dr. Alberto Castro**

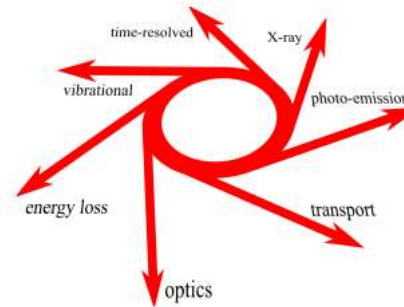
Instituto de Biocomputación y Física de Sistemas Complejos  
acaastro@bifi.es

### Photo-emission Spectroscopy

**Dr. Claudio Verdozzi**

Lund University, Lund, Sweden  
Claudio.Verdozzi@teorfys.lu.se

# Networked “theoretical beamlines”



### Vibrational Spectroscopy

**Prof. Gian-Marco Rignanese**

Université Catholique de Louvain, Louvain-la-Neuve, Belgium  
gian-marco.rignanese@uclouvain.be

### X-Rays Spectroscopy

**Prof. John Rehr**

University of Washington, Seattle, USA  
jjr@phys.washington.edu