Core-level Spectroscopies with FEFF9 and OCEAN

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Supported by DOE BES

UNIVERSITY OF WASHINGTON NIST ETSF

Core-level Spectroscopies with FEFF9 and OCEAN

- **GOAL**: *ab initio* theory
- Accuracy ~ experiment

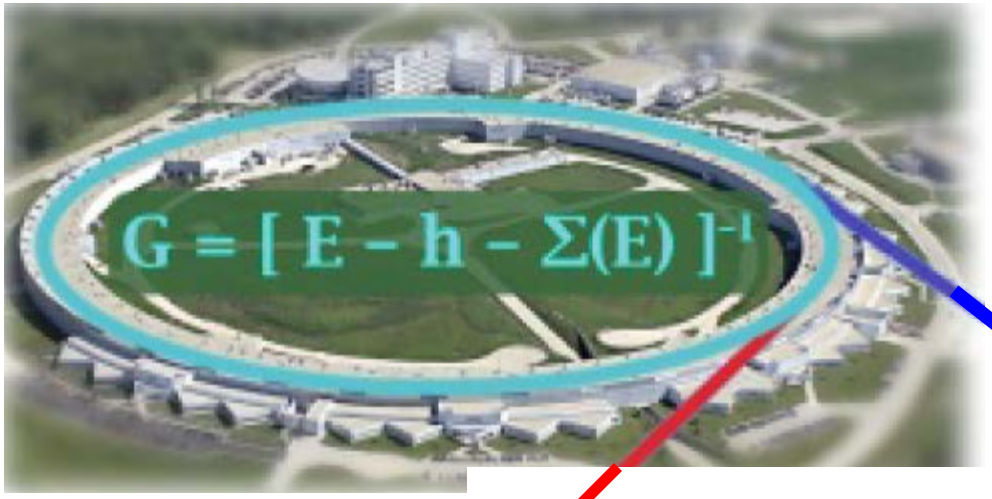
- **TALK**:

I. Introduction

II. FEFF9 Real-space Green's Function - JJR

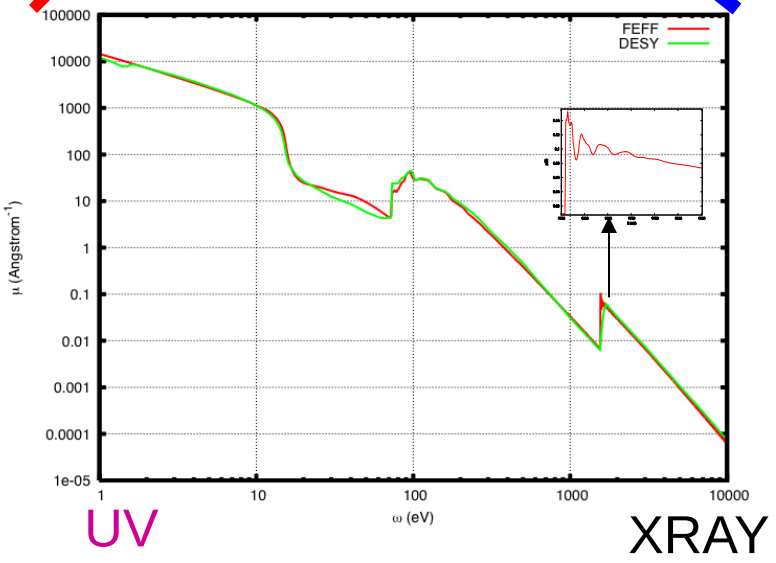
III. BSE – *k* space - KG

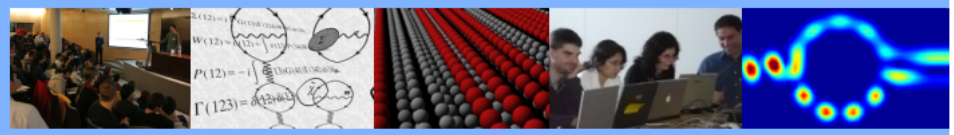
ETSF X-ray Spectroscopy Beamline



XAS
XES
XMCD
NRIXS
RIXS

Full spectrum theoretical tools





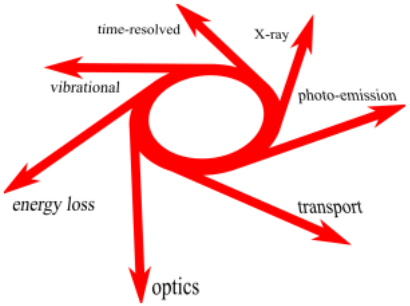
- About the ETSF
- *Beamlines*
  - Energy Loss Spectroscopy
  - Optics
  - Photo-emission Spectroscopy
  - Quantum Transport
  - Time-resolved Spectroscopy
  - Vibrational Spectroscopy
  - X-Rays Spectroscopy
- Services
- Resources
- Funding
- Press
- Impressum

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

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University of Rome Tor Vergata, Rome, Italy
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Energy Loss Spectroscopy

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Ecole Polytechnique, Palaiseau, France
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Quantum Transport

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Time-resolved Spectroscopy

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Photo-emission Spectroscopy

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Vibrational Spectroscopy

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X-Rays Spectroscopy

Prof. John Rehr
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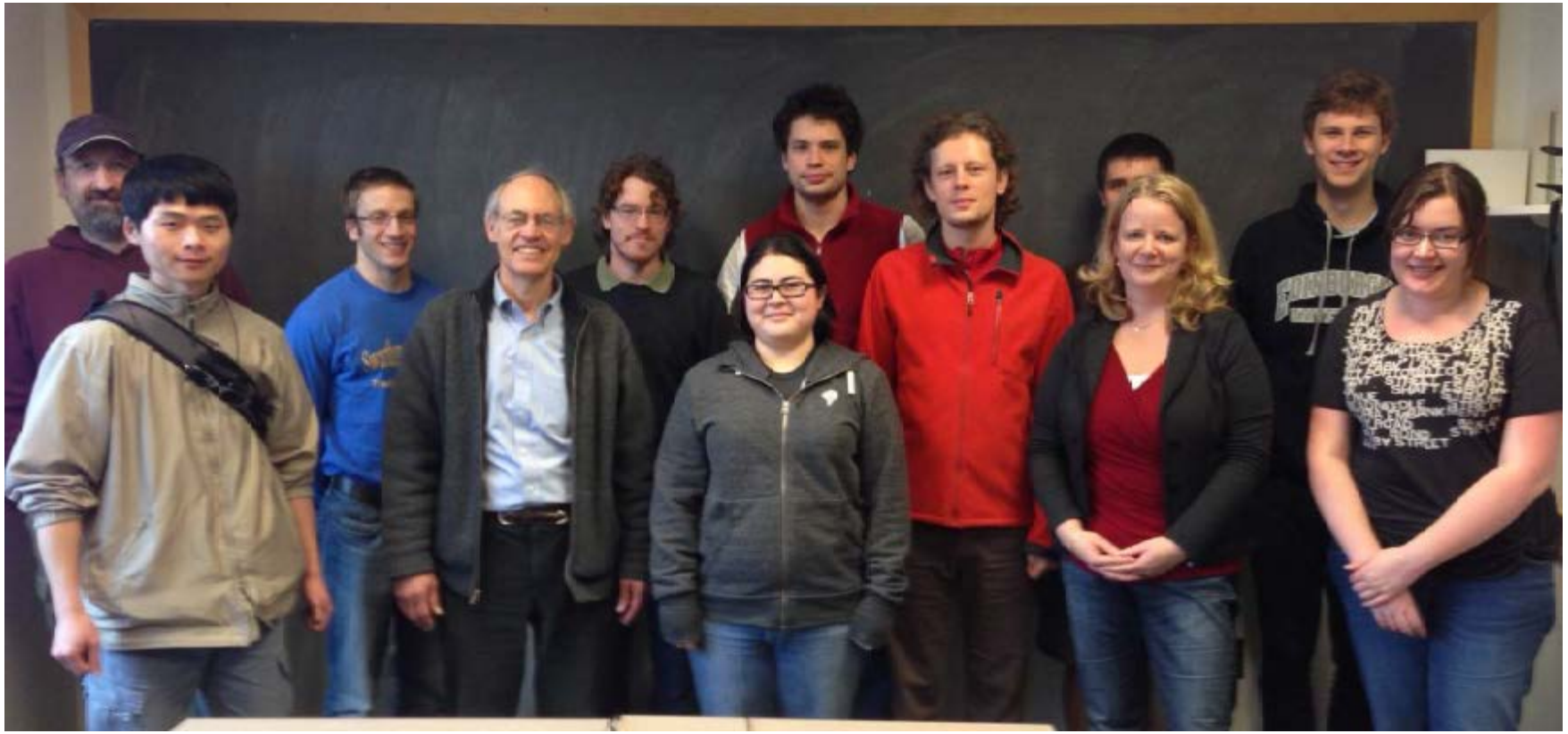
jjr@phys.washington.edu

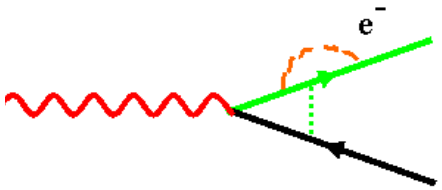
The team: Rehr-Group + collaborators



Thanks to DOE BES, DOE CMCSN,
NSF OCI, and the ETSF

Theoretical ingredients beyond DFT

"Excited State Electronic Structure"

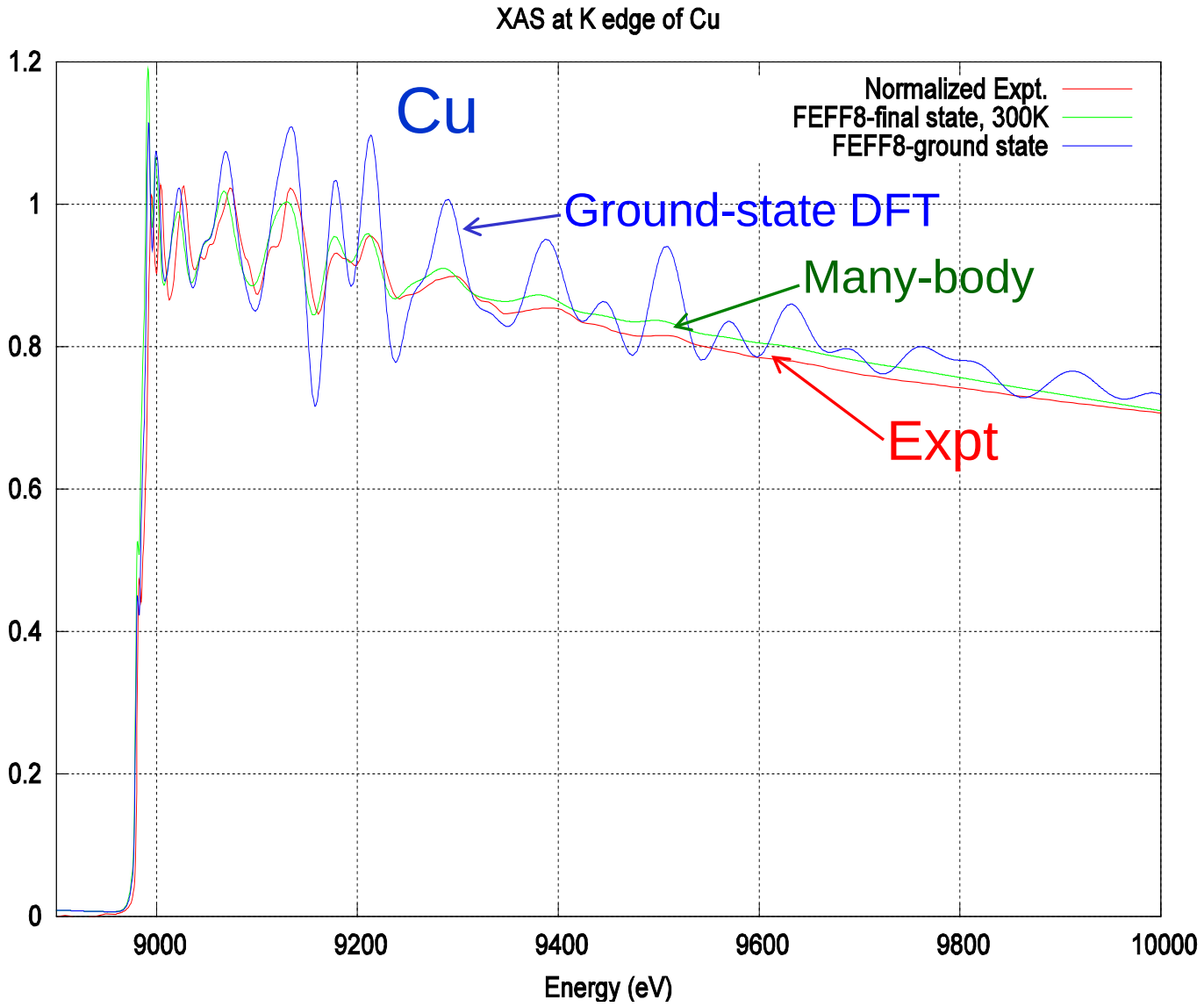


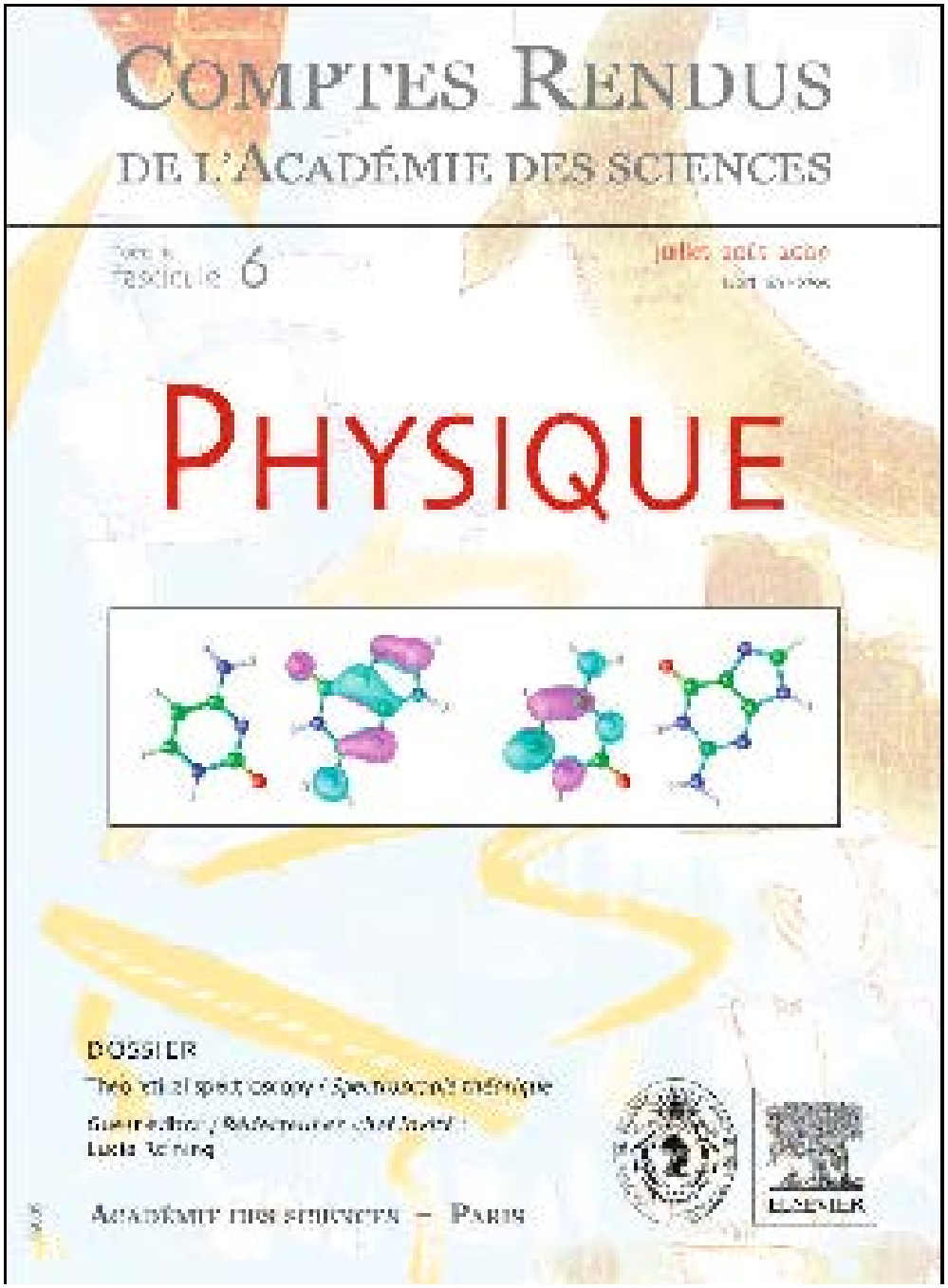
A. Self-energies & mean free paths

B. Screened Core-hole

C. Nuclear motion: Debye Waller factors

Need for corrections to DFT in XAS





FEFF9 reference

Ab initio RSGF Theory

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

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

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

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

Final state rule

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

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

Real-space Green's Function Approach

Golden rule via Wave Functions

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

Paradigm shift:

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

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

No sums over final states !

Implementation: Real-space FEFF 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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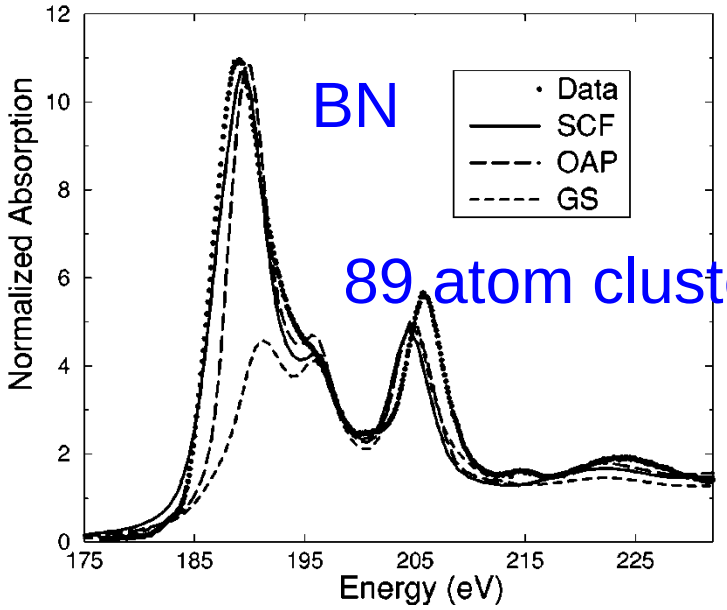
Core-hole SCF potentials

Essential!

Applicable to

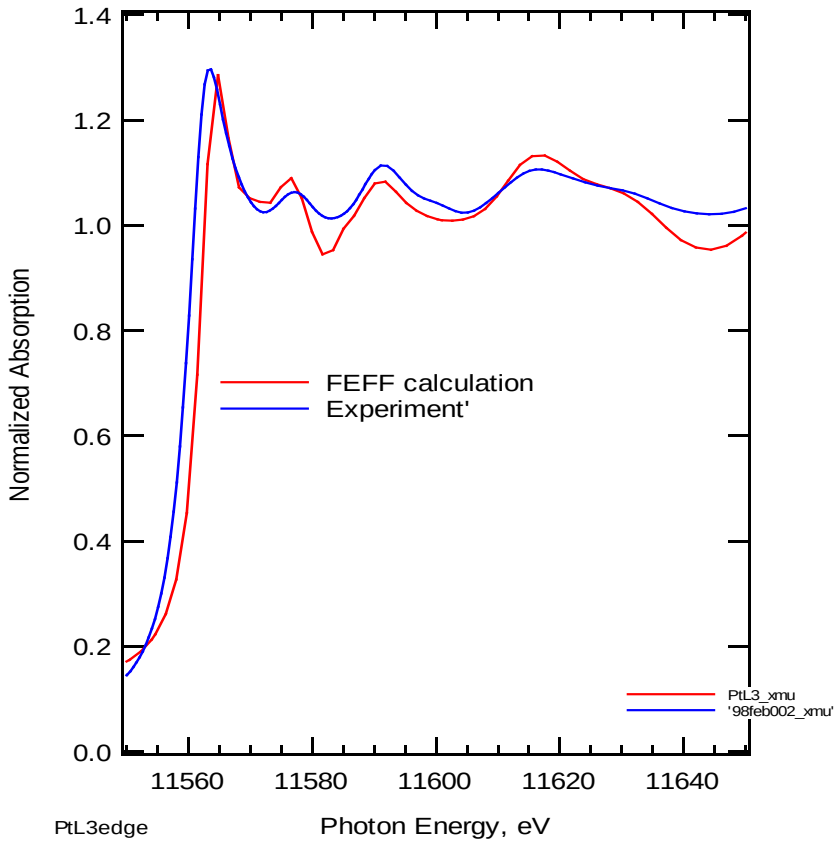
XAS, EELS, XES,
XMCD, DAFS, …



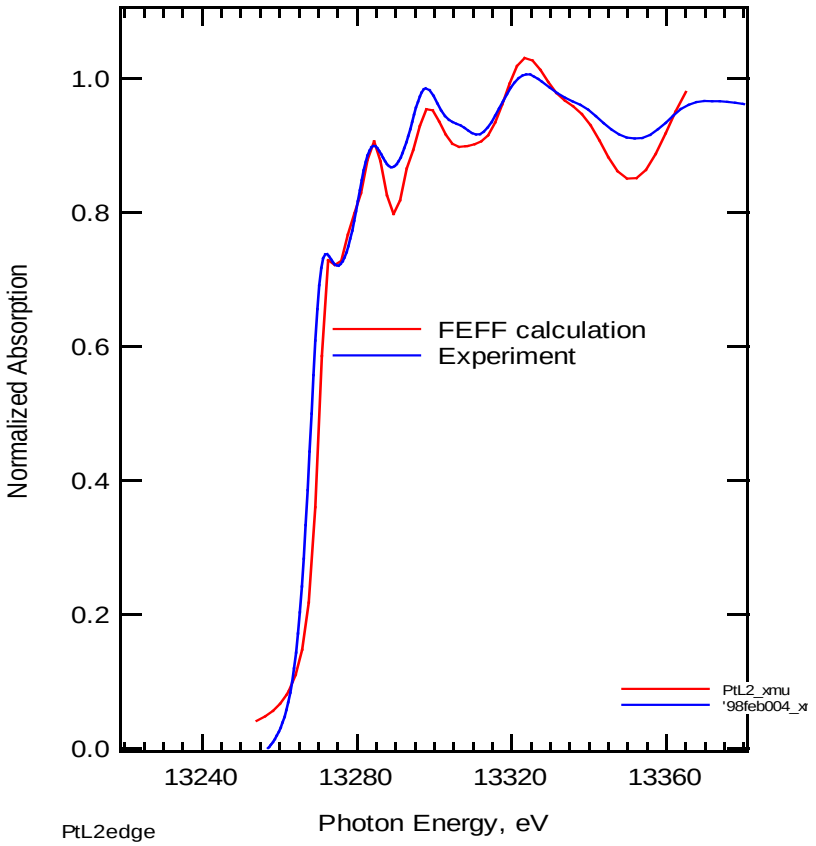
Application: XANES

Pt L_{23}

Pt L_3-edge



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



- ***Dirac relativistic* FEFF8 code reproduces all spectral features**

including absence of white line at L_2-edge

Green's Functions & Parallel Calculations

PHYSICAL REVIEW B, VOLUME 65, 104107

Parallel calculation of electron multiple scattering using Lanczos algorithms

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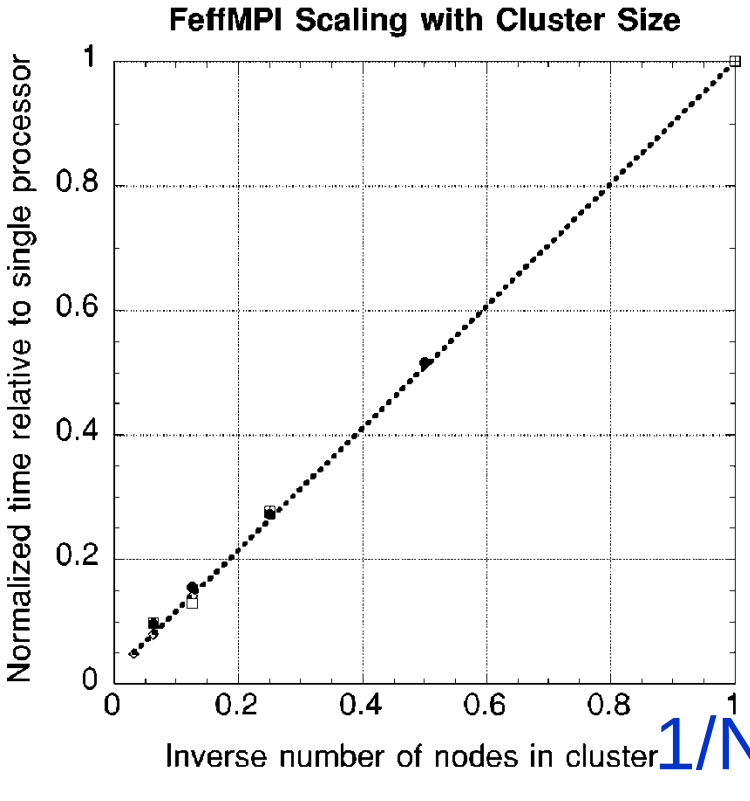

$1/N_{CPU}$

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

Energy E is a **parameter** !

"Natural parallelization"

Each CPU does one energy

Application: RIXS

PHYSICAL REVIEW B 83, 235114 (2011)

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

J. J. Kas,[1] J. J. Rehr,[1,*] J. A. Soininen,[2] and P. Glatzel[3]
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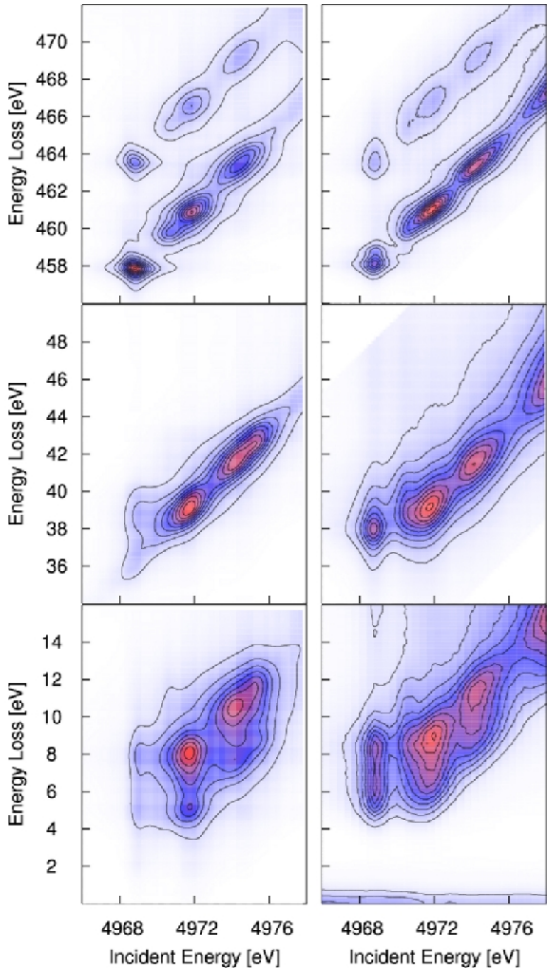
(Received 21 January 2011; revised manuscript received 7 April 2011; published 8 June 2011)

J. Kas et al. Phys. Rev. B **83**, 235114 (2011)



$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{\omega}{\Omega}\sum_F \left| \frac{\sum_M \langle F|\Delta_2^\dagger|M\rangle\langle M|\Delta_1|\Psi_0\rangle}{E_M - \Omega - E_0 + i\Gamma_M} \right|^2 \times \delta(\Omega - \omega + E_0 - E_F).$$

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

~ XES *XAS

Application LDA+ U / GW in FEFF9*

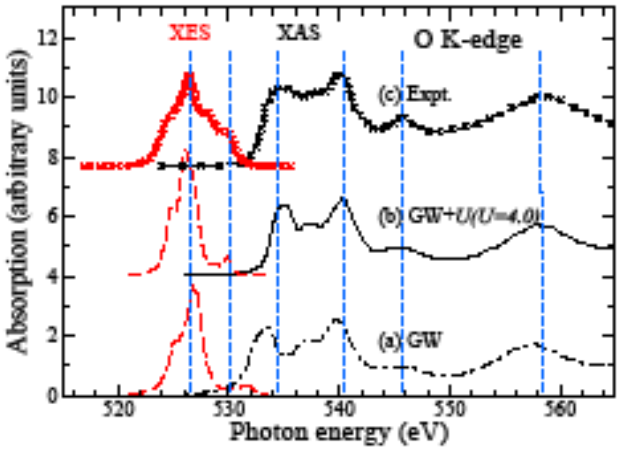
O K-edge MnO

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
Department of Physics, University of Washington, Seattle, Washington 98195, USA
(Received 10 July 2011; revised manuscript received 24 February 2012; published 16 April 2012)

The Hubbard model is implemented in real-space multiple scattering (RSMS) Green's function calculations of x-ray spectra based on a rotationally invariant local density approximation (LDA) + U formalism. Values



Add U as correction to GW self energy:

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

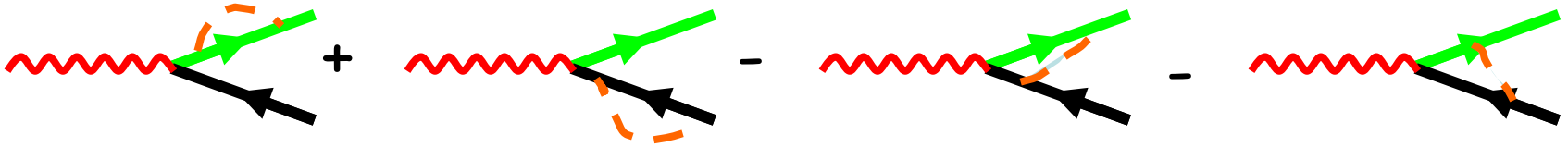
*Phys Rev B 85, 165123 (2012)

Inelastic losses in XAS & XPS

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

$$A(\omega) = -(1/\pi)\ \mathbf{Im}\ g^{++}(\omega)$$

Extrinsic + Intrinsic − 2 x Interference



- Many-body XAS ≈ Convolution of QP XAS with effective spectral function $A(\omega)$

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

Beyond GW: Cumulant Methods

Europhys J. J. B 85, 324 (2012) ‘ see also M. Guzzo et al., PRL **107**, 166401 (2011)

Plasmon Satellites in Valence-band Photoemission Spectroscopy

Ab Initio study of the photon-energy dependence in semiconductors

Matteo Guzzo[1,2], Joshua J. Kas[3], Francesco Sottile[1,2], Mathieu G. Silly[4], Fausto Sirotti[4], John J. Rehr[3], and Lucia Reining[1,2]

Generalized particle/hole cumulant approximation for the electron Green's function

arXiv:1402.0022

J. J. Kas,[1,*] J. J. Rehr,[1,2,†] and L. Reining[3,2,‡]

[1]*Department of Physics, University of Washington Seattle, WA 98195*

[2]*European Theoretical Spectroscopy Facility (ETSF)*

[3]*Laboratoire des Solides Irradiés, École Polytechnique, CNRS, CEA-DSM, F-91128 Palaiseau, France*

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

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

GW Kernel

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

Extension XPS

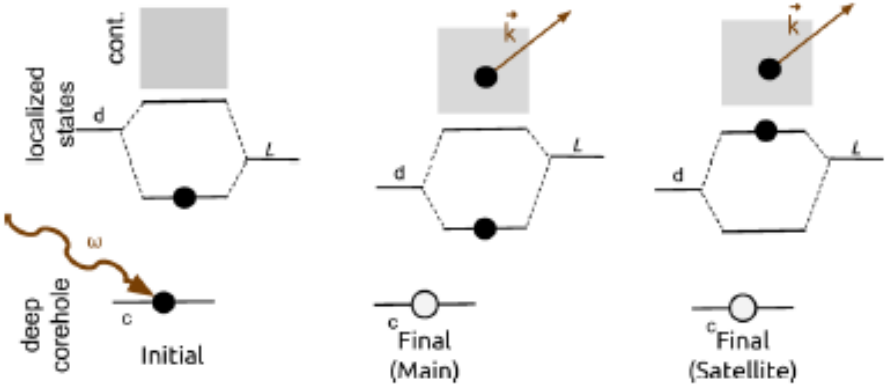
$$\gamma_{ik}(\omega) = \sum_{\mathbf{q}} |g_{\mathbf{q}}|^2 \delta(\omega-\omega_q) = \gamma_i^{int} + \gamma_k^{ext} + \gamma_{ik}^{inf}$$

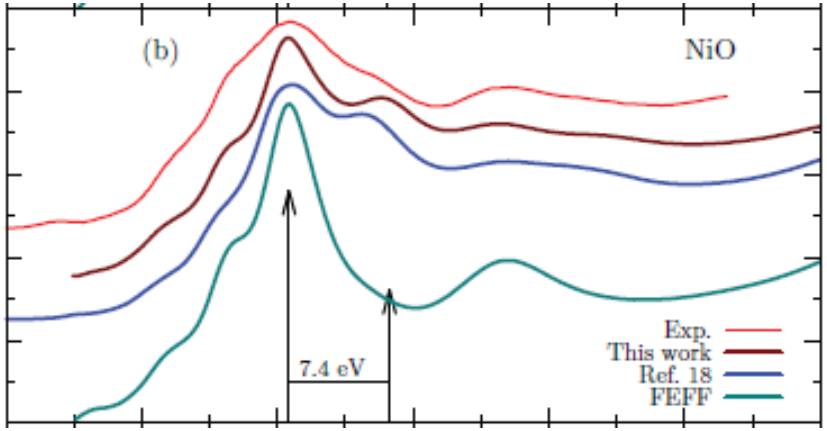
Application: Charge Transfer Satellites

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





Part II GW-BSE OCEAN

Core-Level X-ray Spectroscopy part II

Bethe-Salpeter equation

Keith Gilmore[1], J J Rehr[2], J Kas[2], J Vinson[3], E Shirley[3]

[1] ESRF, Grenoble, France

[2] University of Washington, Seattle, WA, USA

[3] NIST, Gaithersburg, MD, USA

Computational Objective

- Predictive
  - First-principles
  - Minimal free parameters
- Accurate
- Versatile
  - Multiple x-ray techniques
  - Variety of physical / chemical systems
- Efficient
  - 100-1000s atoms
  - Modest run-times / resources
- Usable
  - Simple / intuitive interface & inputs
  - Expertise in DFT not required

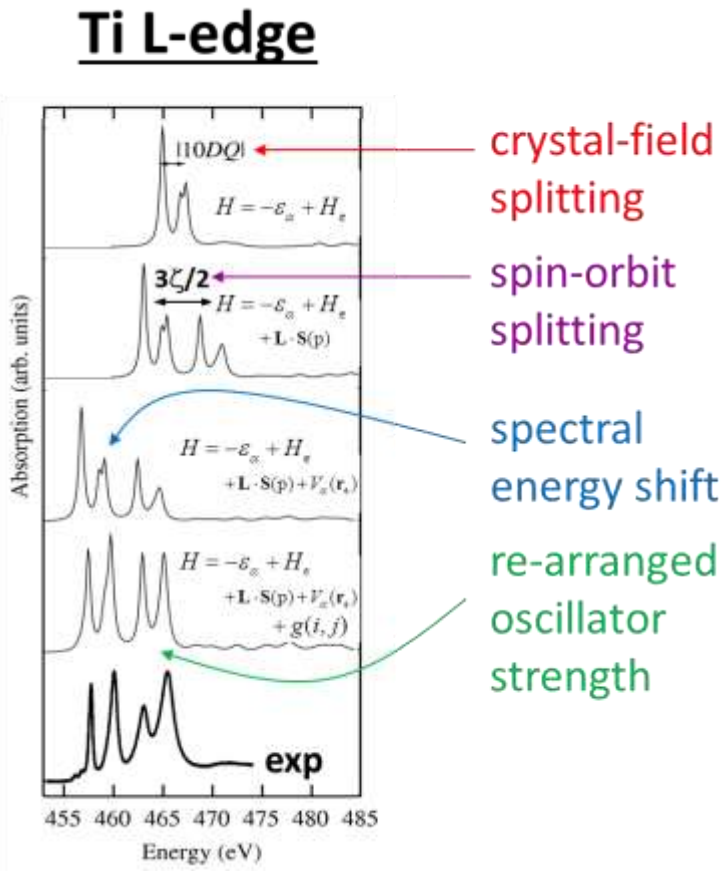
Atomic Multiplets

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

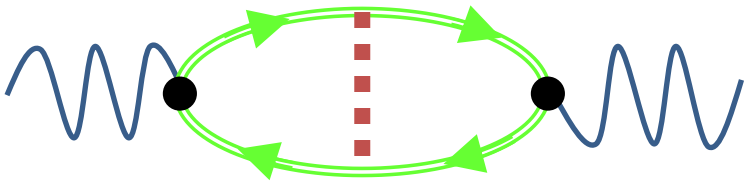
$$H_h = -\varepsilon_\alpha + \zeta L \cdot S$$

$$H_e = T + U + V$$

$$H_{eh} = V_\alpha(r) + g_{ij}$$



Bethe-Salpeter Equation



$$\mu(\omega) = -\frac{1}{\pi} Im\langle 0|\hat{d}^{+}|e,h\rangle \left\langle e,h\left|\frac{1}{\omega - H_{BSE} + i\eta}\right|e',h'\right\rangle \langle e',h'|\hat{d}|0\rangle$$

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

$$H_e = -\frac{\nabla^2}{2} + \int dr' \frac{\rho(r')}{|r - r'|} + V_{xc}[\rho(r)] + \Sigma$$ from DFT or DFT+GW

$$H_h = E_h + \chi_j - i\Gamma_j$$ from atomic DFT or HF

lifetime

Spin-orbit interaction

$$H_{eh} = V_X - V_D$$

$$V_X = \int dr dr' \psi_1^*(r)\psi_2(r)\frac{1}{|r - r'|}\psi_1(r')\psi_2^*(r')$$

$$V_D(\omega) = \int dr dr' \psi_1^*(r)\psi_2(r')\frac{\epsilon^{-1}(r,r';\omega)}{|r - r'|}\psi_1(r)\psi_2^*(r')$$

OCEAN: Obtaining Core-Excitations from Ab-initio electronic structure and the NIST BSE solver

Primary Developers

Eric Shirley
NIST

John Vinson
NIST

Group of
John Rehr
U. Washington

- Systematically improvable many-body approach to calculating spectra
- Based on DFT ground-state electronic structure
- Spectra obtained from 2-particle solutions of the Bethe-Salpeter eq.
- Several efficiencies make calculations practical
- **XAS, XES, RIXS, NRIXS, Auger, optical absorption**

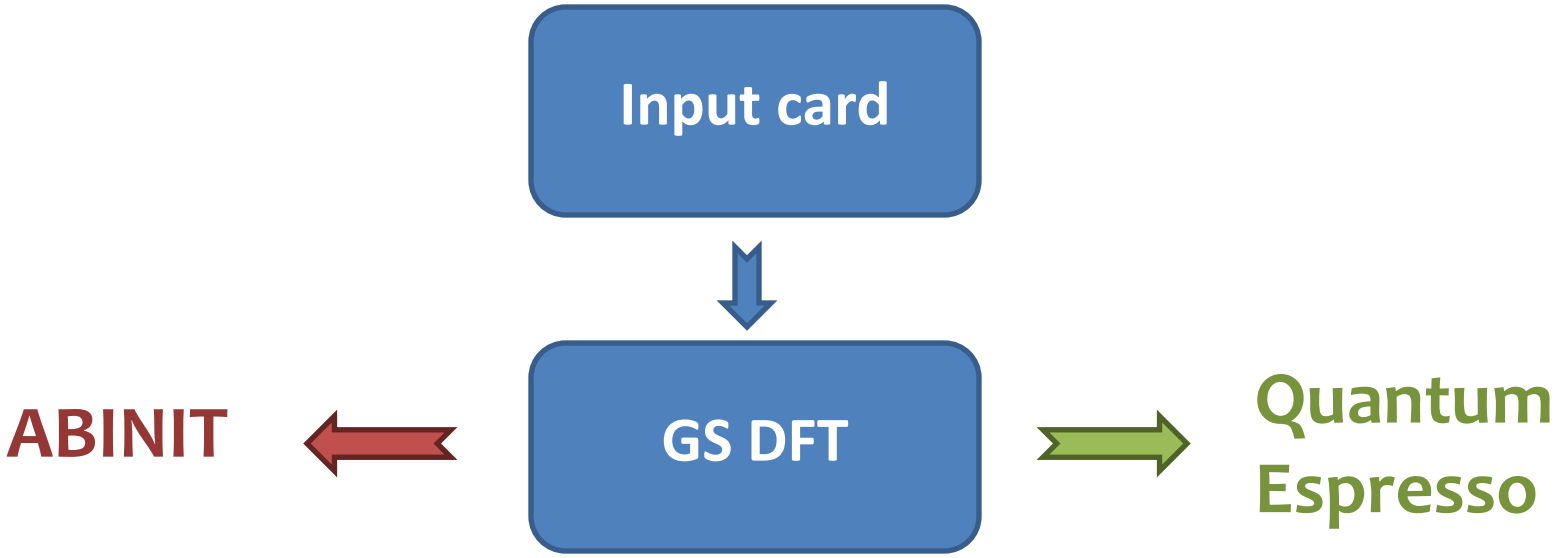
OCEAN process flow

Input card

- single file + pseudopotentials
- useful defaults

- atomic positions
- DFT parameters
- spectrum type (XAS, XES, XRS)
- edge information (atom, K/L, etc)

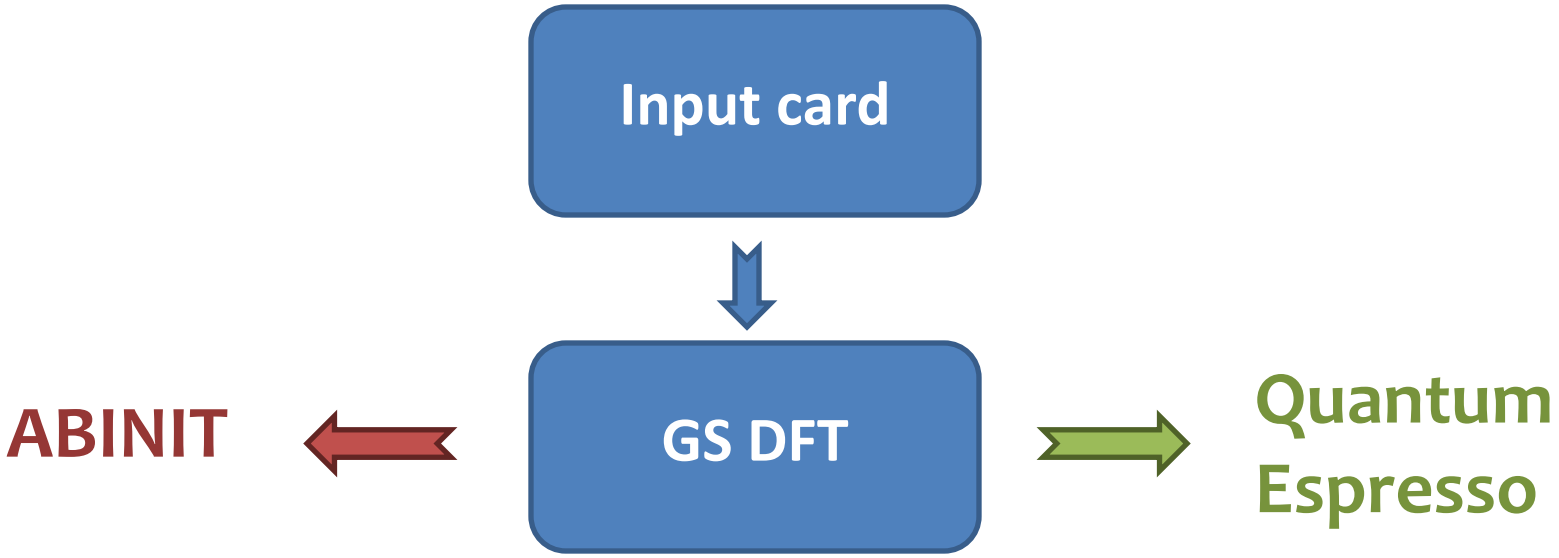
OCEAN process flow



- Freely available
- Well documented, easy to use
- High functionality, actively developed

- Plane-wave basis

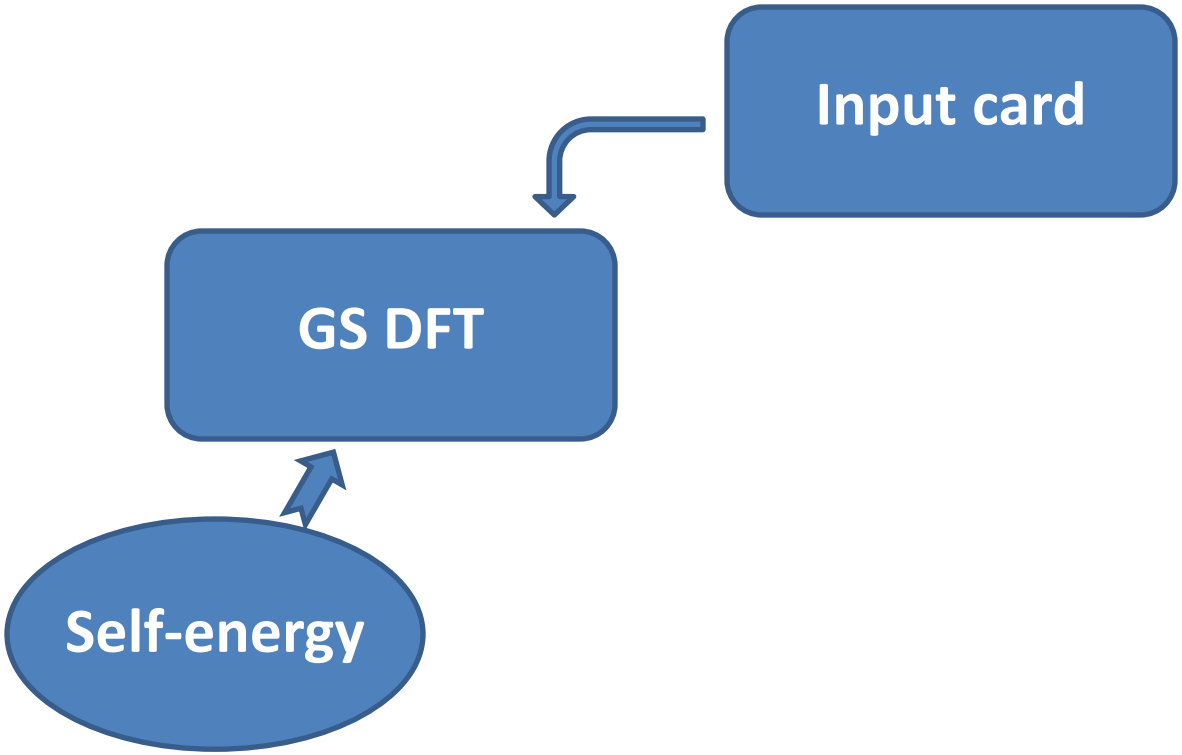
OCEAN process flow



Full periodic table of pseudopotenials available

NC : yes
US : testing
PAW : coming soon

OCEAN process flow



Self energy corrections

- GW: often accurate, but slow

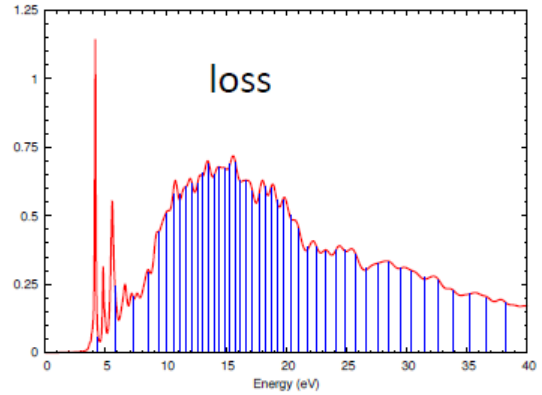
Many-pole self energy (MPSE)

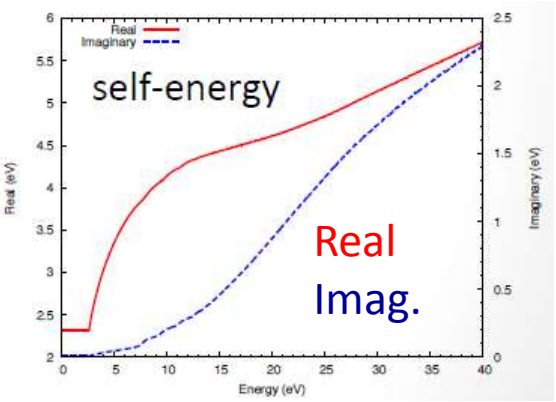
- Fast post-processing; extension of plasmon-pole model
- Calculate loss function (FEFF, optical code)
- Approximate loss function with a series of poles
- Use simple electron gas Green's function

$$-Im[\varepsilon(q,\omega)^{-1}] = \pi \sum_i g_i \omega_i^2 \delta[\omega^2 - \omega_i(q)^2]$$

$$\Sigma(k,E) \approx \mathrm{i} \int \frac{d^3q}{(2\pi)^3} \frac{d\omega}{2\pi} \frac{V(q)}{\varepsilon(q,\omega)} G_{heg}(E,\omega,k)$$

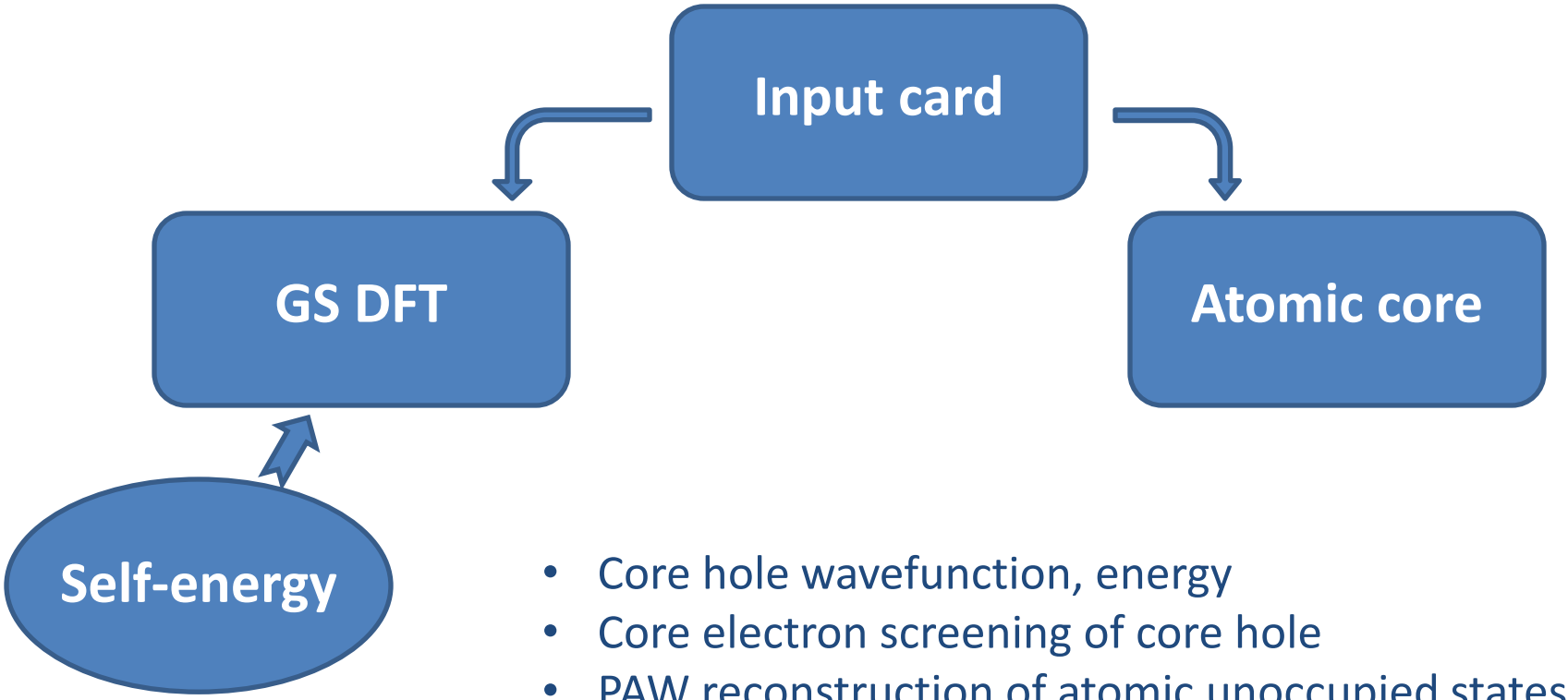
Example: Ice-Ih





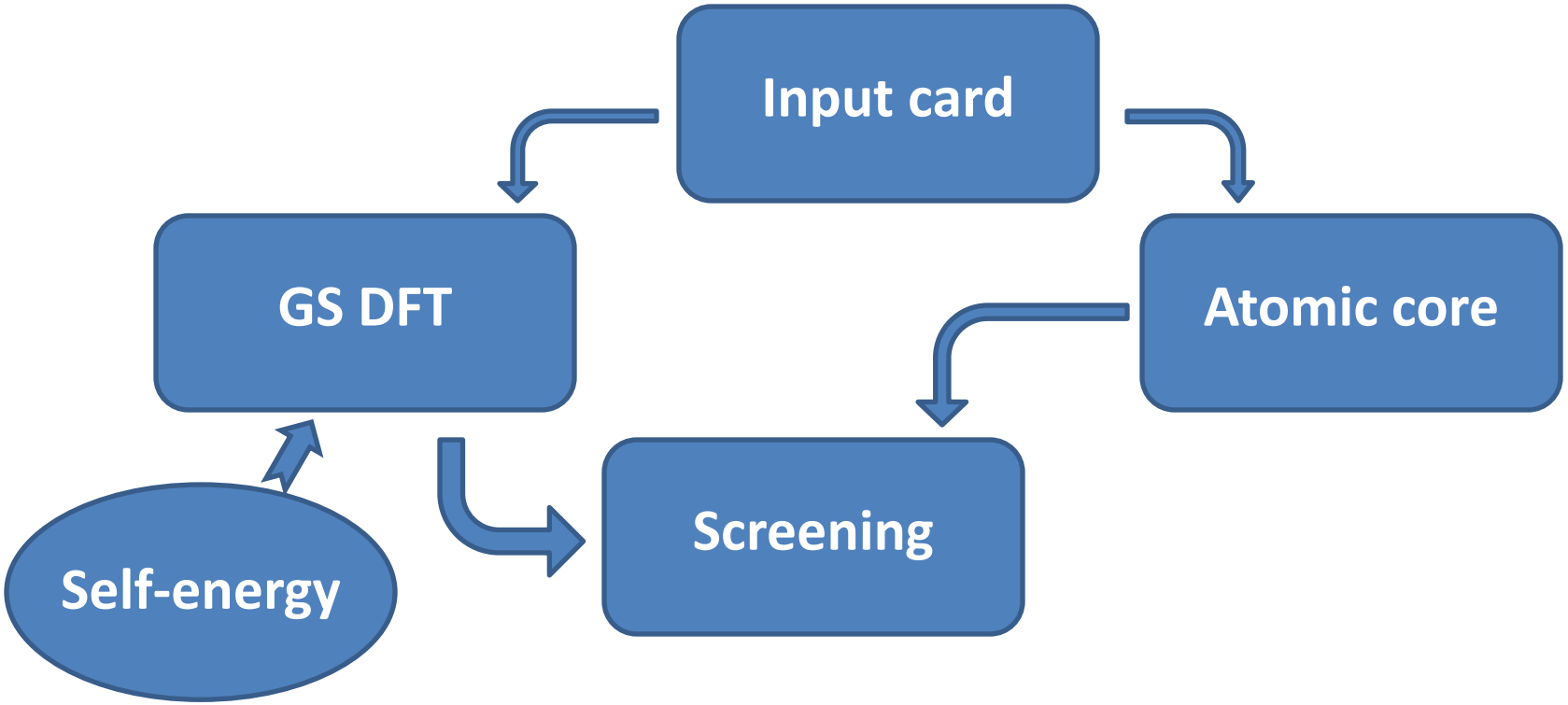
JJ Kas *et al*, *Phys Rev B* **76,** 195116 (2007)

OCEAN process flow



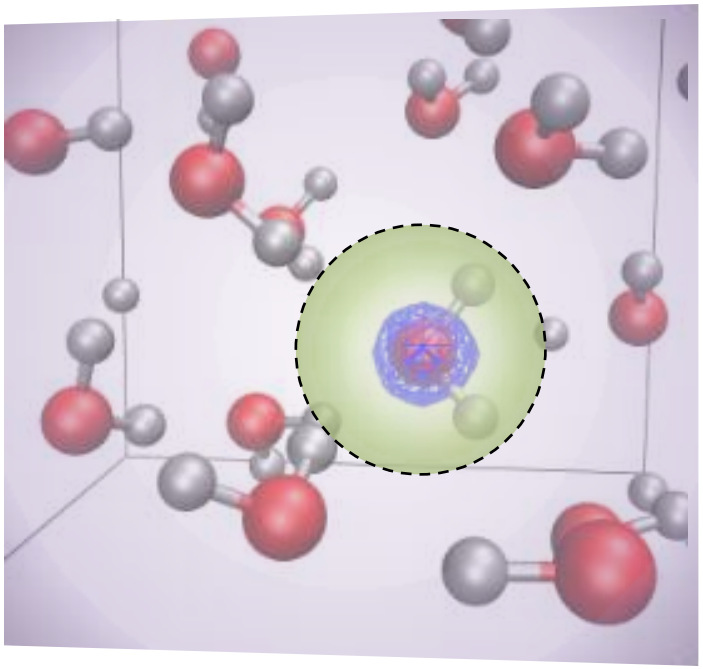
- Core hole wavefunction, energy
- Core electron screening of core hole
- PAW reconstruction of atomic unoccupied states
- Transition matrix elements

OCEAN process flow



Partition space for efficient calculation of screening response

$$W_0(r) = \Delta V_c(r) + W_c{}^{sr}(r) + W_c{}^{lr}(r)$$



Short-range: detailed RPA screening

$$\chi^0(r,r',\omega) = \int d\omega' G^0(r,r',\omega') G^0(r',r,\omega+\omega')$$

Random phase approximate

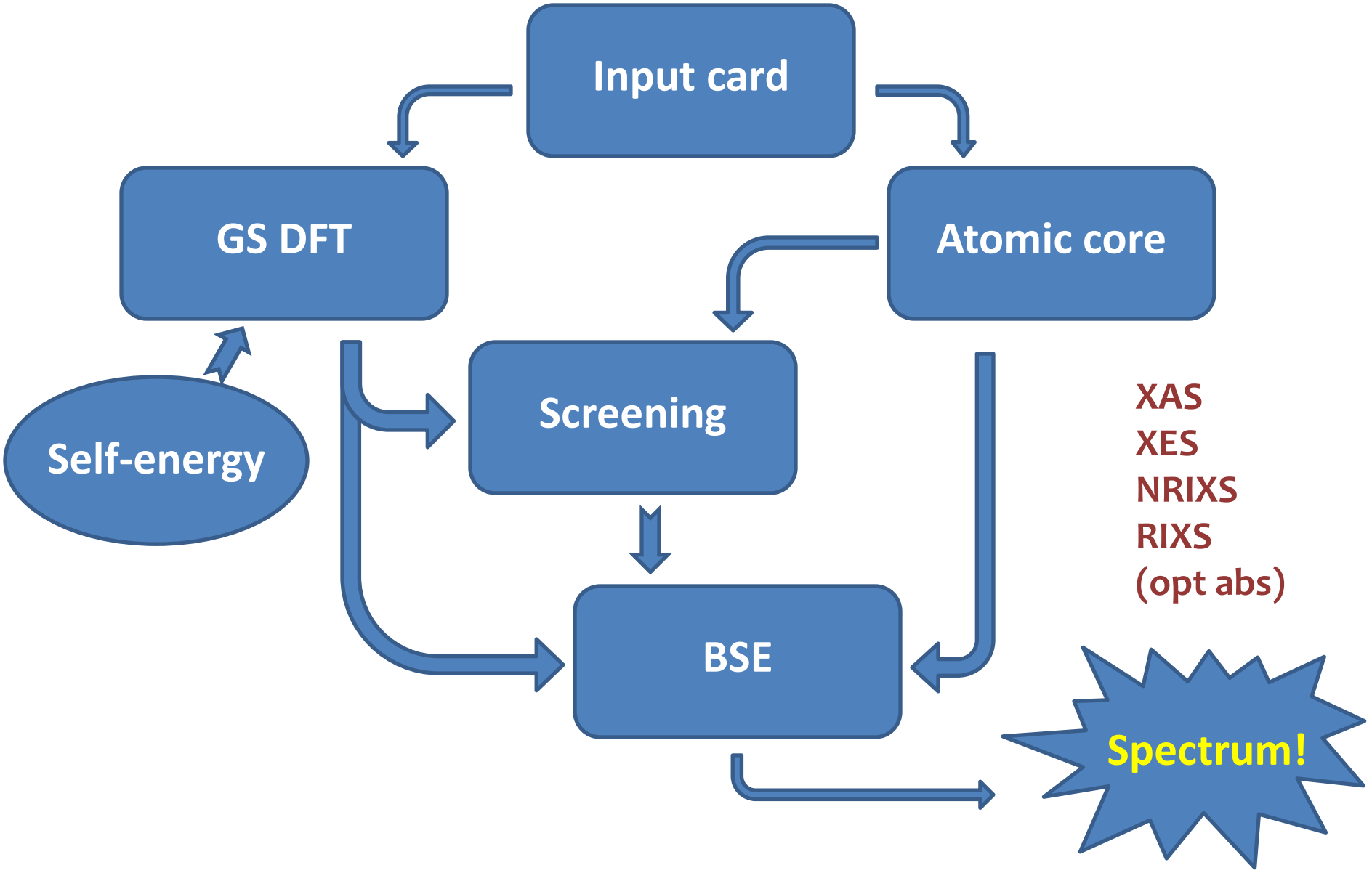
Long-range: model dielectric response

$$\chi_M(r,r') = \nabla \cdot \nabla' \left(\frac{n(r)+n(r')}{2n_0} \right) \left(\int \frac{d^3q}{(2\pi)^3} e^{iq\cdot(r-r')} \frac{\varepsilon_{LL}^{-1}(q,n_0;\varepsilon_\infty)-1}{4\pi} \right)$$

Levine-Louie model dielectric function

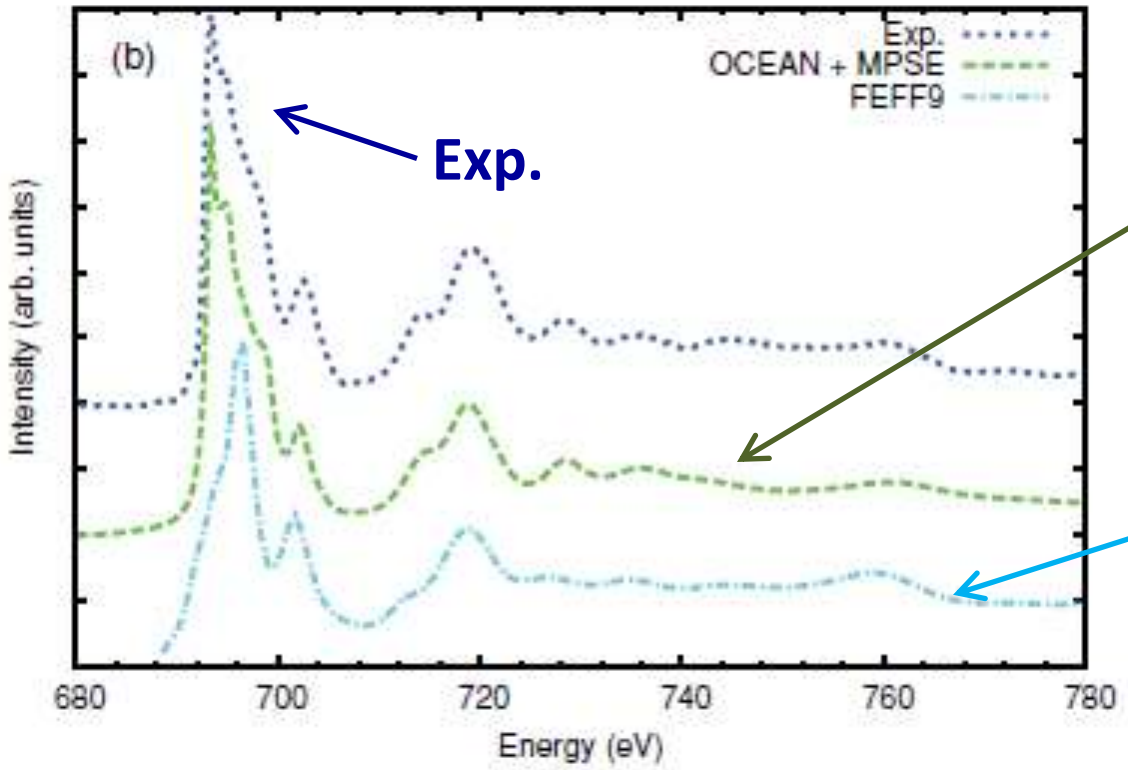
EL Shirley, *Ultramicroscopy* **106,** 986 (2006)

OCEAN process flow



XAS: K-edges

LiF; F K-edge



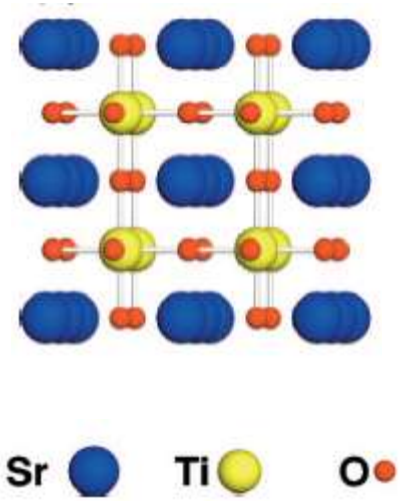
OCEAN accurately reproduces full range of spectrum

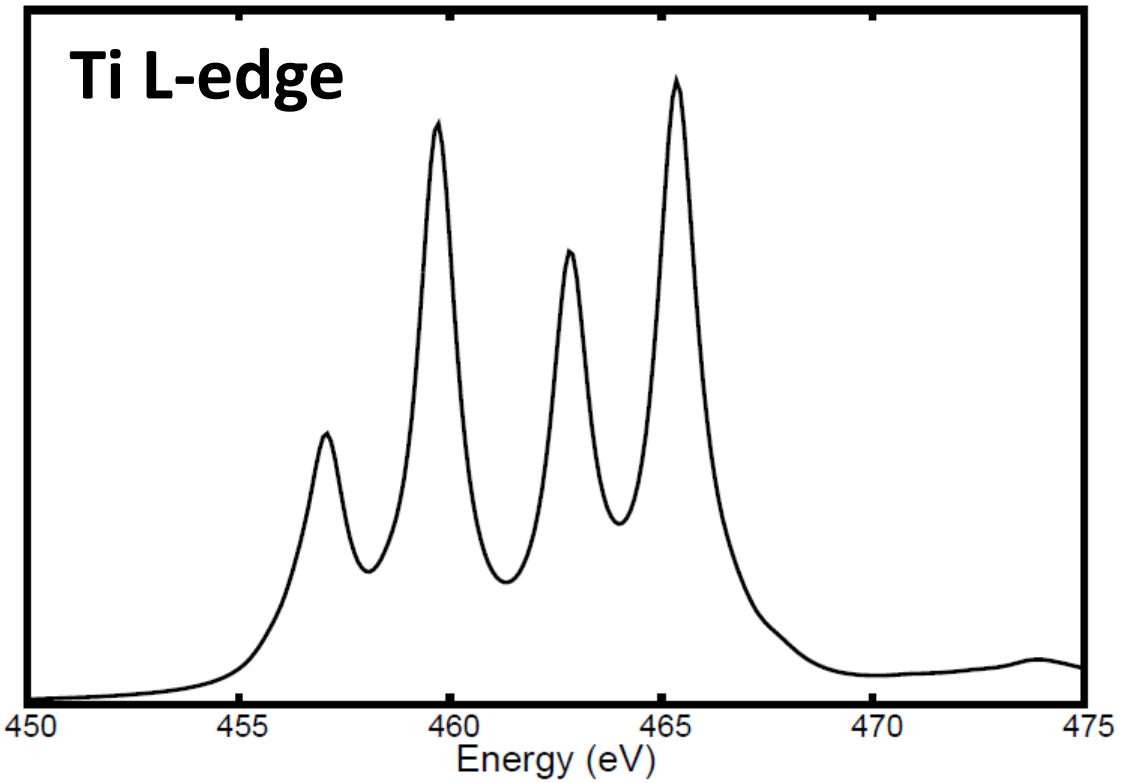
FEFF misses excitonic feature, reproduces extended region

J Vinson *et al*, *Phys Rev B* **83**, 115106 (2011)

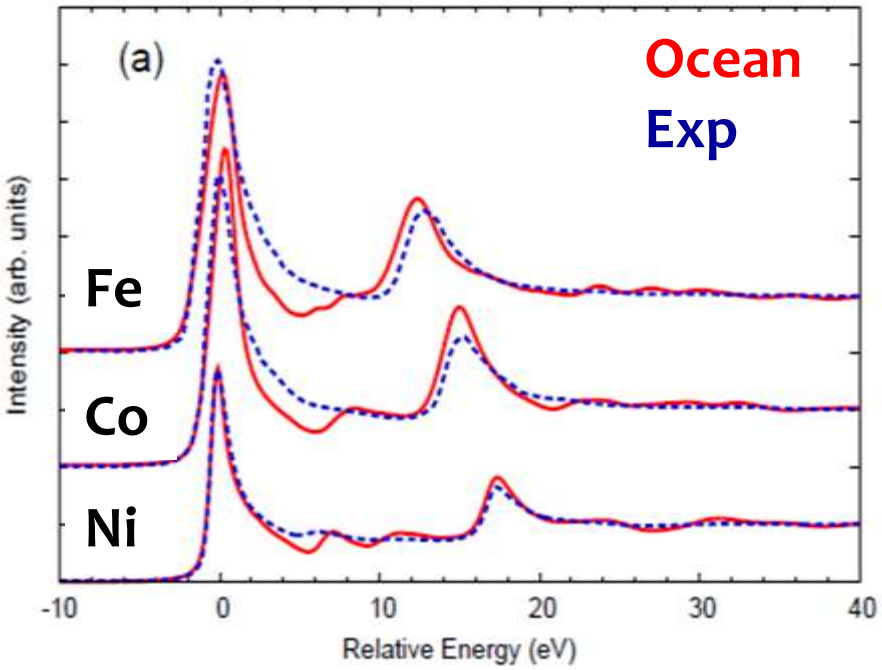
XAS: simple L-edges

$SrTiO_3$





XAS: transition metal L-edges

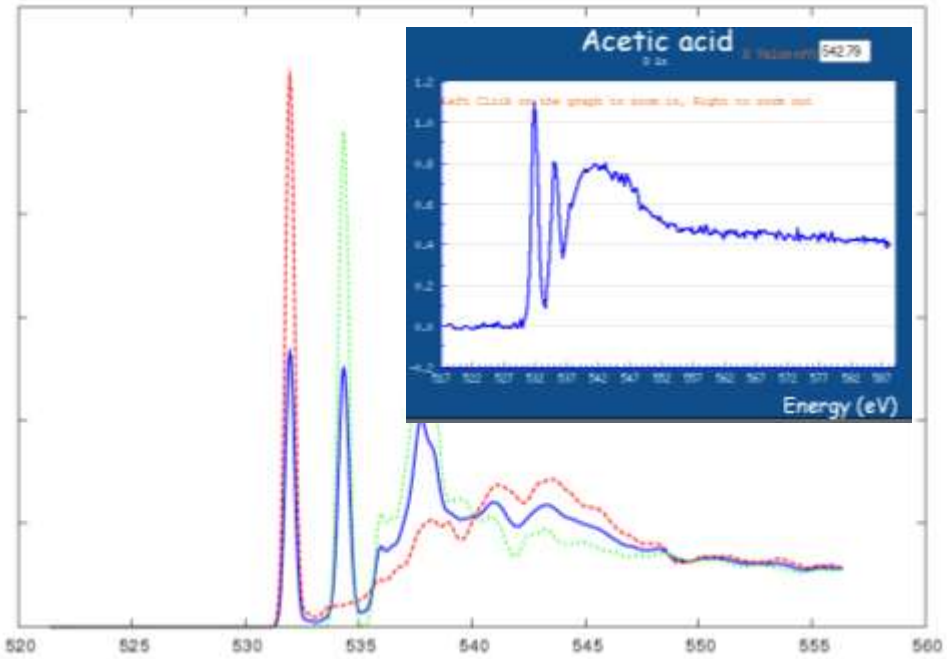


L_3 / L_2 branching ratios

Atom	Z	Exp	OCEAN
Ca	20	0.8	0.8
V	23	1.0	1.1
Fe	26	2.0	1.8
Co	27	2.3	2.0
Ni	28	2.4	2.0
Cu	29	0.9	0.8

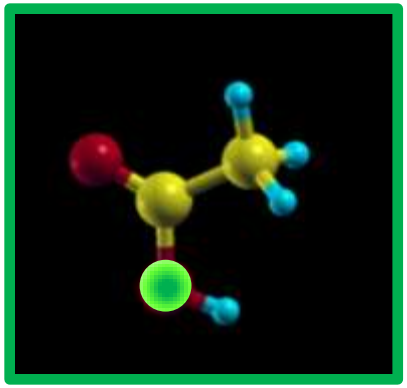
J Vinson and JJ Rehr, *Phys Rev B* **86,** 195135 (2012)

XAS: molecules / liquids



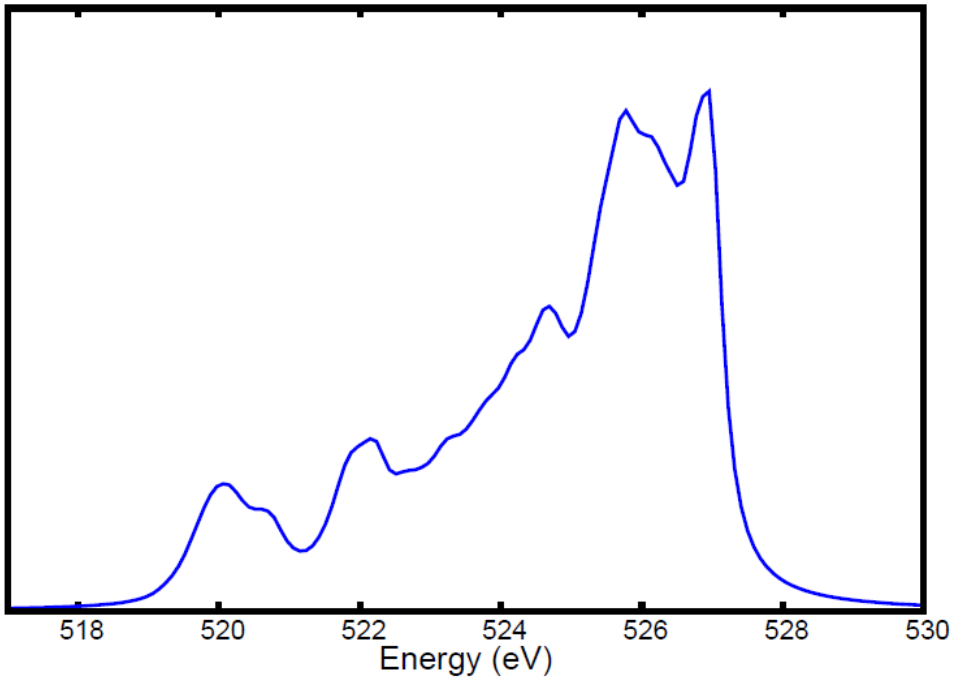
Photon Energy (eV)

Experimental reference spectrum from
Adam Hitchcock, McMaster University, Ontario, CA
unicorn.mcmaster.ca/corex/name-list.html

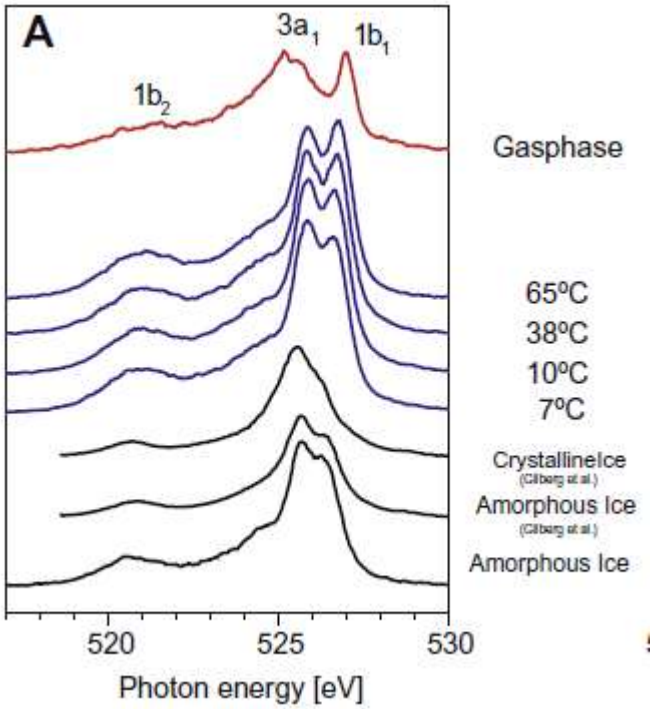


XES: liquid water (with excited-state dynamics)

Water O XES



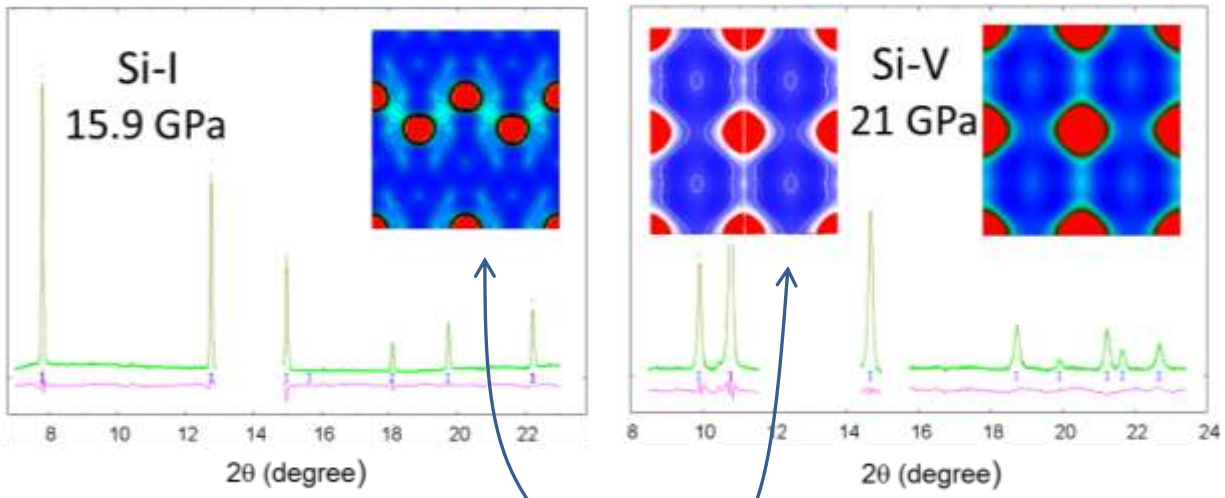
unpublished



Tokushima *et al.*, Chem Phys Lett (2008)

High pressure silicon

Phase change at high pressure

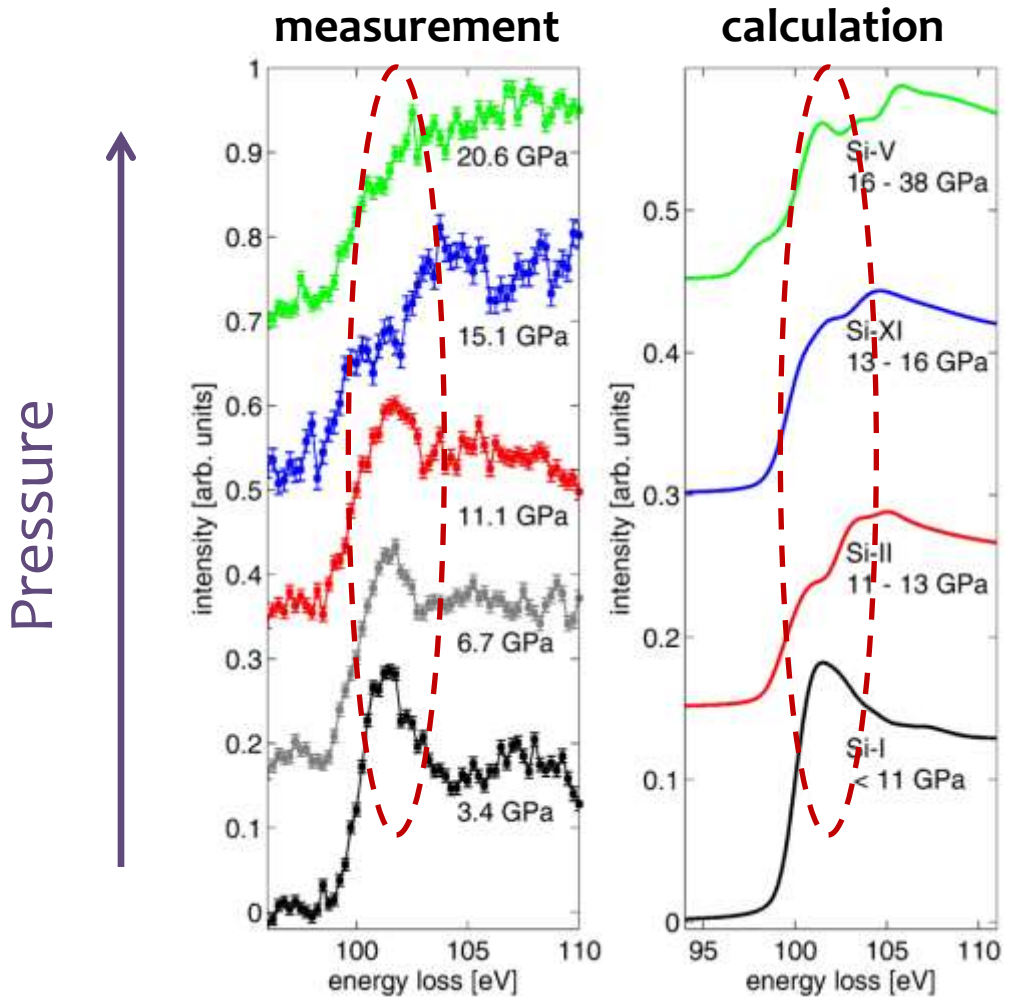


Diffraction performed on ESRF ID09

Redistribution of electron density from s-p hybridized bonding orbitals to d-character orbitals with strong interstitial weight

JS Tse *et al*, J Phys Chem C (2014)

NRIXS: L-edges



Silicon NRIXS

Increasing pressure

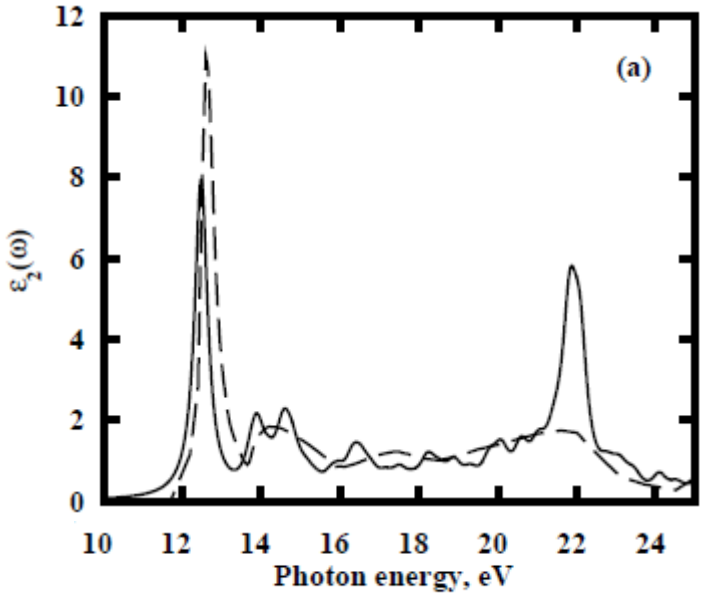
- Phase changes
- Decreasing excitonic peak
- Increasing metallicity

XRS measured on ESRF ID16

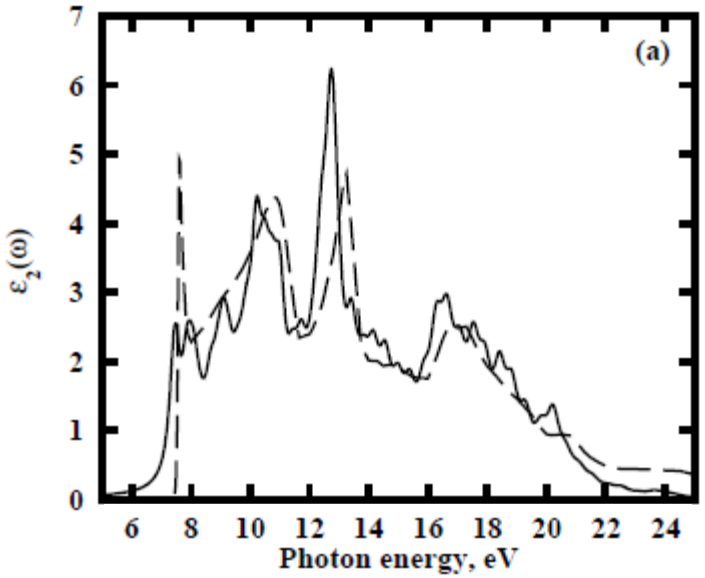
JS Tse *et al*, J Phys Chem C (2014)

Optical absorption

LiF



MgO



—— calculation ------ experiment

LX Benedict *et al*, *Phys Rev Lett* **80**, 4514 (1998)

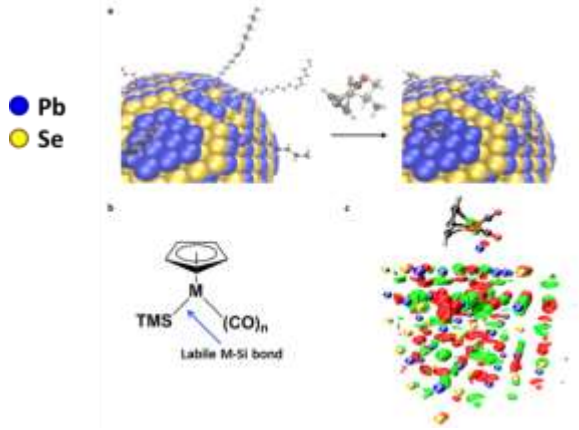
OCEAN: Obtaining Core-Excitations from Ab-initio electronic structure and the NIST BSE solver

- Predictive
  - First-principles, minimal free parameters
- Accurate
- Versatile
  - XAS, XES, (N)RIXS, optical spectra
  - Periodic crystals, liquids, molecules
- Efficient
  - 100s atoms (want 1000s)
  - Needs cluster, but not supercomputer
- Development of release version in progress
  - 'locally' available at the ESRF/Grenoble
  - keith.gilmore@esrf.fr

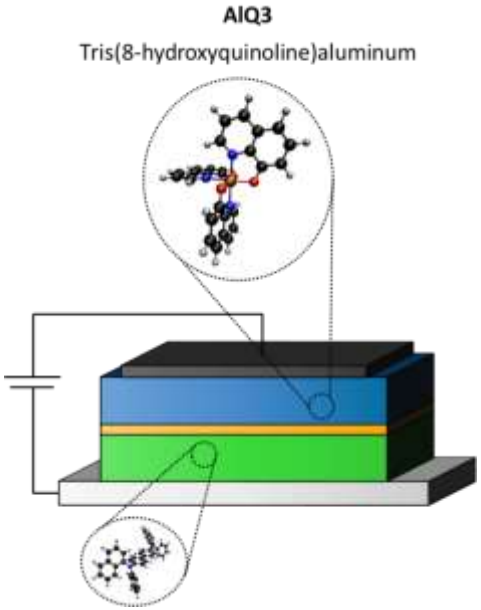
See poster for additional results

keith.gilmore@esrf.fr

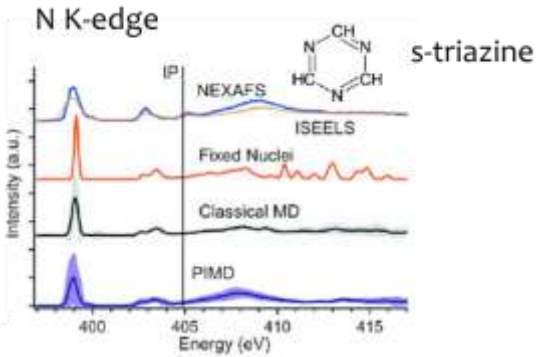
Semiconductor nanocrystals



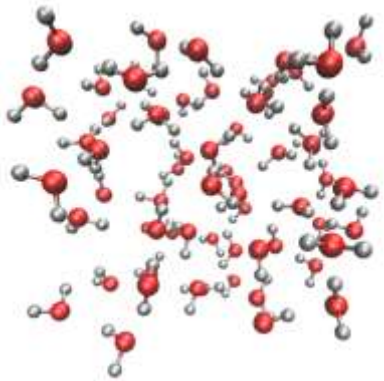
Organic electronics



Vibrational effects

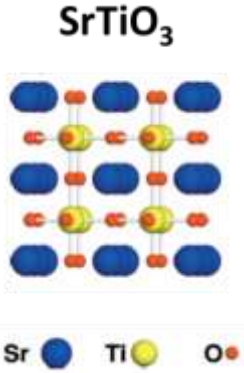


Water

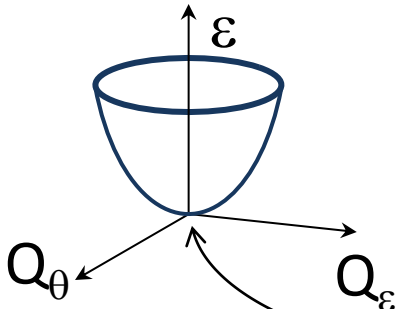


CP Schwartz *et al*, *J Chem Phys* **130**, 184109 (2009)

Explicit inclusion of vibronic coupling: $SrTiO_3$

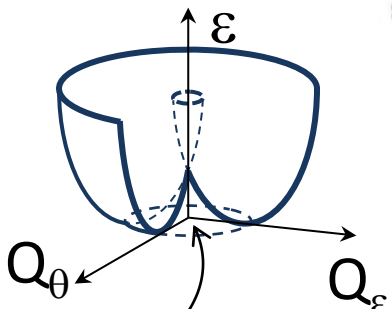


$3d^0$ ground state

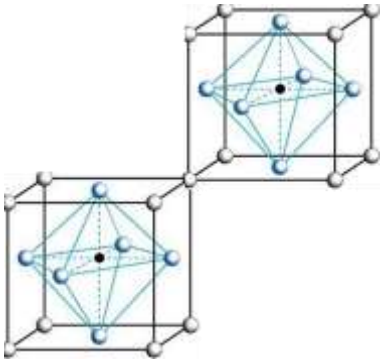


Born-Oppenheimer surfaces

$3d^1$ excited state

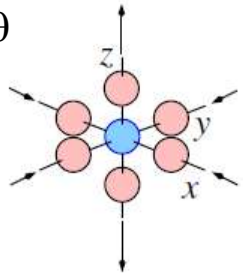


undistorted cubic lattice



Important local vibrational modes

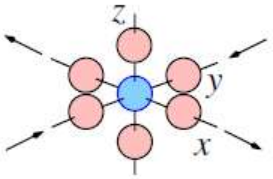
Q_θ



Ti^{4+}

O^{2-}

Q_ε



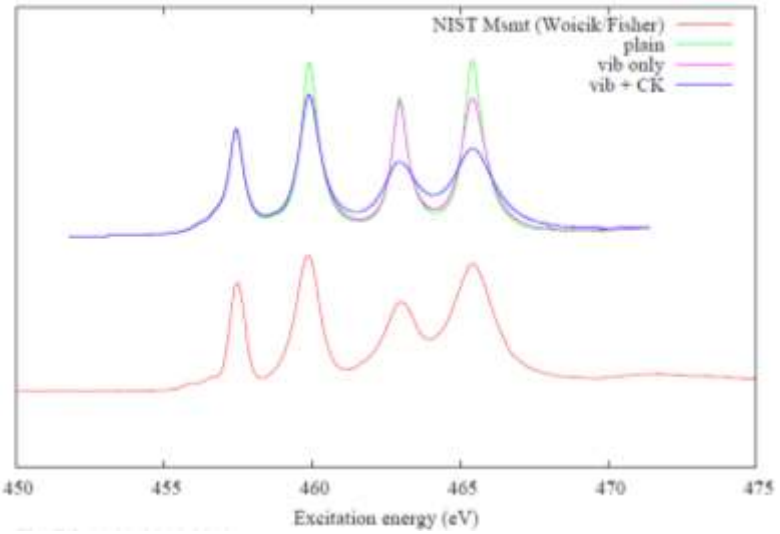
Explicit inclusion of vibronic coupling: $SrTiO_3$

$$\left[\mathbf{H}^{(0)}_{\text{mult}} + \mathbf{H}_{\text{vib}} + \mathbf{W}\right] \chi_K = E\, \chi_K$$

$$\chi_K \;\varepsilon\; |m_\ell^{(2p)}, m_s^{(2p)}; m_\ell^{(3d)}, m_s^{(3d)}; n_\theta, n_\epsilon\rangle$$

(n_θ,n_ε)	(0,0)	(1,0)	(0,1)	(1,1)	…	(N,N)
(0,0)	H’	W	W	0	…	
(1,0)	$W^\dagger$	H’	0	W		
(0,1)	$W^\dagger$	0	H’	W		
(1,1)	0	$W^\dagger$	$W^\dagger$	H’		
⋮	⋮				⋱	
(N,N)						

60 (rows) × 60 (columns)



$$H' = H_{\text{mult}} + \hbar\omega(n_\theta+n_\varepsilon)\,\mathbf{1}_{\text{mult}}$$

N=200 vibrational levels required for convergence

K Gilmore and EL Shirley, *J Phys : Condens Matter* **22**, 315901 (2010)