Introduction to the calculation of X-ray absorption spectra

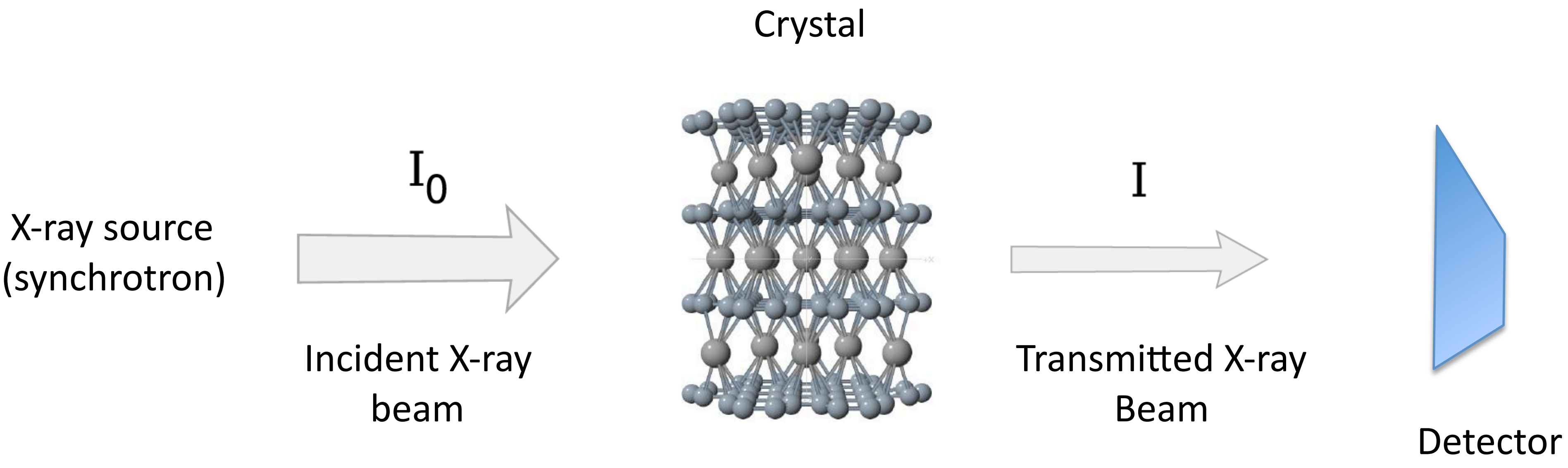
Matteo Calandra and Oana Bunau

/afs/ictp/public/shared/smr2376/Tutorial/XSpectra/Introduction_to_XAS.pdf
or
$WORKSHOP/Tutorial/XSpectra/Introduction_to_XAS.pdf

C. Gougoussis, M. Calandra, A. P. Seitsonen, and F. Mauri
Phys. Rev. B **80**, 075102 (2009)

P. Giannozzi et al., J. Phys. Condens. Matter **21**, 395502 (2009).

What is XAS ?



Crystal

X-ray source
(synchrotron)

I_0

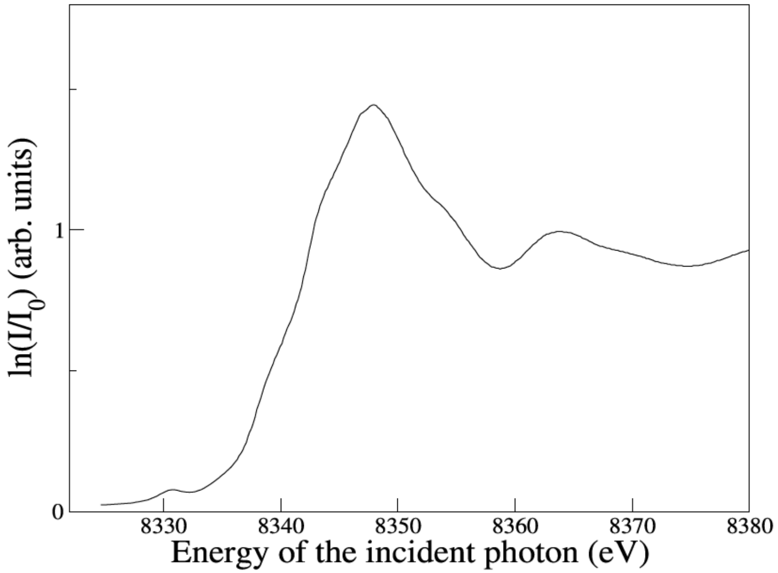
Incident X-ray beam

I

Transmitted X-ray Beam

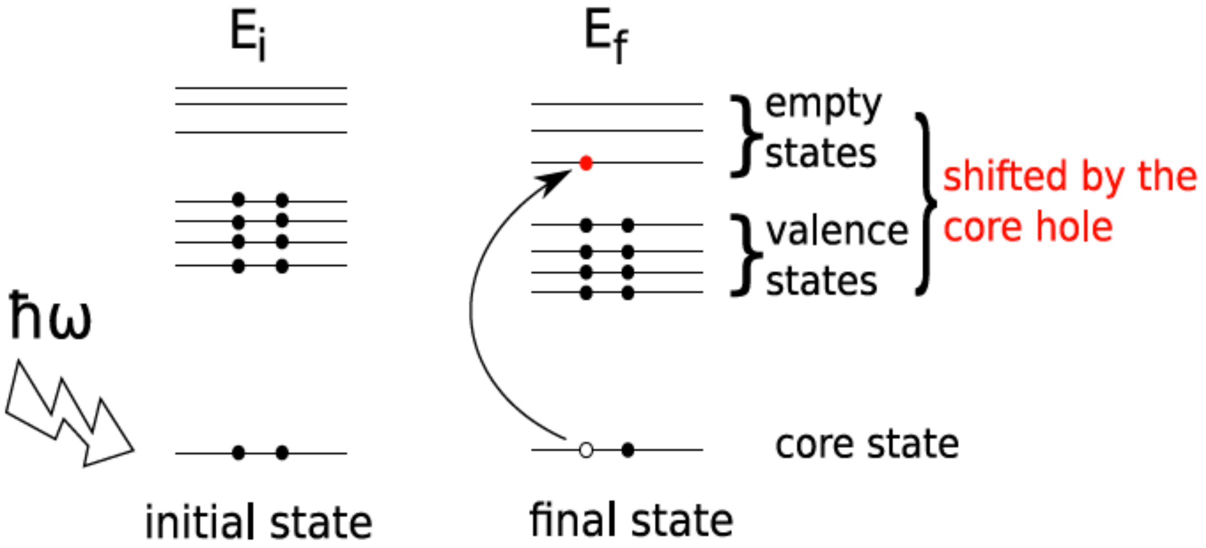
Detector

Result :



Ni K-edge XAS of NiO

XAS Physical process



Challenge: describe core-hole attraction from first principles.

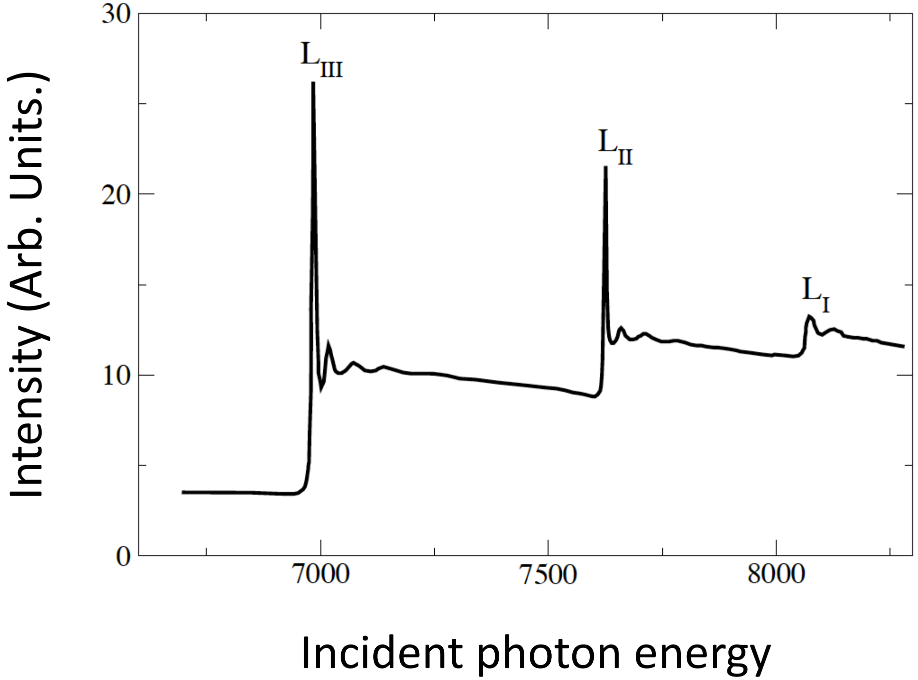
Chemical and Orbital selectivity

The choice of the incident photon energy selects the core electron excited.
Experimentalists are then free to choose:

(i) the atom from which the electron is excited (absorbing atom).

(ii) the atomic level from which the electron is excited.

Example: Eu L_1, L_2, L_3 edges



Core state	Edge name
1s	K
2s	L_1
$2p_{1/2}$	L_2
$2p_{3/2}$	L_3
3s	M_1

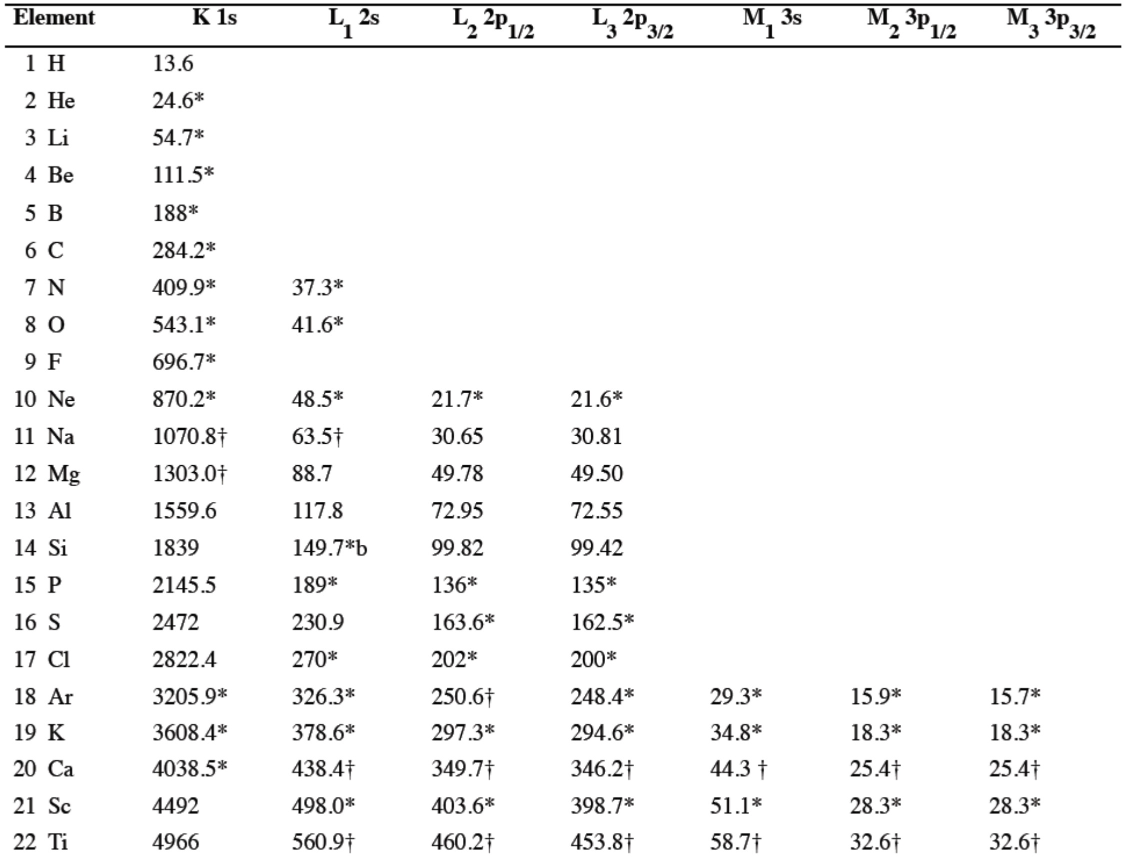
Chemical and Orbital selectivity

The choice of the incident photon energy selects which core electron is excited.
Experimentalists are then free to choose:

(i) the atom from which the electron is excited (absorbing atom).

(ii) the atomic level from which the electron is excited.

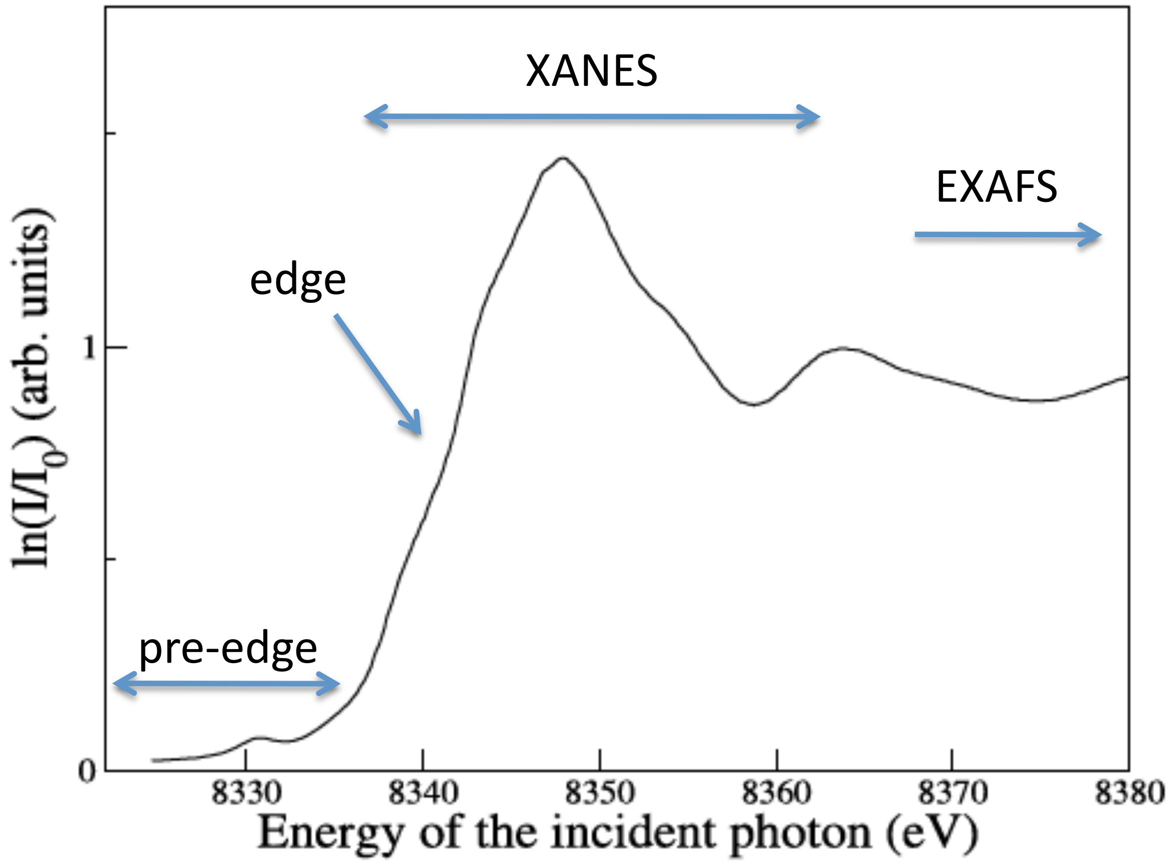
Note that core-sate binding energies of atoms are very different:



Element	K 1s	L_1 2s	L_2 $2p_{1/2}$	L_3 $2p_{3/2}$	M_1 3s	M_2 $3p_{1/2}$	M_3 $3p_{3/2}$
1 H	13.6						
2 He	24.6*						
3 Li	54.7*						
4 Be	111.5*						
5 B	188*						
6 C	284.2*						
7 N	409.9*	37.3*					
8 O	543.1*	41.6*					
9 F	696.7*						
10 Ne	870.2*	48.5*	21.7*	21.6*			
11 Na	1070.8†	63.5†	30.65	30.81			
12 Mg	1303.0†	88.7	49.78	49.50			
13 Al	1559.6	117.8	72.95	72.55			
14 Si	1839	149.7*b	99.82	99.42			
15 P	2145.5	189*	136*	135*			
16 S	2472	230.9	163.6*	162.5*			
17 Cl	2822.4	270*	202*	200*			
18 Ar	3205.9*	326.3*	250.6†	248.4*	29.3*	15.9*	15.7*
19 K	3608.4*	378.6*	297.3*	294.6*	34.8*	18.3*	18.3*
20 Ca	4038.5*	438.4†	349.7†	346.2†	44.3 †	25.4†	25.4†
21 Sc	4492	498.0*	403.6*	398.7*	51.1*	28.3*	28.3*
22 Ti	4966	560.9†	460.2†	453.8†	58.7†	32.6†	32.6†

For more see http://xdb.lbl.gov/

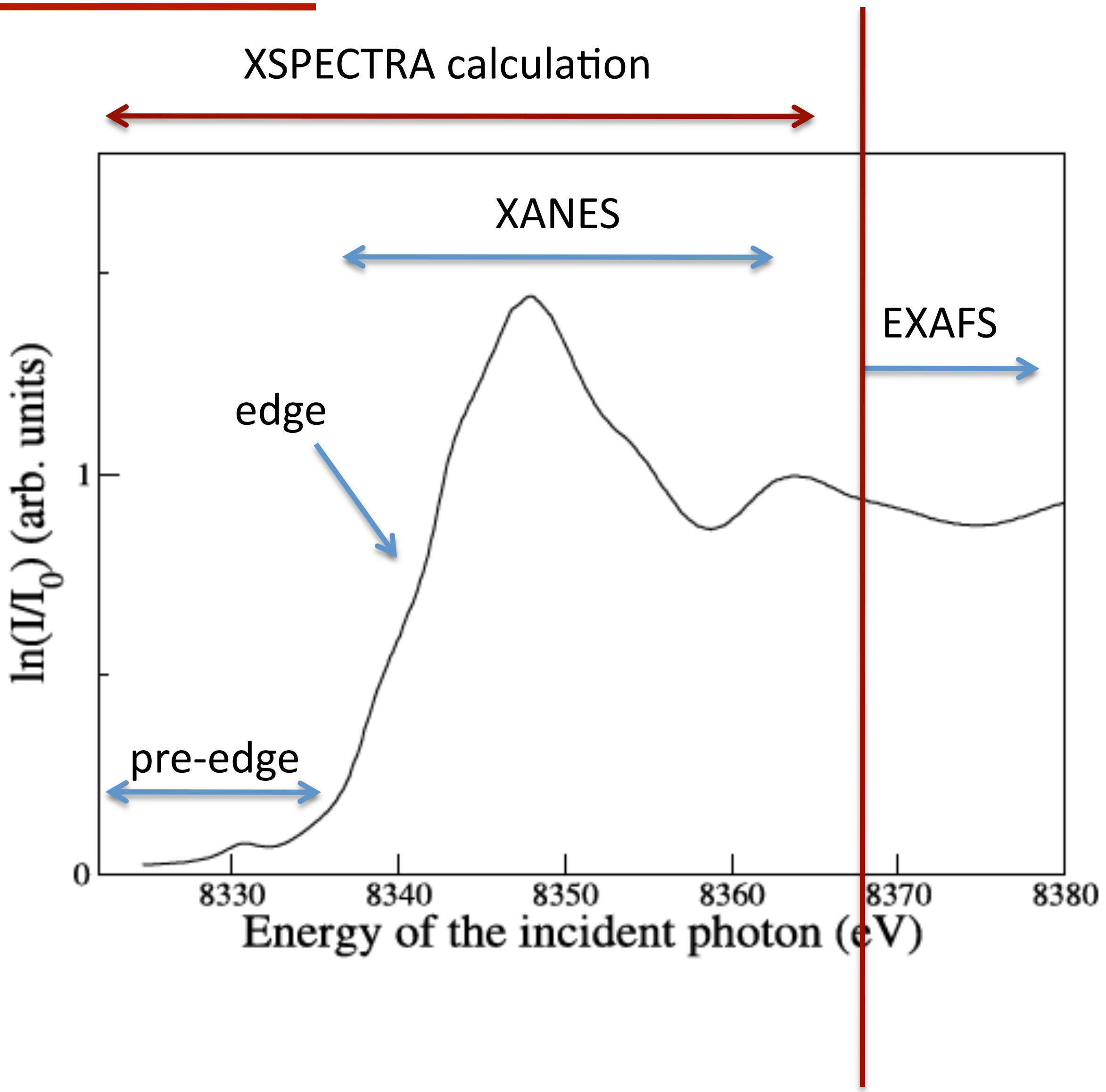
Name of XAS structures



XANES=X-ray near edge structures.

EXAFS=Extended X-Ray Absorption Fine Structure.

Name of XAS structures



XANES=X-ray near edge structures.

EXAFS=Extended X-Ray Absorption Fine Structure.

XAS cross section

From Fermi golden-rule:

$$\sigma(\hbar\omega) = 4\pi^2\alpha\hbar\omega \sum_f |\langle f|\mathcal{O}|i\rangle|^2 \, \delta(E_f - E_i - \hbar\omega)$$

Final state with
a core-hole

Initial state:
no core-hole

Incident-photon
energy

The matrix element is:

$$\mathcal{O} = \boldsymbol{\epsilon}\cdot\boldsymbol{r} + \frac{i}{2}(\boldsymbol{k}\cdot\boldsymbol{r})(\boldsymbol{\epsilon}\cdot\boldsymbol{r})$$

electric dipole

1s →p states

electric quadrupole

1s →d states

See Ch. Brouder, J. Phys. Cond. Matt. **2**, 701 (1990) for more details.

XAS cross section

In the absence of a magnetic field the cross section can be separated in dipolar and quadrupolar terms (cross terms are zero in this case):

$$\sigma = \sigma_D + \sigma_Q$$

with:

$$\begin{aligned}\sigma_D &= 4\pi^2\alpha\hbar\omega \sum_f \left| \langle f | \sum_j \epsilon \cdot \mathbf{r}_j | i \rangle \right|^2 \delta(E_f - E_i - \hbar\omega) \\ \sigma_Q &= 4\pi^2\alpha\hbar\omega \sum_f \left| \langle f | \frac{1}{2} \sum_j (\epsilon \cdot \mathbf{r}_j)(\mathbf{k} \cdot \mathbf{r}_j) | i \rangle \right|^2 \delta(E_f - E_i - \hbar\omega)\end{aligned}$$

and the two terms can be calculated separately.

The quadrupolar part is in the pre-edge region.

XAS cross section needs all-electron states

$$\sigma(\hbar\omega) = 4\pi^2\alpha\hbar\omega \sum_f |\langle f|\mathcal{O}|i\rangle|^2 \, \delta(E_f - E_i - \hbar\omega)$$

All-electron
Final state with
a core-hole

Initial state:
no core-hole

Incident-photon
energy

ALL ELECTRON STATES

XAS cross section needs all-electron states

However we have pseudopotentials and we do not have all-electron states!

$$\sigma(\hbar\omega) = 4\pi^2\hbar\omega\sum_f |\langle\tilde{f}|\mathcal{O}|i\rangle|^2\delta(E_f - E_i - \hbar\omega)$$

↓

PSEUDO WAVE FUNCTION

labeled by a tilde from now on

How to solve this problem ?

Use the projected augmented wave (PAW) method!

P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994)

PAW for XAS – short explanation

As we use pseudopotentials, the electron wavefunction that we obtain in our simulation is different from the all-electron wavefunction:

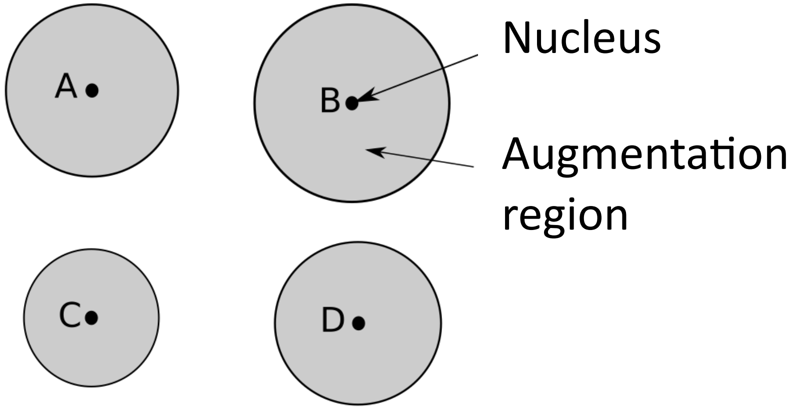
ALL ELECTRON　　　　MAPPING　　　　PSEUDO

$$|\psi\rangle \xleftrightarrow{\hspace{3cm}} |\tilde{\psi}\rangle$$

Assume that a linear mapping exists between the two wavefunctions:

$$|\psi\rangle = \mathcal{T}|\tilde{\psi}\rangle$$

As the *pseudowavefunction differs from the AE one only in the augmentation region* (core region) then *the mapping operator is different from the identity only in the augmentation region.*



P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994)

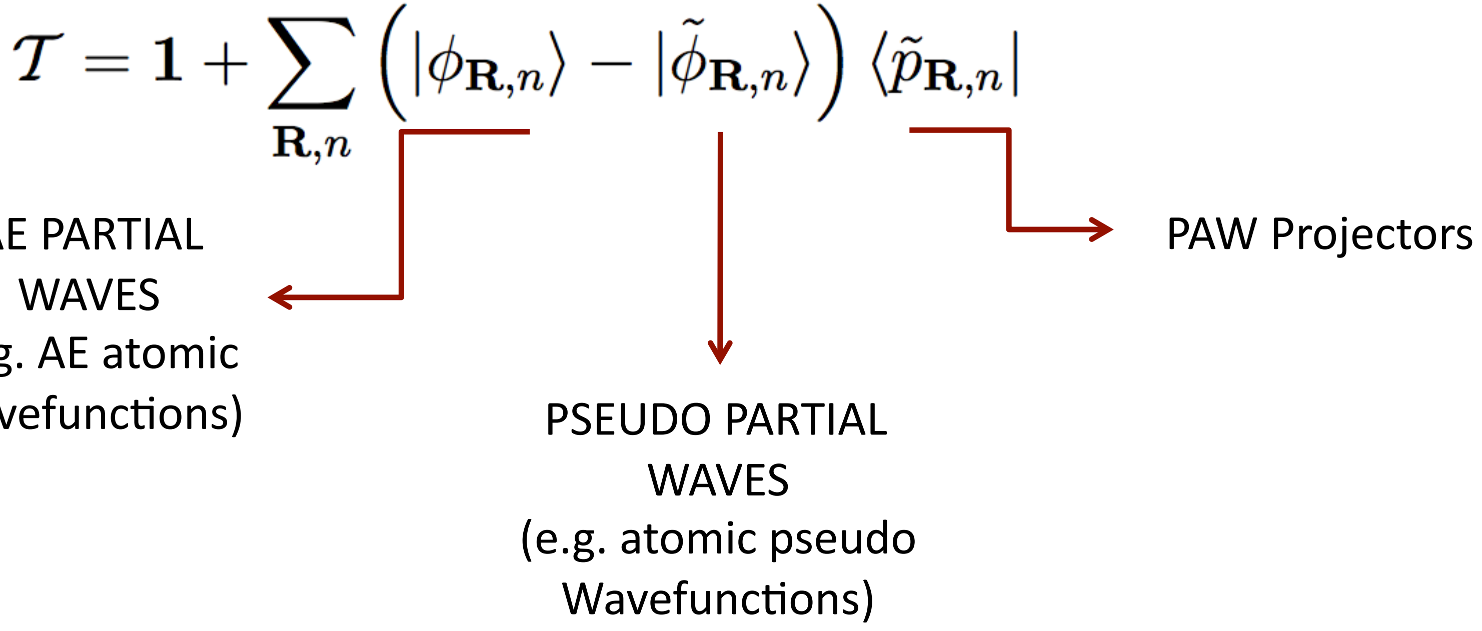
PAW for XAS – short explanation

The mapping is written as:

$$\mathcal{T} = 1 + \sum_{\mathbf{R}} \mathcal{T}_{\mathbf{R}}$$

R= coordinates of the nuclei

with



$$\mathcal{T} = \mathbf{1} + \sum_{\mathbf{R},n} \left(|\phi_{\mathbf{R},n}\rangle - |\tilde{\phi}_{\mathbf{R},n}\rangle \right) \langle \tilde{p}_{\mathbf{R},n}|$$

AE PARTIAL WAVES (e.g. AE atomic wavefunctions)

PSEUDO PARTIAL WAVES (e.g. atomic pseudo Wavefunctions)

PAW Projectors

Note that:

$$\phi_{\mathbf{R}n}(\mathbf{r}) = \tilde{\phi}_{\mathbf{R}n}(\mathbf{r})$$

Outside the augmentation region.

P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994)

PAW for XAS – short explanation

The mapping is written as:

$$\mathcal{T} = 1 + \sum_{\mathbf{R}} \mathcal{T}_{\mathbf{R}}$$

R= coordinates of the nuclei

with

$$\mathcal{T} = \mathbf{1} + \sum_{\mathbf{R},n} \left(|\phi_{\mathbf{R},n}\rangle - |\tilde{\phi}_{\mathbf{R},n}\rangle \right) \langle \tilde{p}_{\mathbf{R},n}|$$

PAW Projectors are built to satisfy identified the conditions

$$\langle \tilde{p}_{\boldsymbol{R},n} | \tilde{\phi}_{\boldsymbol{R}',n'} \rangle = \delta_{\boldsymbol{RR}'} \delta_{nn'}$$

orthogonality

$$\sum_n |\tilde{p}_{\mathbf{R}n}\rangle\langle\tilde{\phi}_{\mathbf{R}n}| = 1$$

completeness

Within the augmentation region.

$$\phi_{\mathbf{R}n}(\mathbf{r}) = \tilde{\phi}_{\mathbf{R}n}(\mathbf{r})$$

outside the augmentation region.

P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994)

PAW for XAS – short explanation

By replacing $\mathcal{T} = \mathbf{1} + \sum_{\mathbf{R},n} \left(|\phi_{\mathbf{R},n}\rangle - |\tilde{\phi}_{\mathbf{R},n}\rangle \right) \langle \tilde{p}_{\mathbf{R},n}|$ in the XAS matrix element

$$\langle f|\mathcal{O}|i\rangle = \langle \tilde{f}|\mathcal{O}|i\rangle + \sum_{\mathbf{R}n} \langle \tilde{f}|\tilde{p}_{\mathbf{R}n}\rangle \langle \phi_{\mathbf{R}n}|\mathcal{O}|i\rangle - \sum_{\mathbf{R}n} \langle \tilde{f}|\tilde{p}_{\mathbf{R}n}\rangle \langle \tilde{\phi}_{\mathbf{R}n}|\mathcal{O}|i\rangle$$

Since the projectors satisfy the condition, $\sum_{n} |\tilde{p}_{\mathbf{R}n}\rangle \langle \tilde{\phi}_{\mathbf{R}n}| = 1$ we get:

$$\langle f|\mathcal{O}|i\rangle = \sum_{\mathbf{R}n} \langle \tilde{f}|\tilde{p}_{\mathbf{R}n}\rangle \langle \phi_{\mathbf{R}n}|\mathcal{O}|i\rangle$$

M. Taillefumier *et al.* PRB 66, 195107 (2002)

PAW for XAS – short explanation

As the core state $\psi_i(\mathbf{r})$ is localized on the absorbing atom site $\mathbf{R}_0$

we drop all terms with $\mathbf{R} \neq \mathbf{R}_0$

$$\langle f|\mathcal{O}|i\rangle = \sum_{\mathbf{R}n} \langle \tilde{f}|\tilde{p}_{\mathbf{R}n}\rangle\langle\phi_{\mathbf{R}n}|\mathcal{O}|i\rangle \approx \langle \tilde{f}|\tilde{p}_{\mathbf{R_0}n}\rangle\langle\phi_{\mathbf{R_0}n}|\mathcal{O}|i\rangle$$

Thus the all-electron matrix element is written only in terms of all-electron atomic partial waves, paw projectors and the core initial state.

Thus from an all-electron calculation on the isolated atom we can get the state

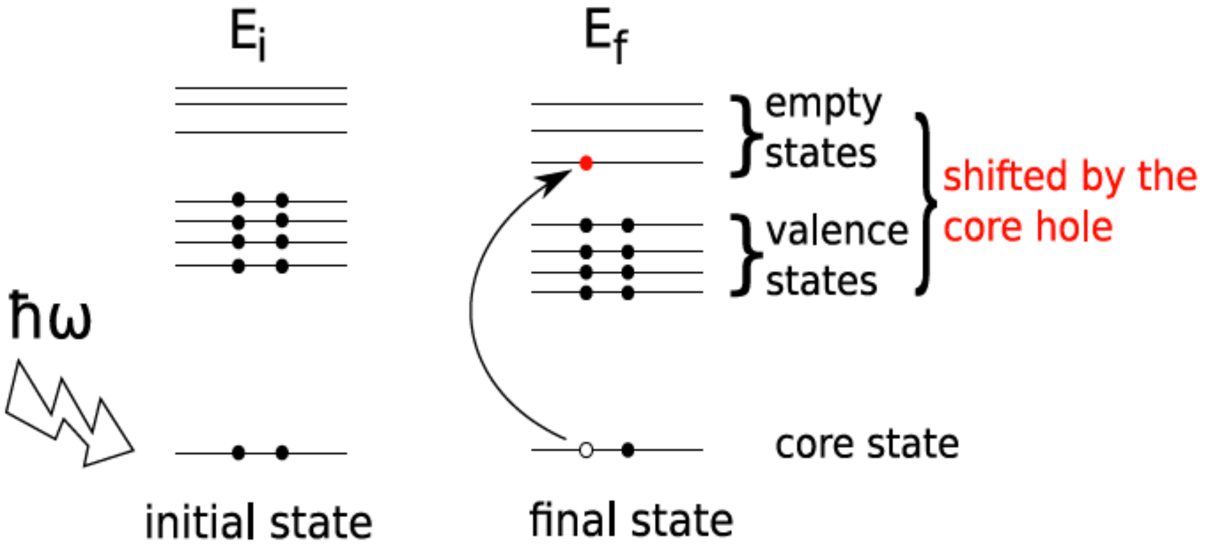
$$|\tilde{\chi}_{\mathbf{R}_{0n}}\rangle = |\tilde{p}_{\mathbf{R}_{0n}}\rangle\langle\phi_{\mathbf{R}_{0n}}|\mathcal{O}|i\rangle$$

such that:

$$\boxed{\langle f|\mathcal{O}|i\rangle = \langle \tilde{f}|\tilde{\chi}_{\mathbf{R}_{0n}}\rangle}$$

M. Taillefumier *et al.* PRB 66, 195107 (2002)

XAS Physical process



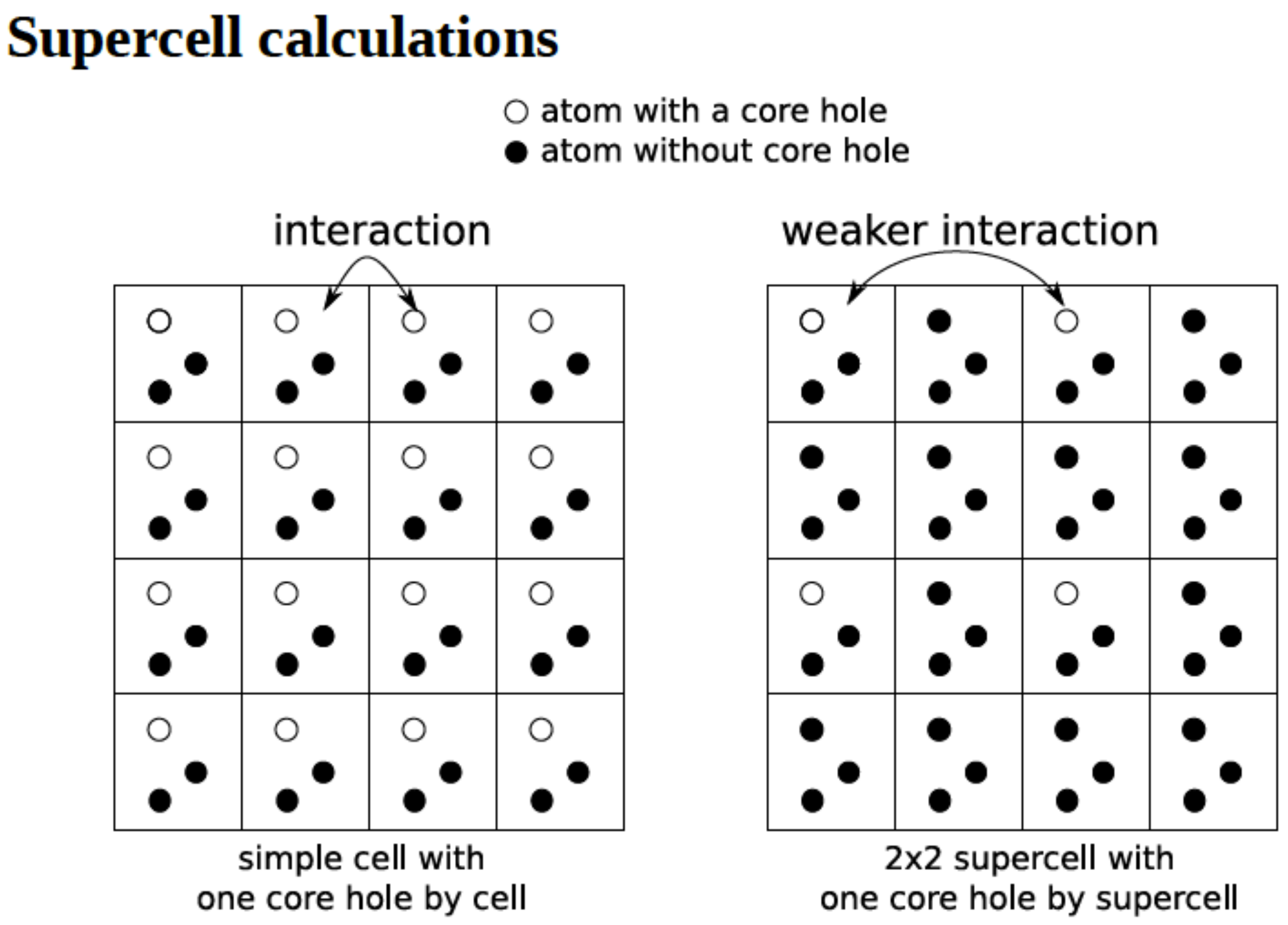
Challenge: describe core-hole attraction from first principles.

XSPECTRA (Modeling the core hole)

The core-hole is modeled in a supercell approach.

The pseudopotential of the absorbing atom has a core-hole in the core-state.

As we work with periodic boundaries we build a supercell to minimize the interaction between the core-hole and its periodic images



Supercell calculations

simple cell with
one core hole by cell

2x2 supercell with
one core hole by supercell

How does it works in practice ?

K-edge

Weakly correlated materials (SiO_2, Cu, ….)

Correlated materials (NiO, Cuprates…)

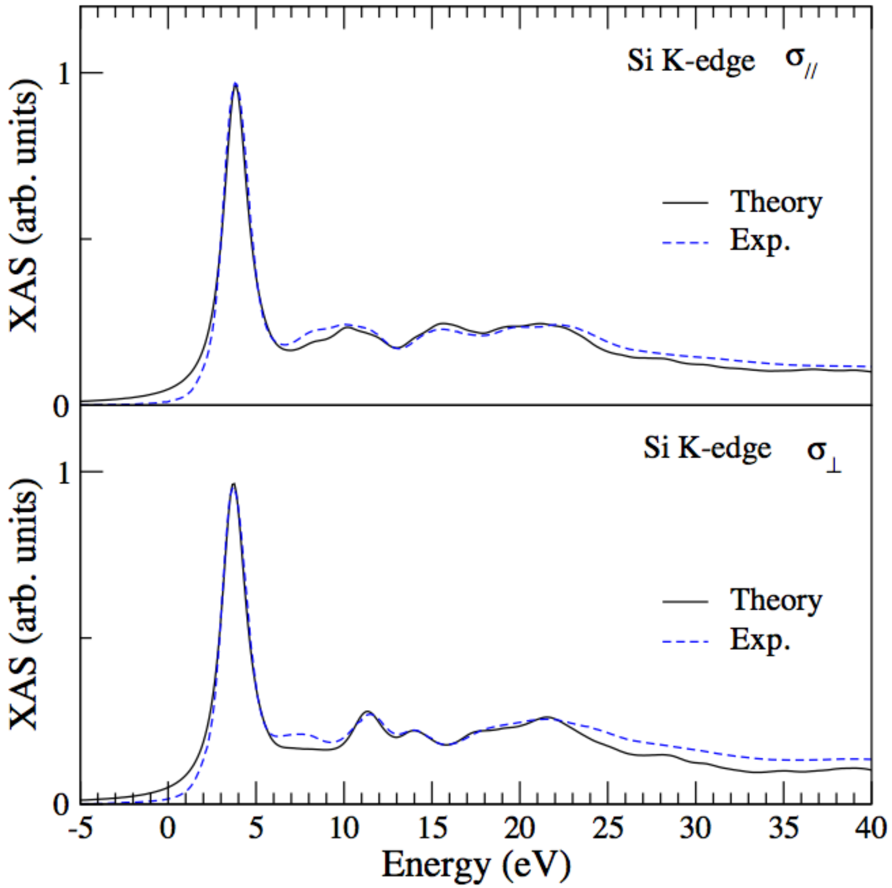
Large and correlated systems (Telephone number compound)

The patological case of Diamond!

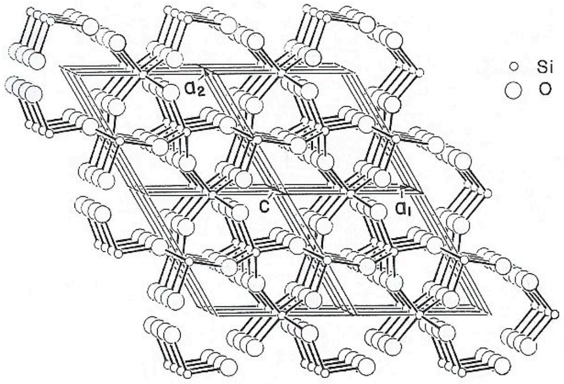
$L_{2,3}$-edges

Copper, Cuprite

Si K-edge in SiO_2 (alpha – Quartz)



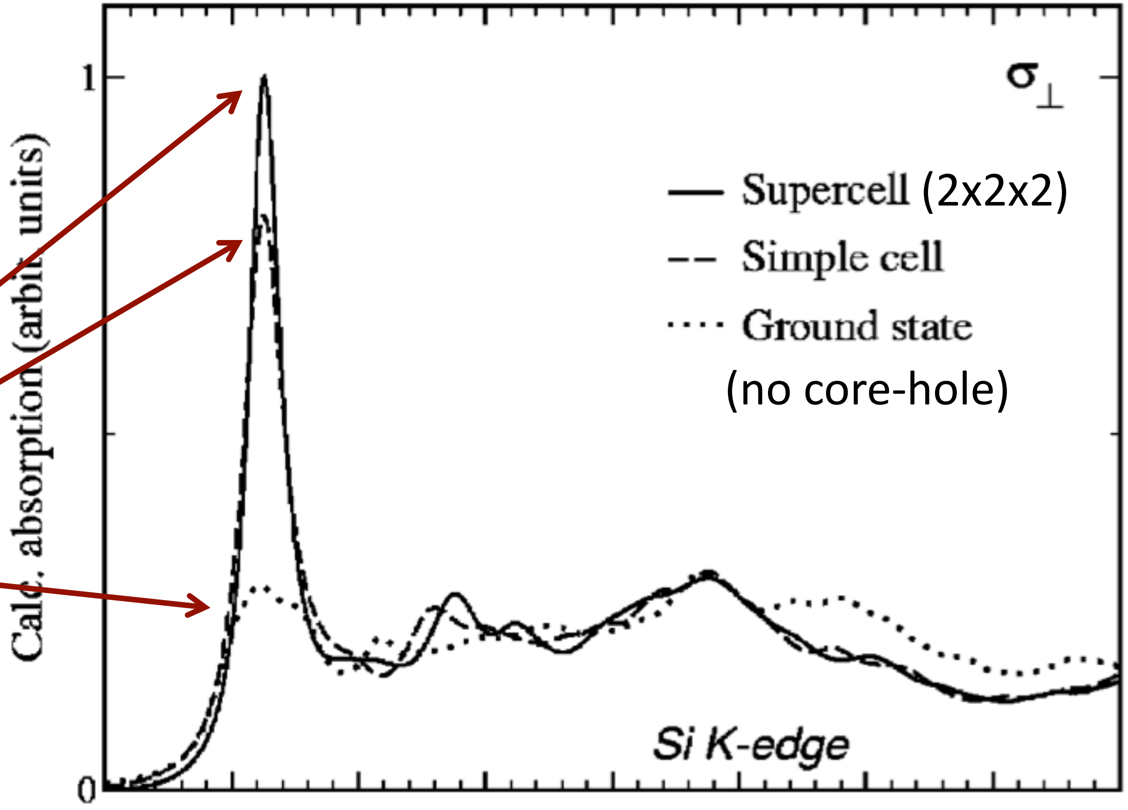
$[Si]=1s^2 2s^2 2p^6 3s^2 3p^2$



Excellent agreement Theory - Experiment

M. Taillefumier *et al.* PRB 66, 195107 (2002)

Core-hole effects ?



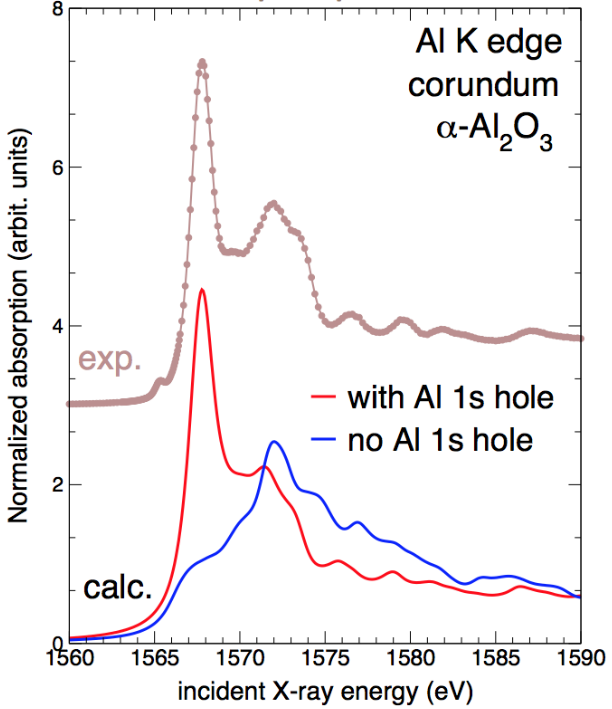
Huge
core-hole
effects

M. Taillefumier *et al.* PRB 66, 195107 (2002)

Do we really need the core-hole ?

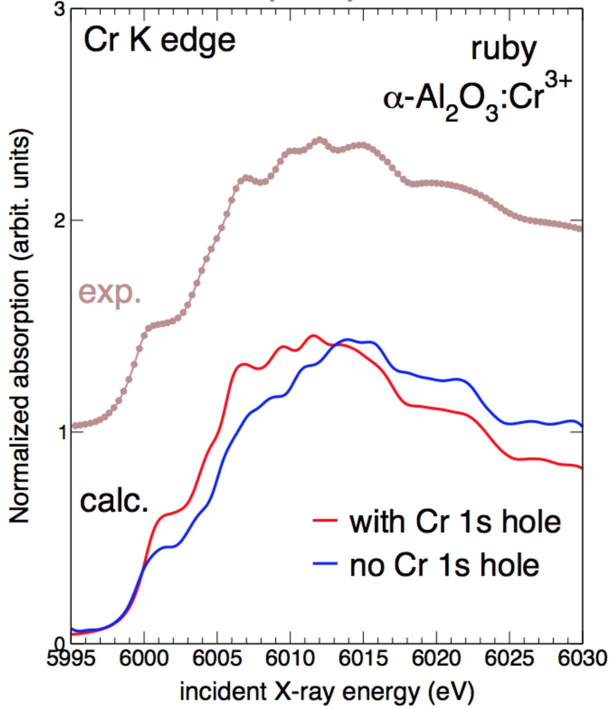
Huge core-hole effects.

isotropic spectra



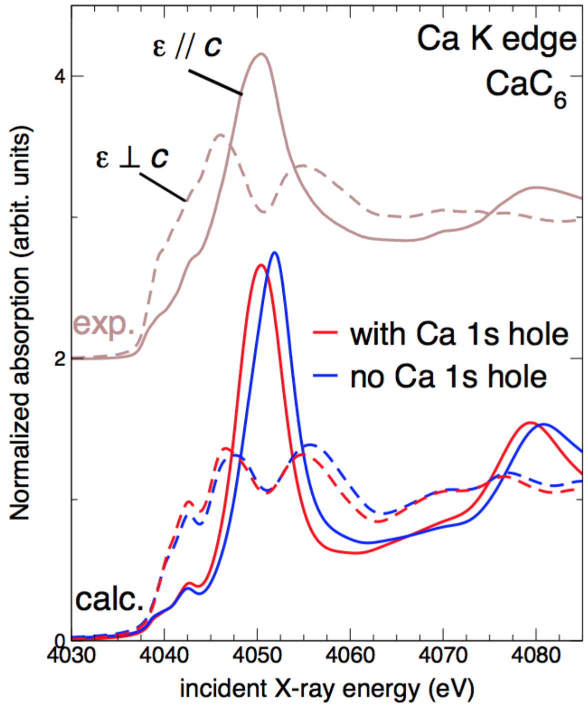
Moderate core-hole effects.

isotropic spectra



Weak core-hole effects.

polarized spectra



YES! Core-hole effects can be huge (usually they are smaller in metals).

Courtesy of Delphine Cabaret

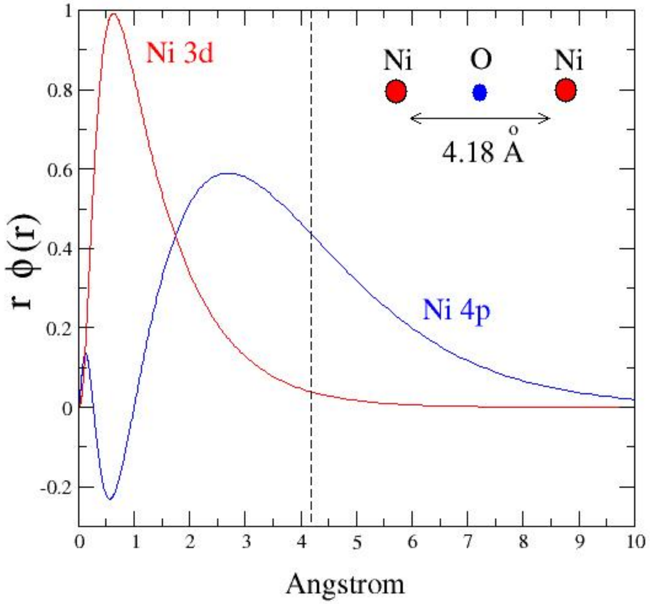
Intersite 4p-3d hybridization

Ch. Gougoussiss *et al.* Phys. Rev. B 79, 045118

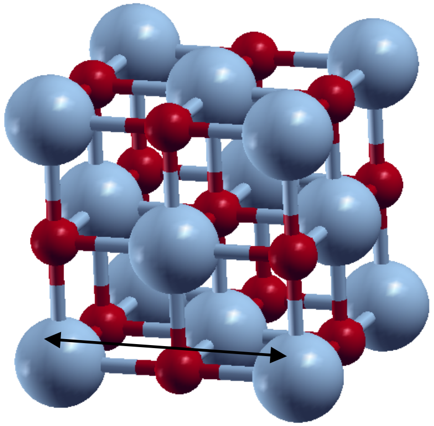
An example: NiO

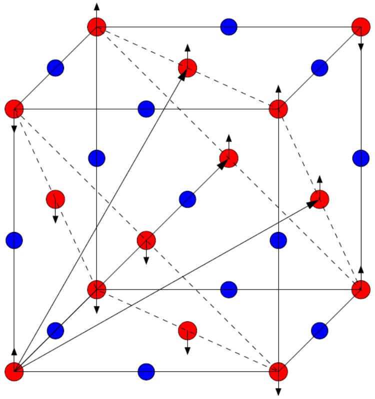
What atomic states
form the dipolar part ?

Ni atomic states



NiO





4.18 A

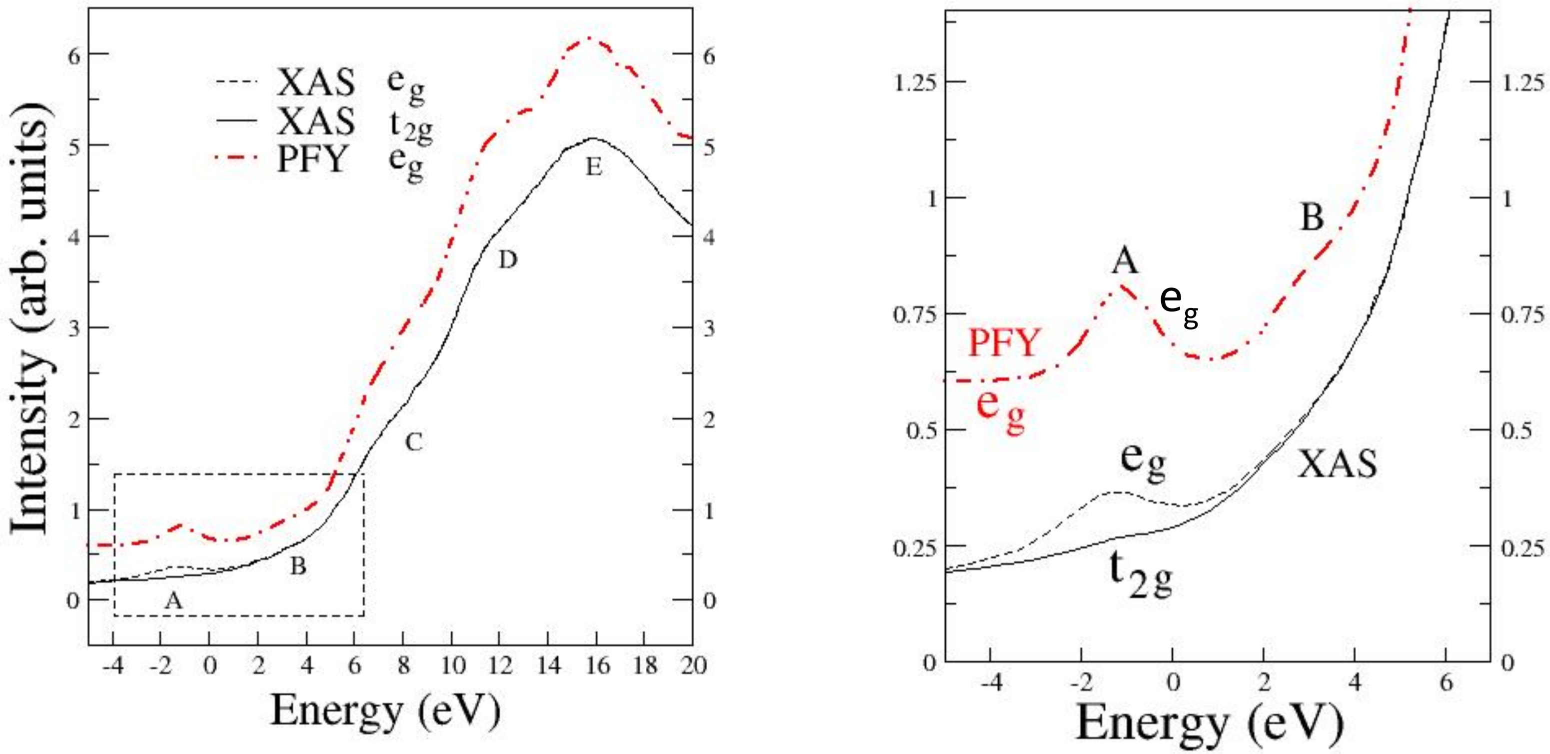
Ni atomic 4p states are very extended: hybridization with off-site Ni 3d states is possible.

Can 4p states promote transition to
off-site Ni 3d states in dipolar Ni K-edge XAS ?
Are these transition visibles ?

T. Uozumi *et al.* Europhys. Lett **18**, 85 (1992)

Ni K-edge XAS in NiO - Experiments

t_{2g} : **ε** // [100] **k** // [010] e_g : **ε** // [110] **k** // [-100]

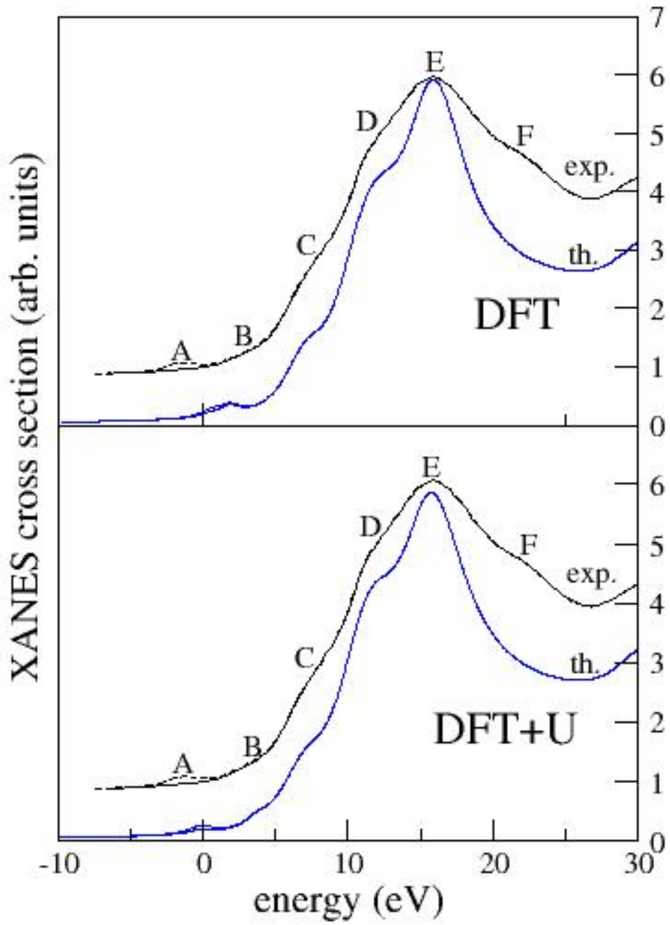


<u>Open problems:</u>

- Excitations in the pre-edge and near-edge region, attribution unclear,
  A is considered quadrupolar in literature, all the others are clearly dipolar.
- Can any of the dipolar feature be related to intersite 4p-3d hybridization?

Ni K-edge XAS in NiO - Theory

Experiments: D. Heumann, G. Dräger, S. Bocharov - J. Phys. IV, **7** 699 (1997)



- U=7.6 eV (CALCULATED!)
- Very good agreement up to the near-edge region

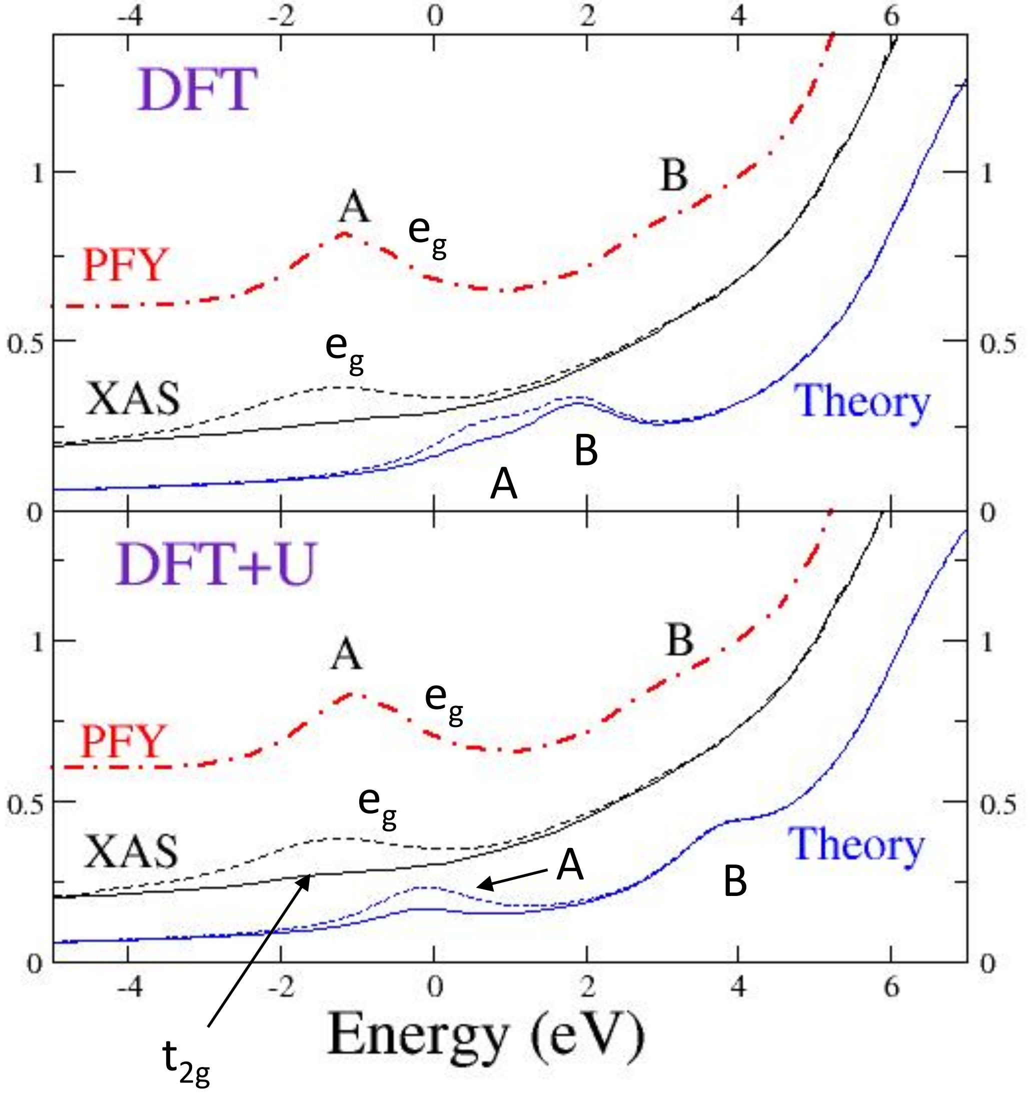
- U seems to have no effect close to the edge.

However in the pre-edge region…

Ch. Gougoussiss *et al.* Phys. Rev. B 79, 045118

Ni K-edge XAS in NiO - Theory

t_{2g} : $\boldsymbol{\varepsilon}$ // [100] $\mathbf{k}$ // [010] e_g : $\boldsymbol{\varepsilon}$ // [110] $\mathbf{k}$ // [-100]



- In DFT peak position and angular dependence are both incorrect.

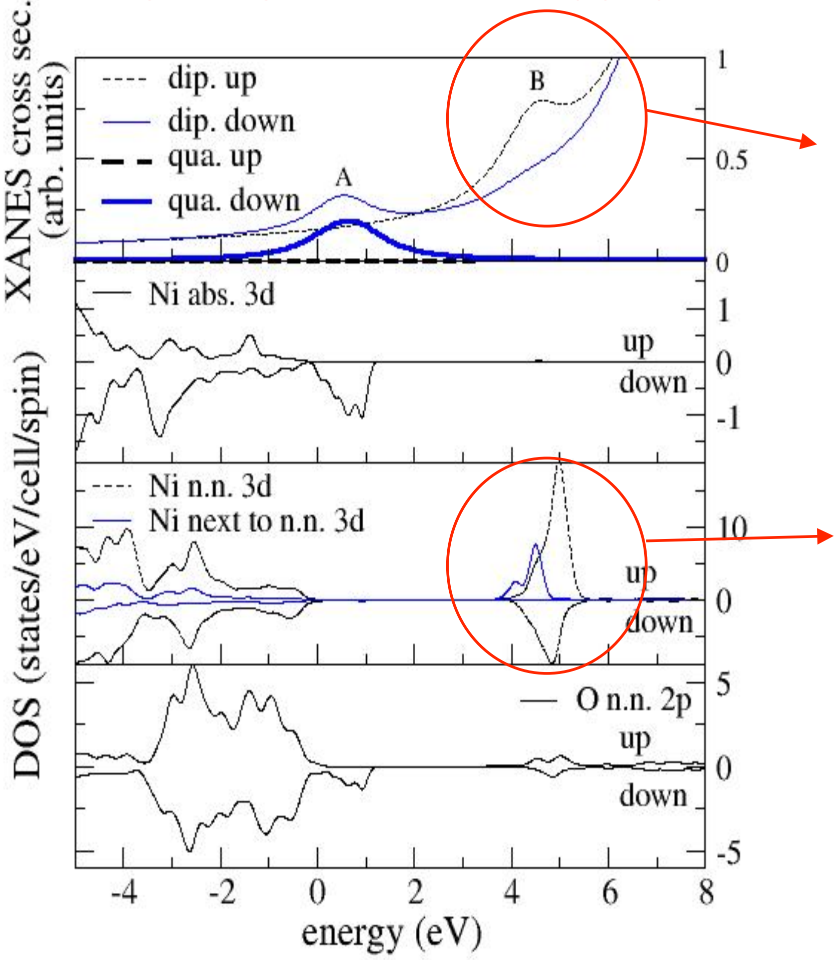
- DFT+U corrects the error.

The use of U is mandatory to describe pre-edges of correlated magnetic insulators!!!

Ch. Gougoussiss *et al.* Phys. Rev. B 79, 045118

Ni K-edge XAS in NiO - B peak interpretation (XSpectra+projwfc.x@QE)

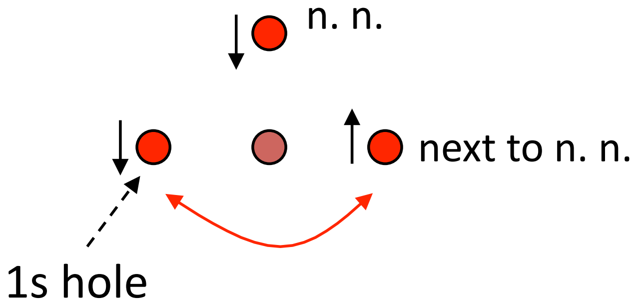
core-hole effects included!



The absorbing atom has up spin.

- The B peak is due to transitions to up spin states, but the absorbing atom has 3d up states occupied!

- The B peak is due to transitions to up spin states of next-to-nearest neighbouring Ni atoms.



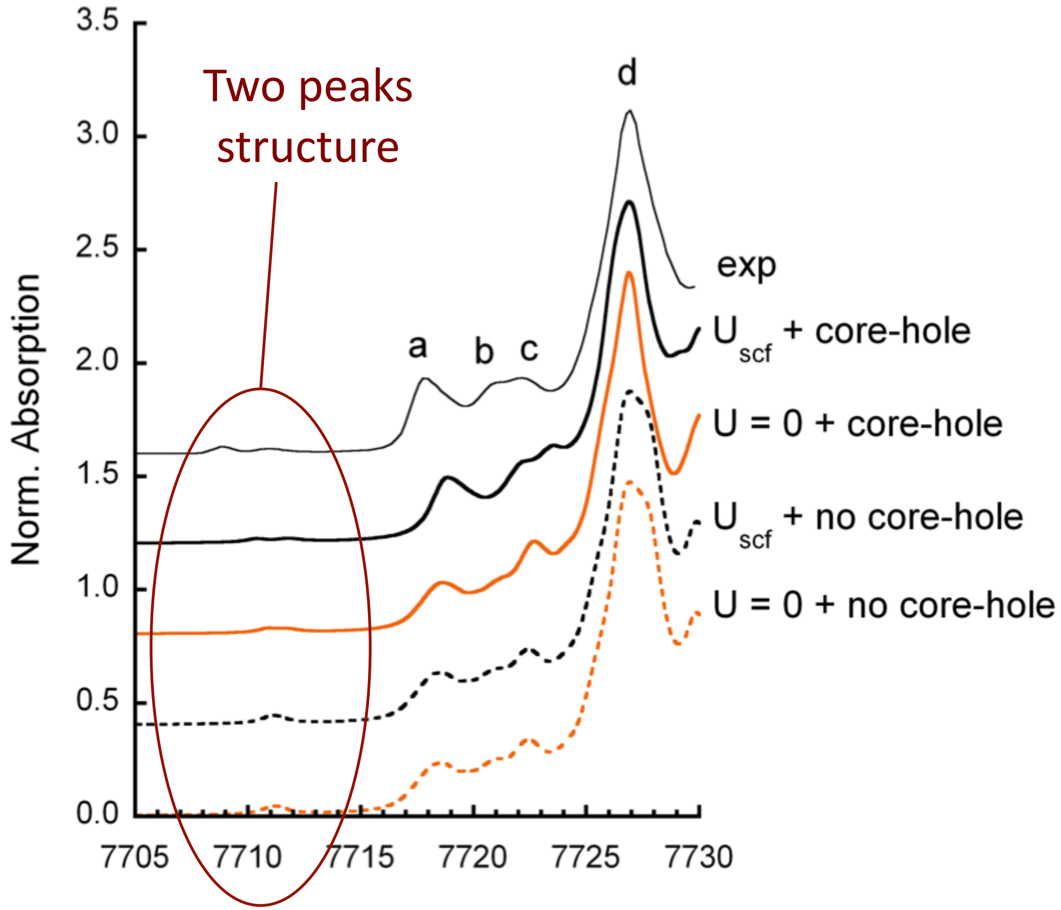
Intersite Ni 4p-Ni 3d hybridization!!!!

Ch. Gougoussiss *et al.* Phys. Rev. B 79, 045118

Co K-edge XAS in $LiCoO_2$

check isn't that O K-edge?

Competition betxeen core-hole attraction and electron-electron repulsion.



Best Agreement U+Core-hole

The two peak structure needs U+core-hole.

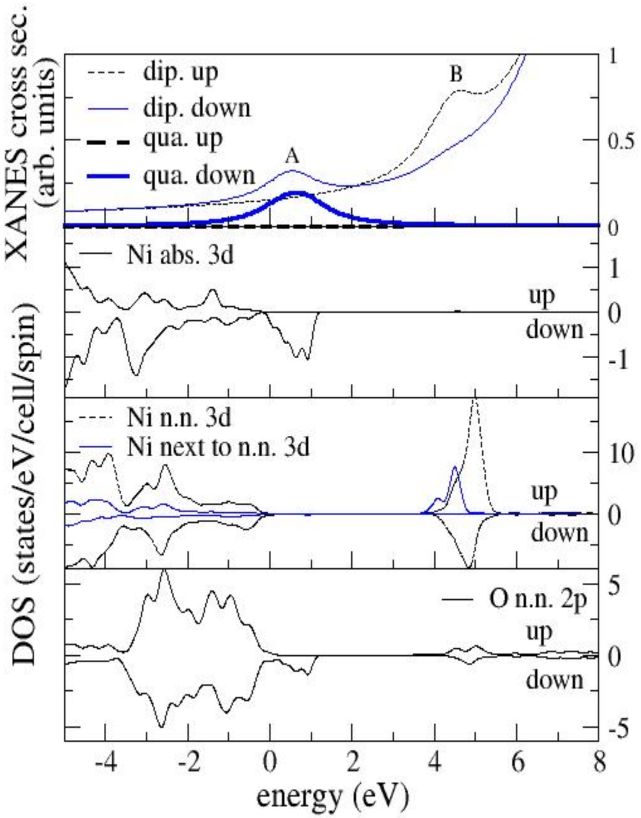
A. Juhin *et al.* Phys. Rev. B **81**, 115115

NiO/LiCoO$_2$ What did we learn ?

- Strong non-local effects in the dipolar part of K-edge XAS

- Hubbard U necessary to obtain agreement in the pre-edge region

This is fairly general for correlated oxides.



Note:

Couple Xspectra with projwfc.x to obtain decomposition of XAS in partial dos.

XAS in large systems – O K-edge in Telephone-number cuprates

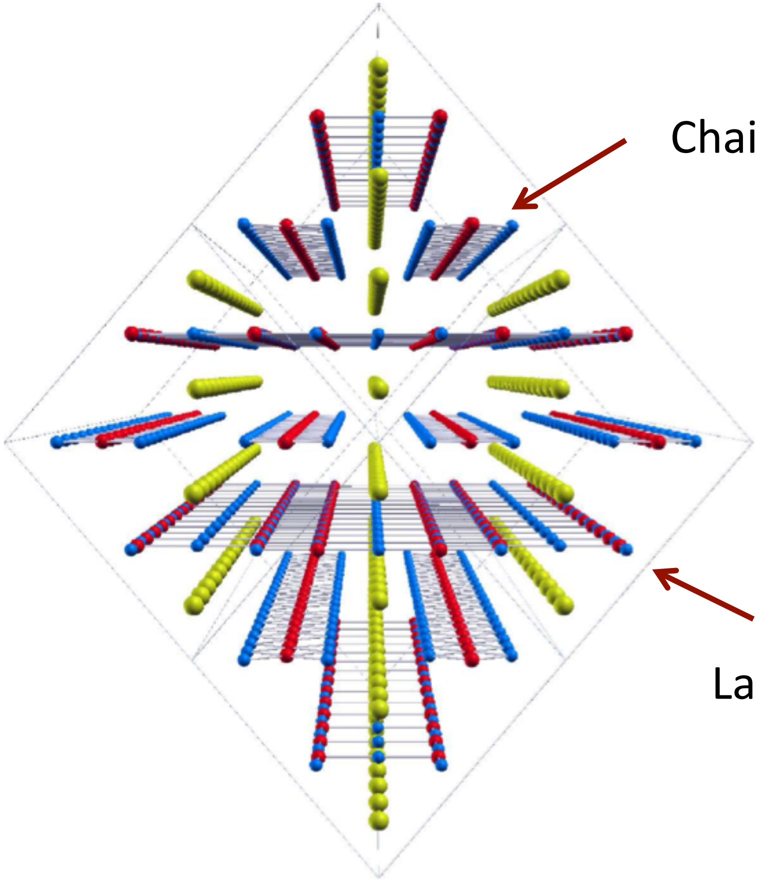
$Sr_{14}Cu_{24}O_{41}$

Naturally doped compound.

Fondamental question:
Where are hole sitting, chain or ladders ?

Incommensurate crystal structure
(infinite number of atoms / cell)

What is the best periodic approximand?
4 chain/5 chain periodicity ?

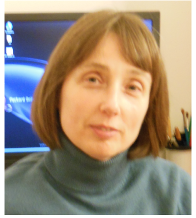


Chains

Ladders

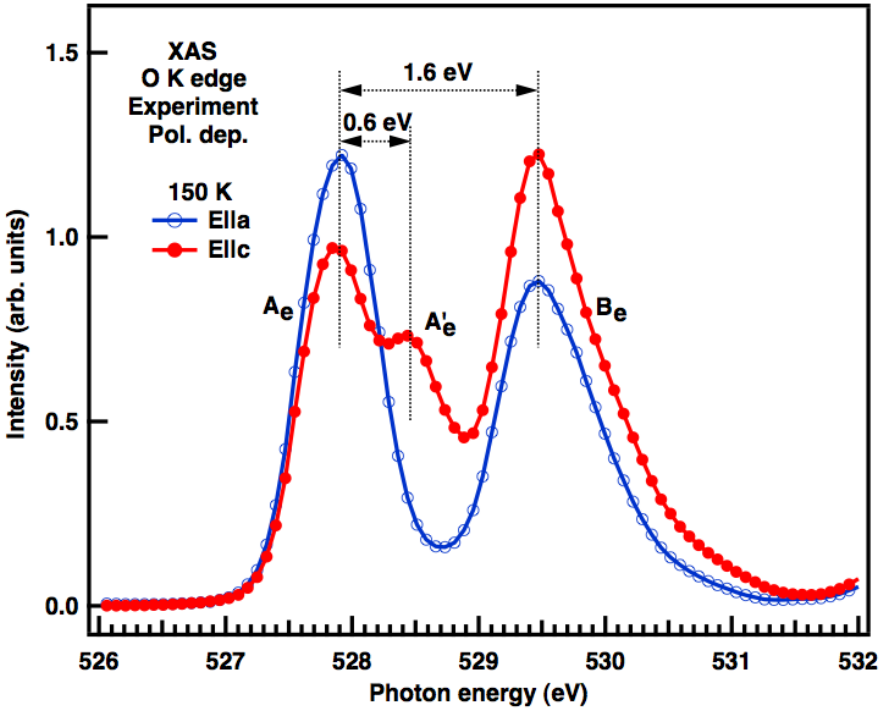
- 316 atoms AF unit cell
-Correlation effects (U)
-Core-hole effects

V. Ilakovac *et al.,* Phys. Rev. B **85**, 075108



XAS in large systems – O K-edge in Telephone-number cuprates

$Sr_{14}Cu_{24}O_{41}$



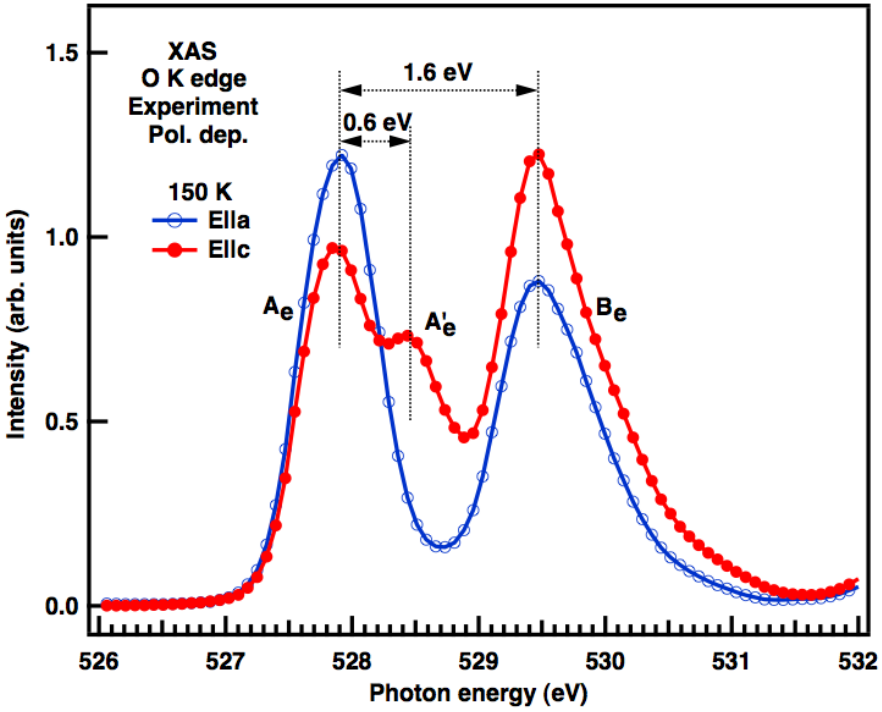
C=Chain
L=Ladder Legs
R=Ladder Rungs

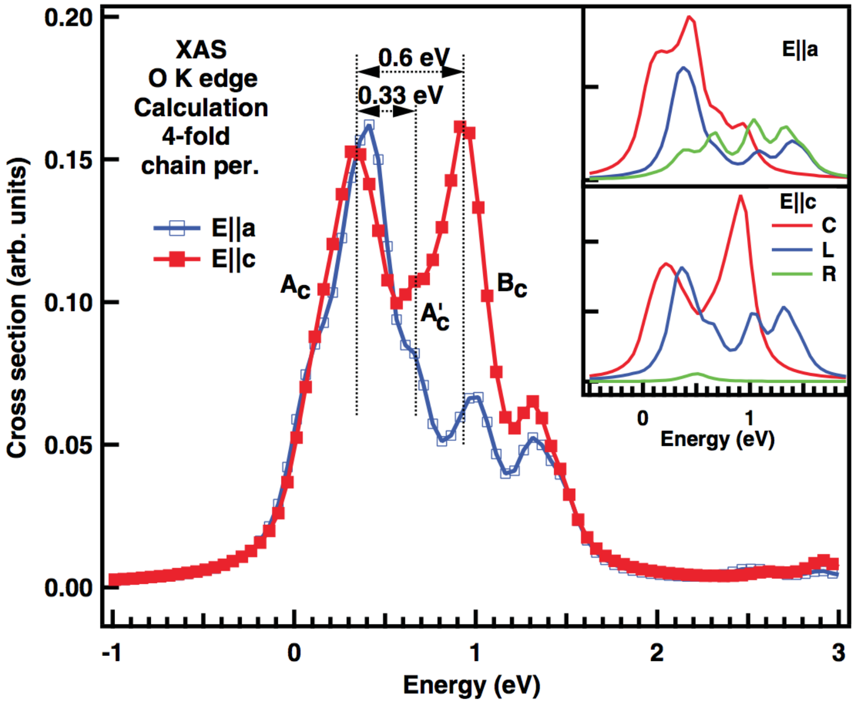
V. Ilakovac *et al.,* Phys. Rev. B **85**, 075108

XAS in large systems – O K-edge in Telephone-number cuprates

4-fold chain periodicity in disagreement with experiments

$Sr_{14}Cu_{24}O_{41}$





Reduced gap = reduced distance between peaks

C=Chain

L=Ladder Legs

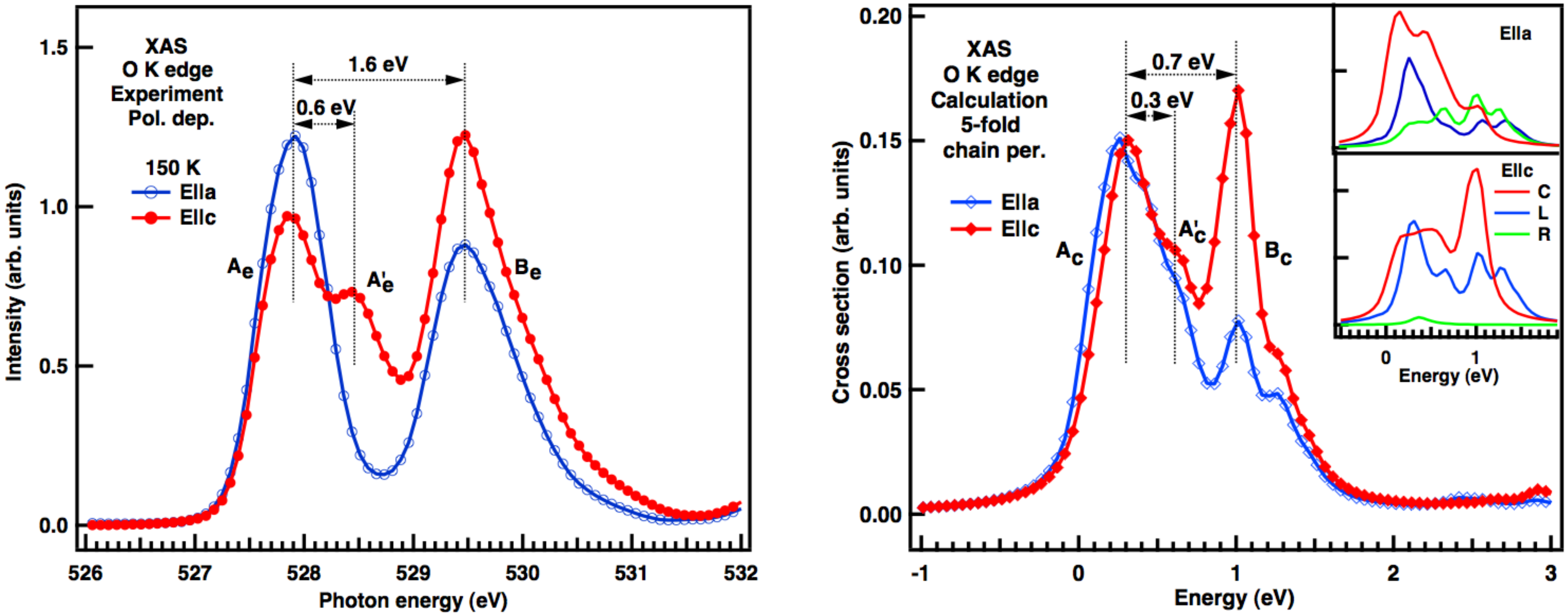
R=Ladder Rungs

V. Ilakovac *et al.,* Phys. Rev. B **85**, 075108

XAS in large systems – O K-edge in Telephone-number cuprates

5-fold chain periodicity in better agreement with experiments

$Sr_{14}Cu_{24}O_{41}$

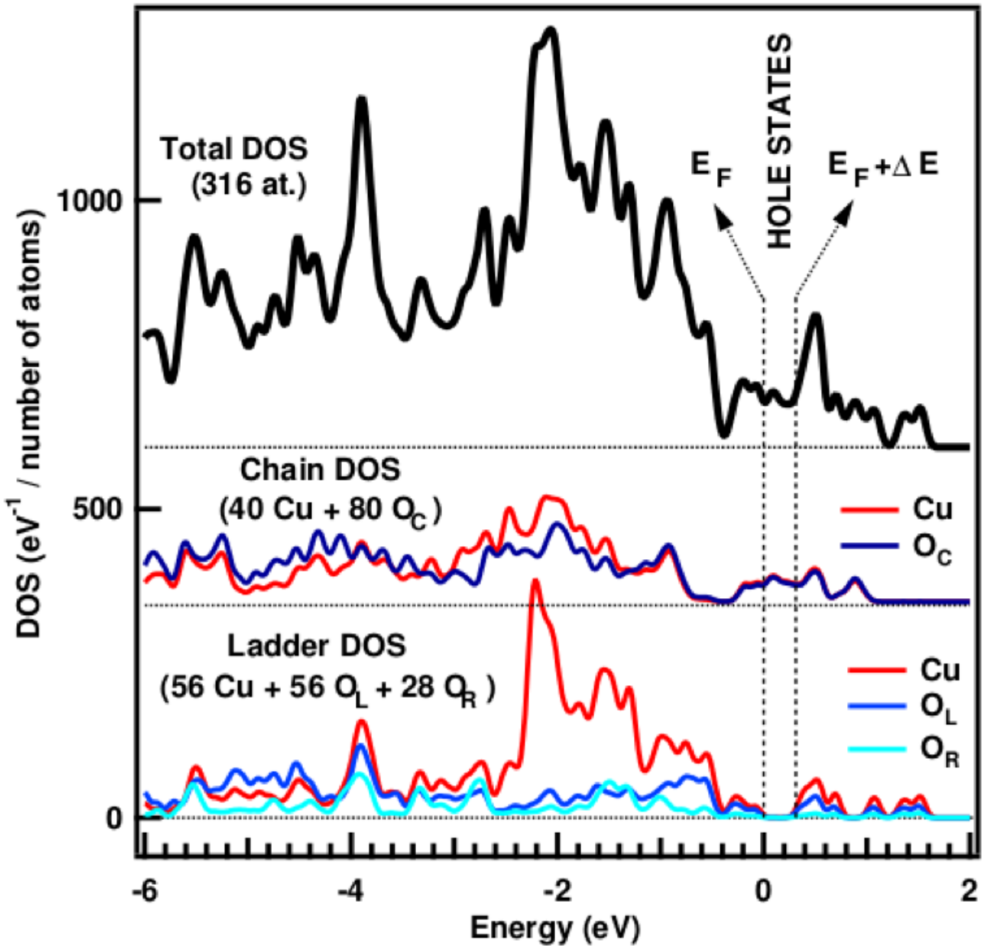


Long distance structural effects!

C=Chain
L=Ladder Legs
R=Ladder Rungs

V. Ilakovac *et al.*, Phys. Rev. B **85**, 075108

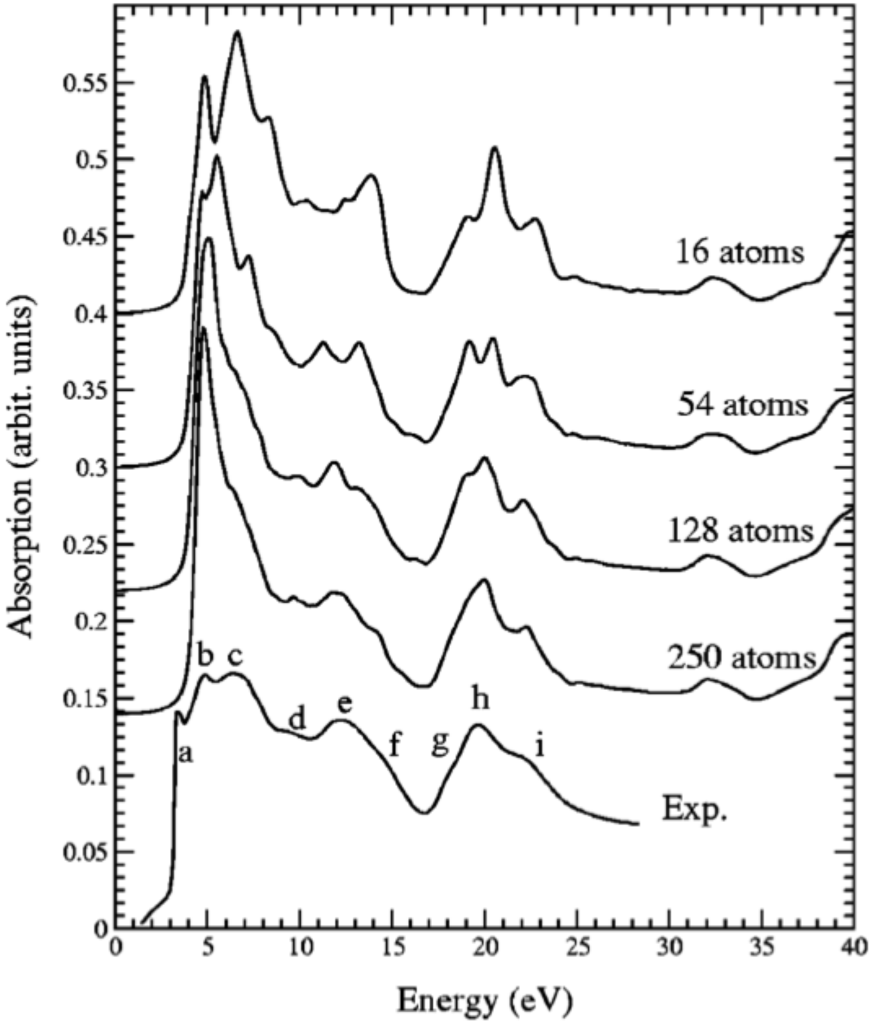
XAS in large systems – O K-edge in Telephone-number cuprates



Contrary to all previous analysis, based on semi-empirical models, U and antiferromagnetic ordering favor the strong chain hole-attraction.

V. Ilakovac *et al.,* Phys. Rev. B **85**, 075108

The pathological case of diamond!

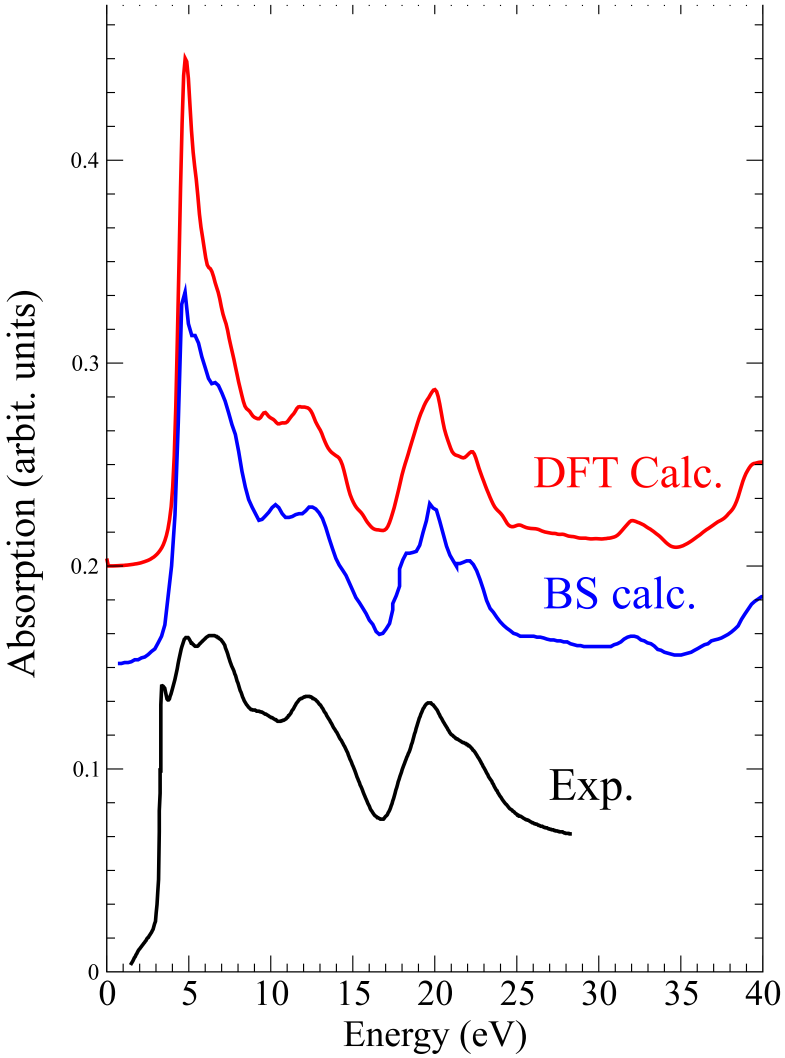


Very big size-effects, the simulation converges with 250 atoms. Note that peak A is not well described in DFT.

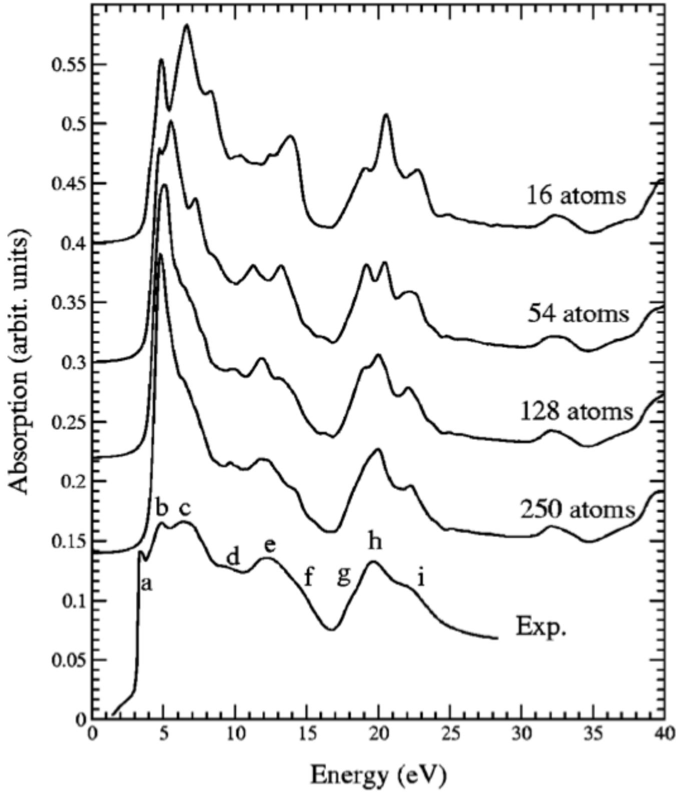
M. Taillefumier, D. Cabaret and F.Mauri PRB 66, 195107 (2002)

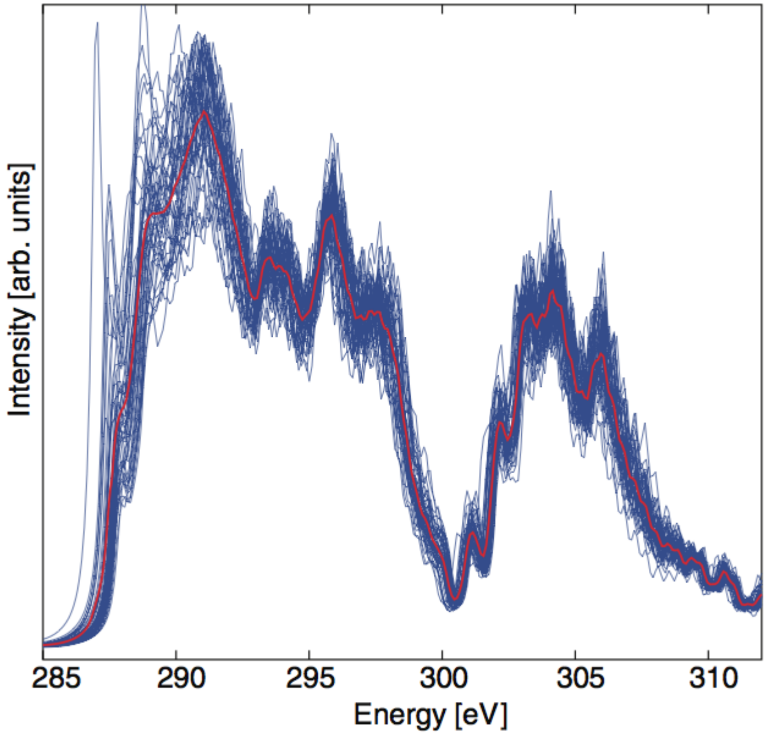
Correlation effects ?

NON!
Bethe-Salpeter almost the same as DFT!



Vibrational effects !





M.P. Ljungberga, J.J. Mortensenb, L.G.M. Petterssona, Journal of Electron Spectroscopy and Related Phenomena 184, 427 (2011)

$L_{2,3}$ - edges

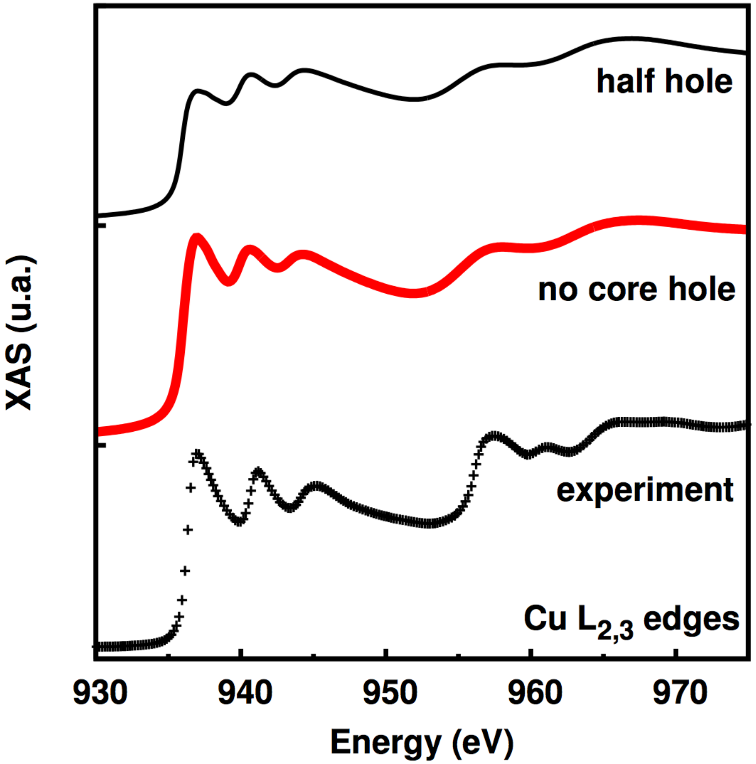
O. Bunau and M. Calandra, in preparation
Next XSpectra school (?).

$L_{2,3}$-edges : dipolar transition between $2p_{1/2,3/2}$ to empty d (mostly) and s states.

More difficult problem then K-edge, more important correlation effects.
Difficult to explain at the DFT level.

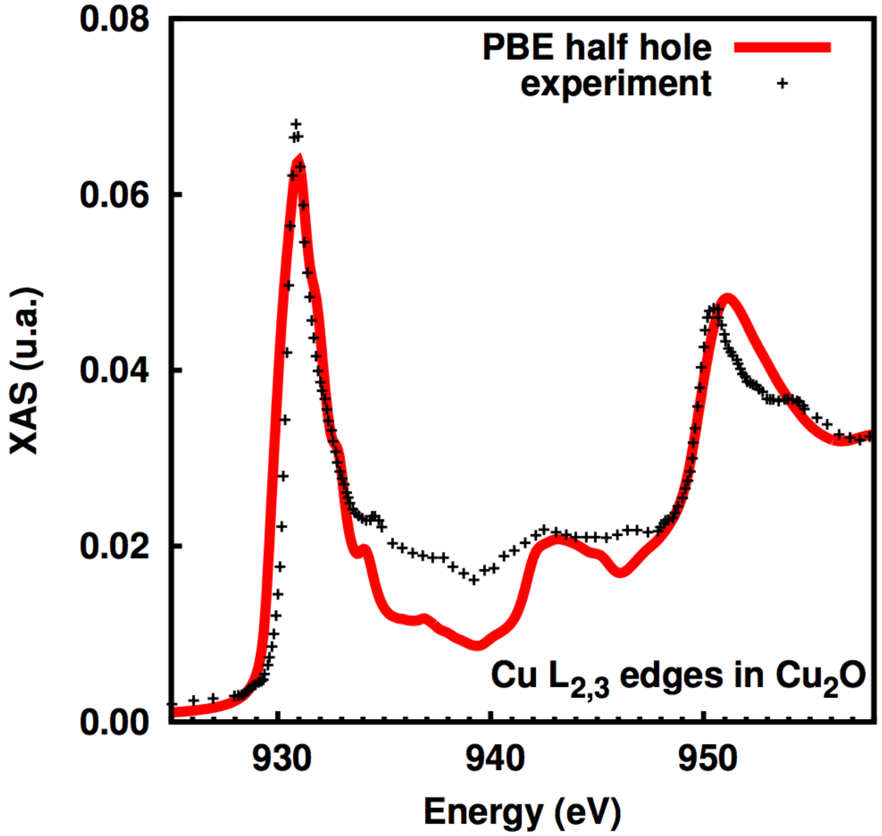
Next XSpectra version will include this feature.

Cu $L_{2,3}$ - edges



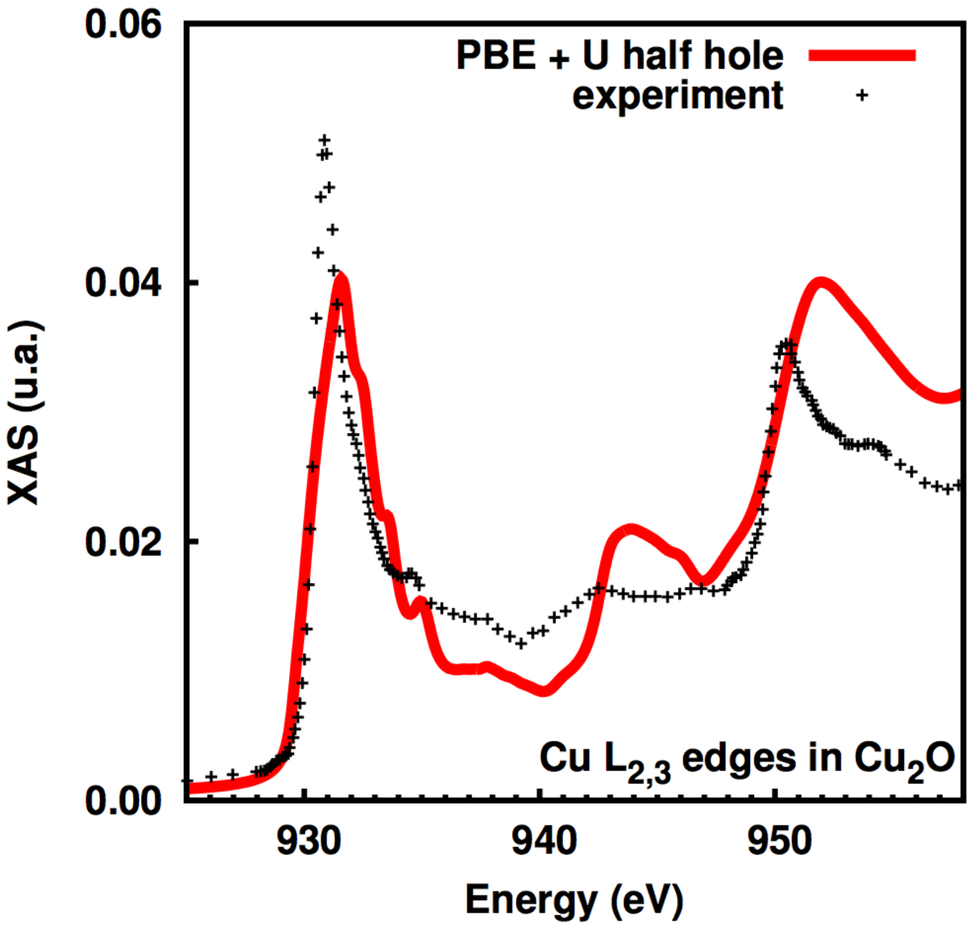
Metallic Cu: fully screened core-hole.
Excellent agreement.

Cu $L_{2,3}$ – edges in Cu_2O



In $L_{2,3}$ edges core-hole effects seem less important.
Best agreement half core-hole (somewhat empirical…).

Cu $L_{2,3}$ – edges in Cu_2O, What about U ?



Using Hubbard U the agreement get worst…. Not the good kind of correlation!

Resumé

- ➔ XSpectra @ QE is a useful tool to describe K-edge and (soon) $L_{2,3}$ absorption edges in the pre-edge, edge and near-edge region.

- ➔ Current implementation includes:
  - ✓ Norm-conserving and Ultrasoft pseudopotentials.
  - ✓ Lanczos method to avoid calculating occupied states.
  - ✓ DFT+U method.
  - ✓ Treatment of static core-hole in a supercell approach.

- ➔ Coupled to projwfc.x @ QE allows attribution of XAS features to atomic orbitals.

- ➔ Large systems can be tackled at a reasonable costs (316 atoms < 10000h sp3)

If you find XSpectra useful, please cite the following works in your publications:

C. Gougoussis, M. Calandra, A. P. Seitsonen, and F. Mauri Phys. Rev. B **80**, 075102 (2009)

M. Taillefumier, D. Cabaret and F.Mauri PRB **66**, 195107 (2002)

P. Giannozzi et al., J. Phys. Condens. Matter **21**, 395502 (2009).