Ab initio simulations of X-ray Absorption Spectroscopy data The case of Cu(II) ions in water

Giovanni La Penna, Velia Minicozzi. Silvia Morante, Giancarlo Rossi, Francesco Stellato

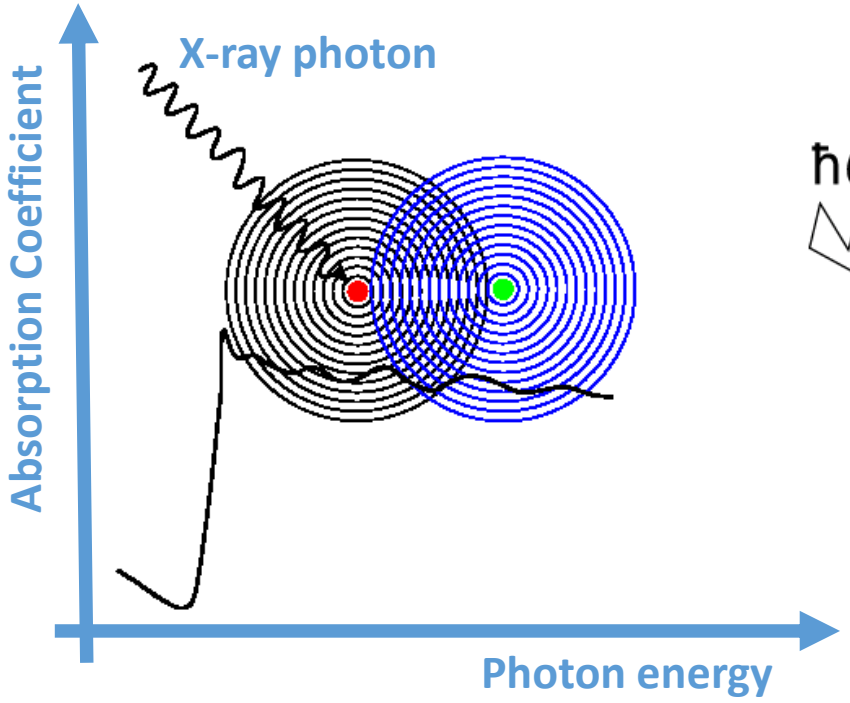
Dipartimento di Fisica & I.N.F.N. – Roma Tor Vergata

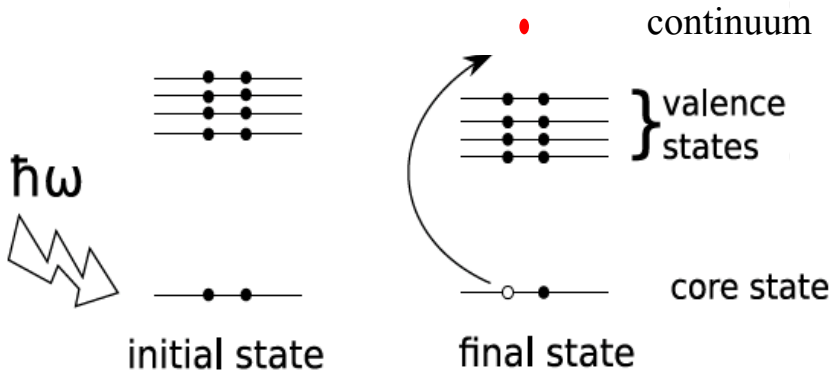
Outline

- X-ray Absorption Spectroscopy
- *Ab initio* calculations of XAS spectra
- Theoretical simulations *vs* experimental data
- Conclusions and Outlook

X-ray Absorption Spectroscopy

Measurement of the X-ray Absorption coefficient μ(E)





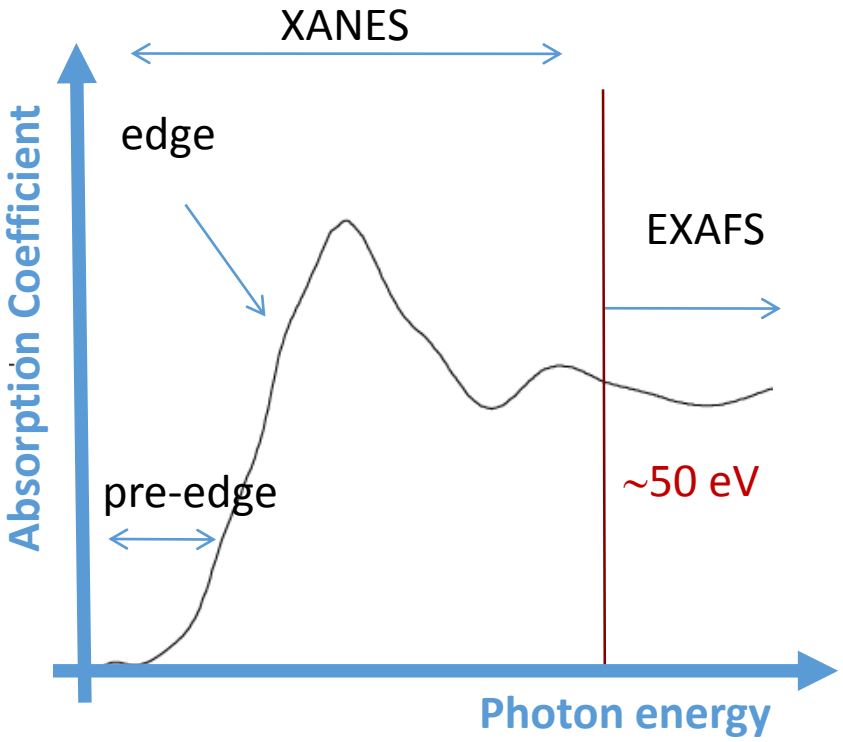
XAS features

✓Selective for the absorber

✓Local probe (~5 Å)

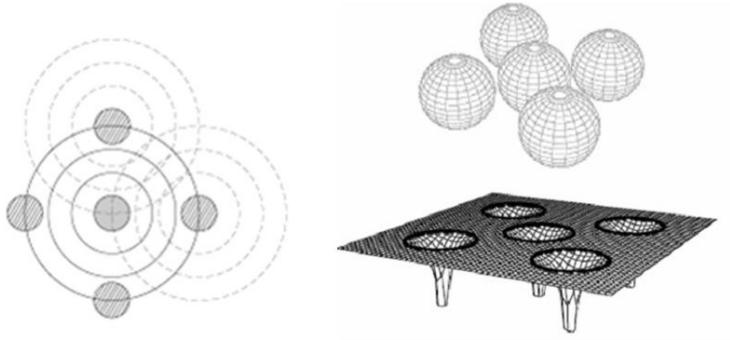
✓No crystals needed

X-ray Absorption Spectroscopy



XANES=X-ray near edge structures.
EXAFS=Extended X-Ray Absorption Fine Structure

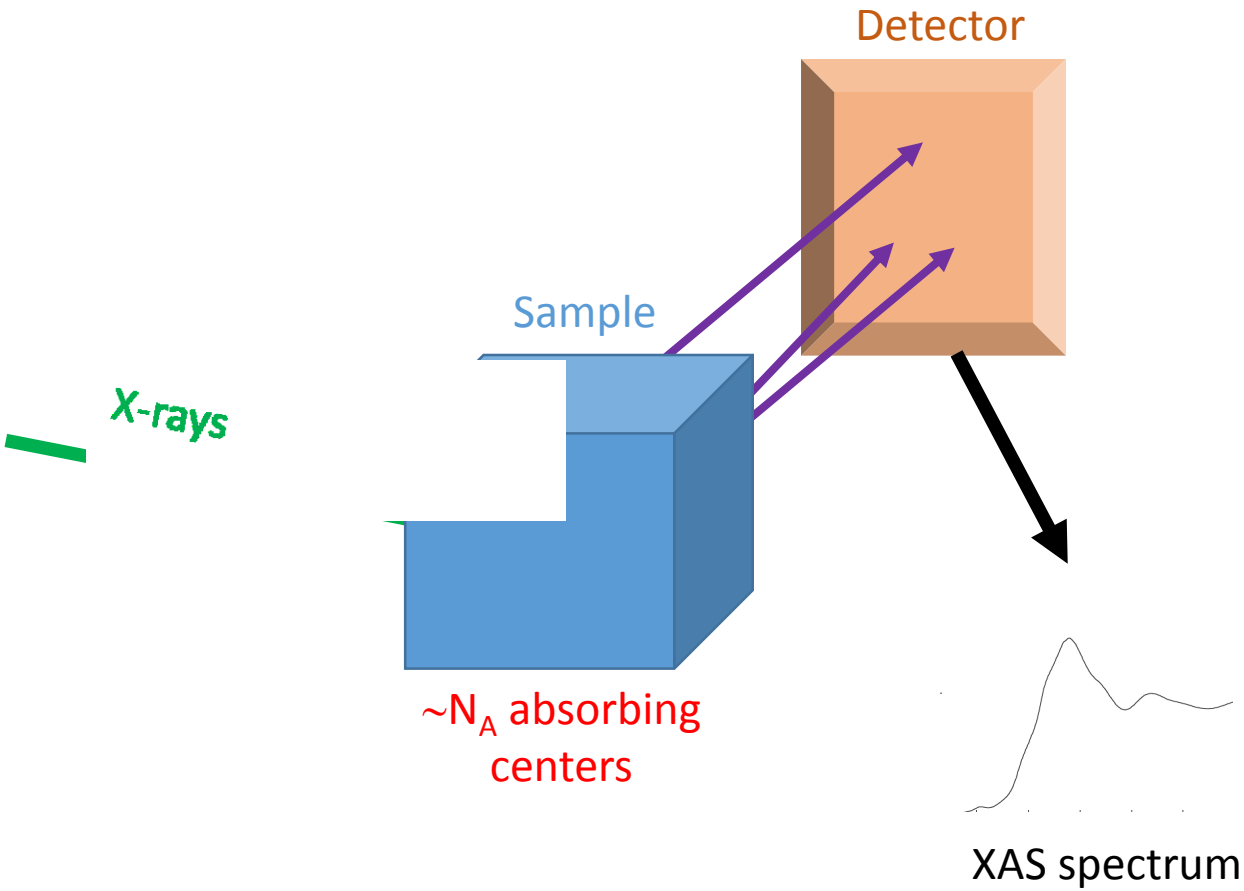
The absorption coefficient in the XANES region is very sensitive to the potential V(**r**) seen by the photoelectron in the vicinity of the absorbing atom



The potential V(**r**) depends on the electronic wave-functions of the whole system and on the atomic positions. The more accurate the description of V(**r**) is, the better the calculation of the XANES spectra.

X-ray Absorption Spectroscopy

A typical XAS experiment

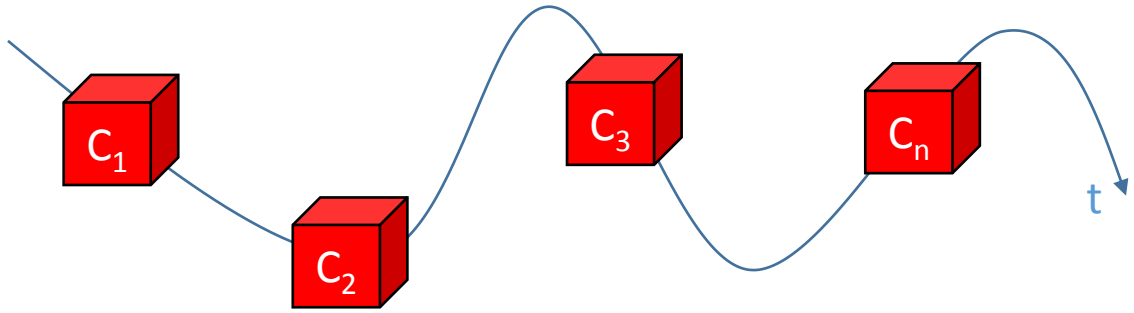


The XAS spectrum is the average of the $\sim N_A$ absorption spectra originated by $\sim N_A$ absorbing centers, each one living in a potentially slightly different configuration

Ab initio XAS spectra calculation

Under the ergodic hypothesis, the ensemble of ~N_A configurations seen by the X-rays could be taken as the ~N_A single configurations along a molecular dynamics trajectory

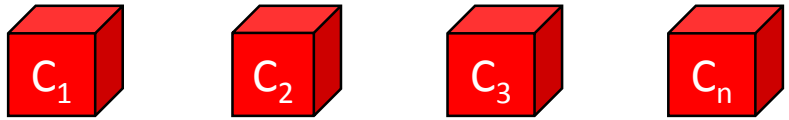
Molecular dynamics trajectory



This is computationally too expensive (at the moment)

Classical starting models are instead built to sample at best configurations space

Classical starting models



Ab initio XAS calculations

The XAS cross section is given by

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

Final state with a core-hole

Initial state: no core-hole

Incident-photon energy

ALL ELECTRON STATES

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

Dipole

Quadrupole

The Schrödinger equation can be solved numerically

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

Ab initio XAS calculations

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

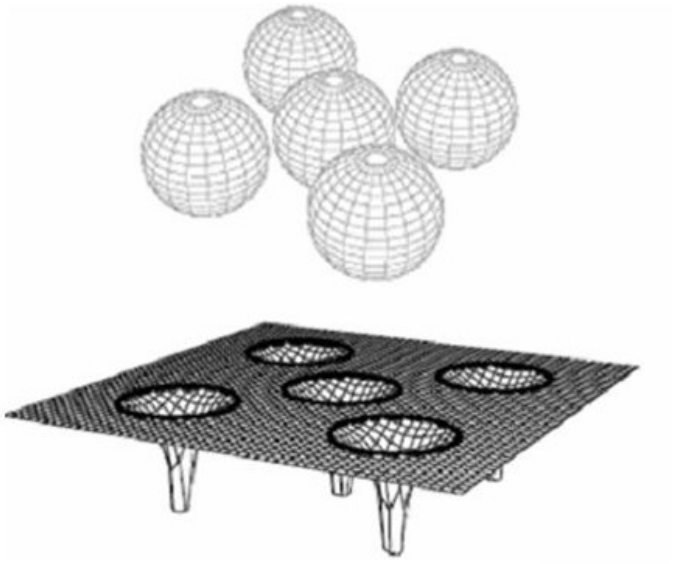
Final state with a core-hole

Initial state: no core-hole

Incident-photon energy

Initial State

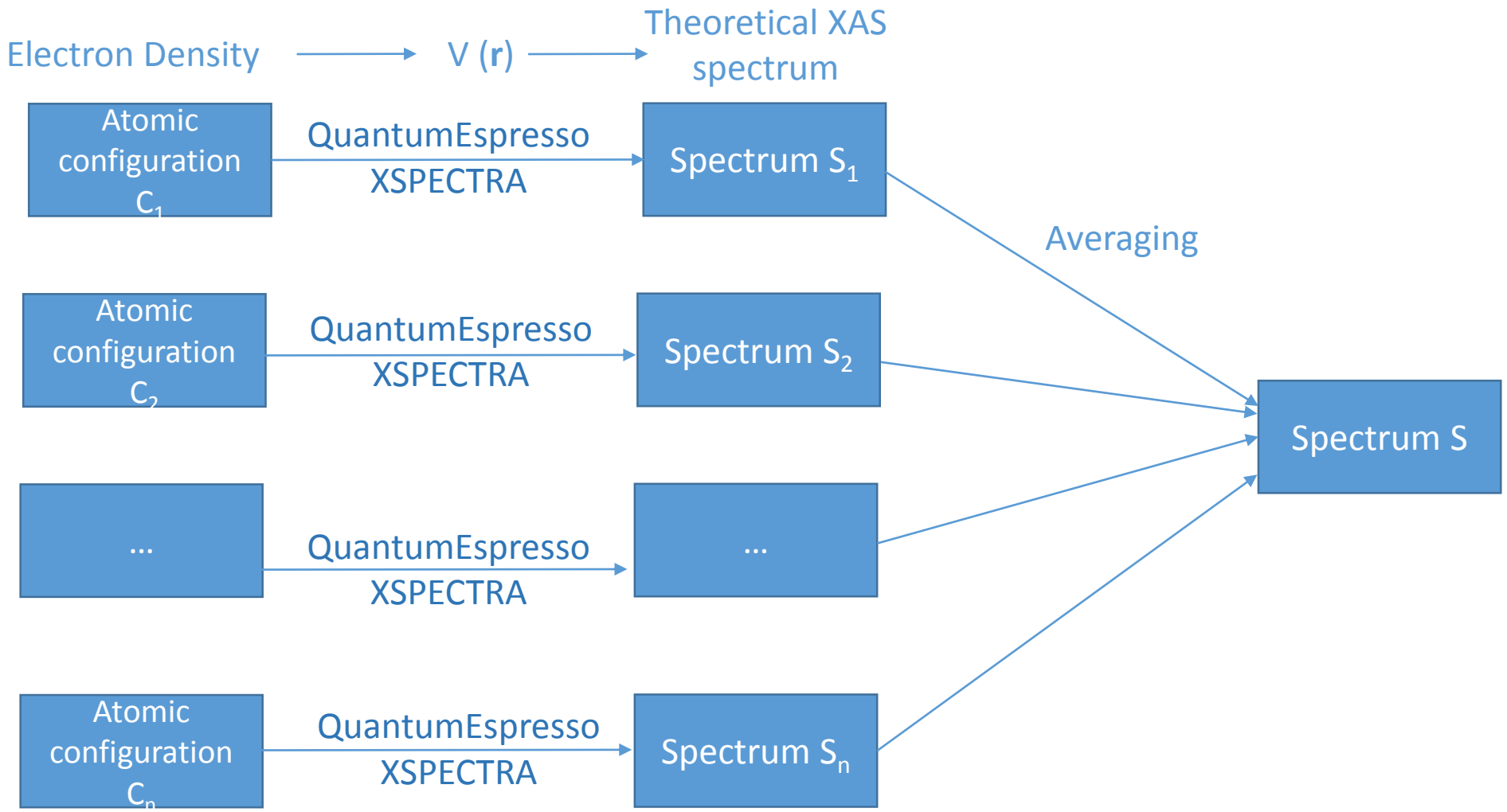
$$\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r}\right)|i\rangle = E|i\rangle$$



Final State

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)|f\rangle = E|f\rangle$$

Ab initio XAS calculations

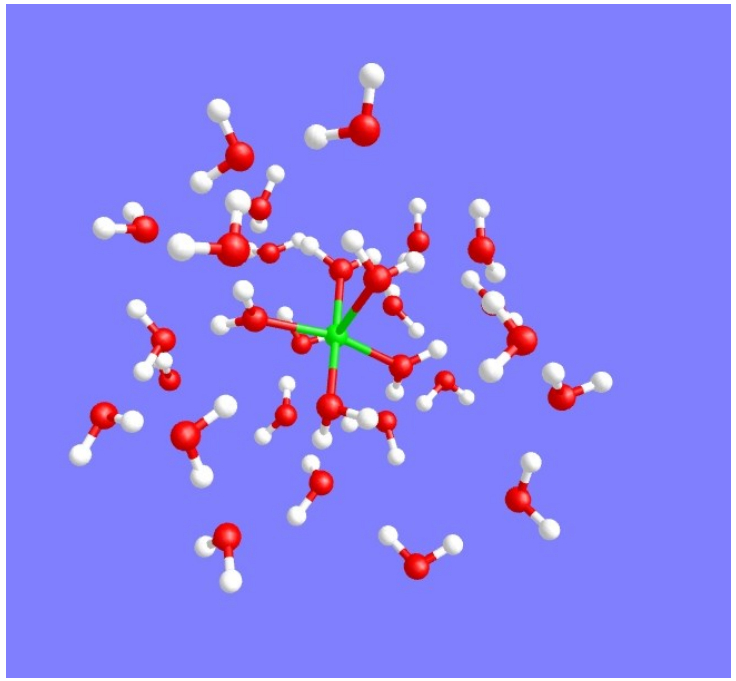


QuantumESPRESSO
Giannozzi, P. *et al.* (2009 *Journal of Physics: Condensed Matter* 21: 395502.

XSPECTRA
Gougoussis, C., Calandra, M., Seitsonen, A. P., & Mauri, F. (2009) *Physical Review B*,*80*(7), 075102.

The Model System

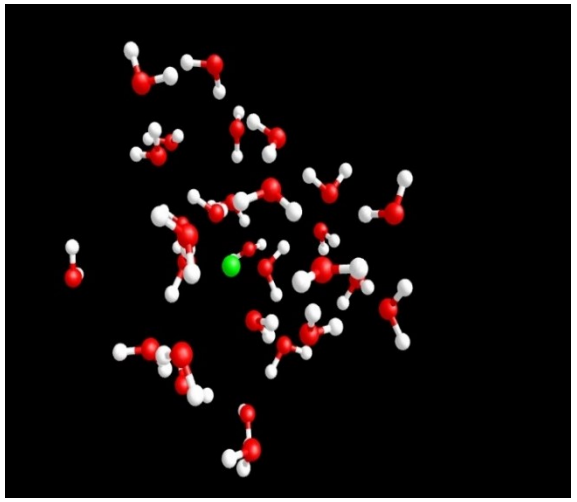
Cu(II) in water
29 water molecules in a 22 Å cubic box
88 atoms
113 electrons



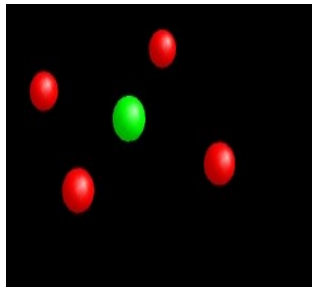
There are many XAS (and non-XAS) studies aimed at elucidating the Cu(II) coordination mode in water

Models with 4 and 5 oxygen atoms in the vicinity of the metal have been proposed

Two Configurations

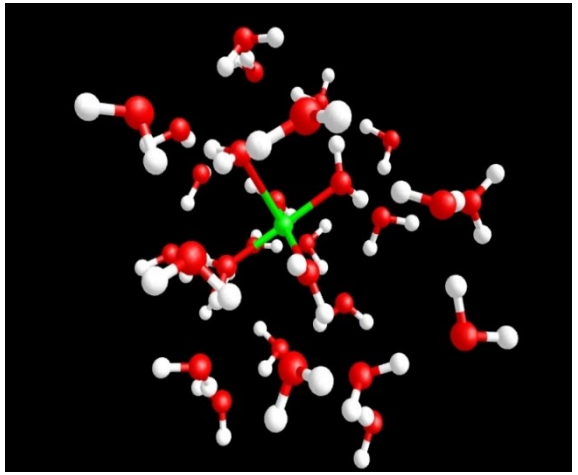


4 water molecules within 2.50 Å from Cu(II)

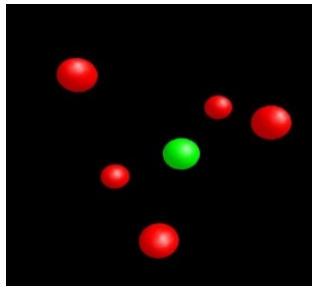


Atom	r (Å)
O	1.95
O	1.97
O	1.97
O	1.98

Configurations with 4 and 5 water molecules coordinated to the Cu(II) have been classically built

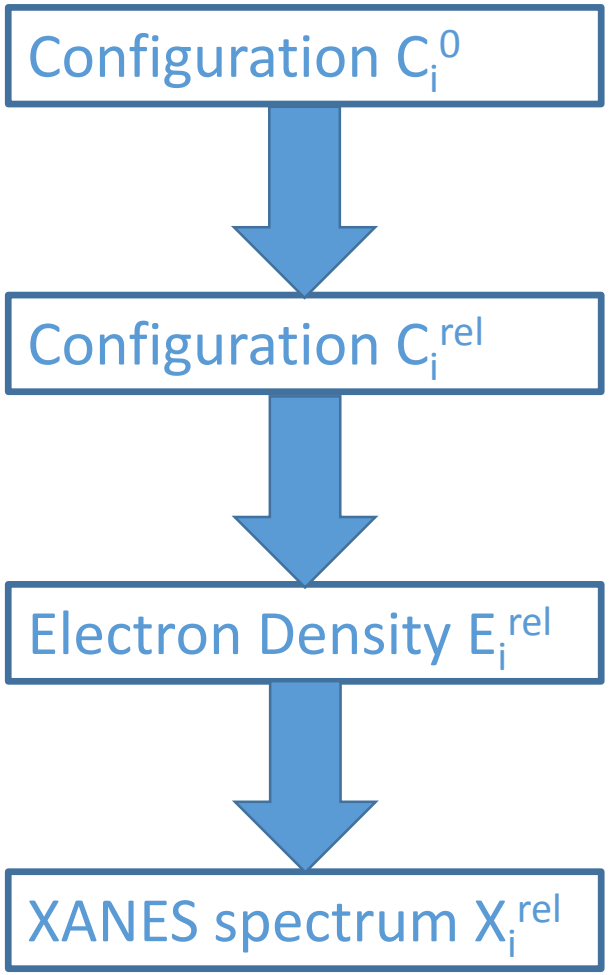


5 water molecules within 2.50 Å from Cu(II)



Atom	r (Å)
O	2.00
O	2.01
O	2.02
O	2.10
O	2.23

XAS Spectrum Simulation

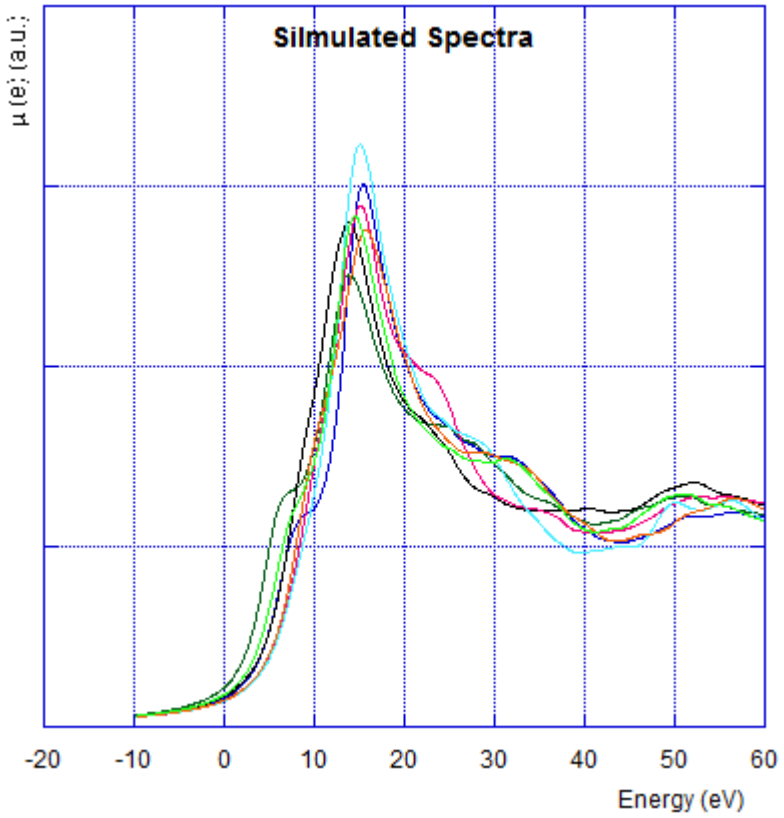


QuantumEspresso
pw.x – relax calculation – 10 iterations

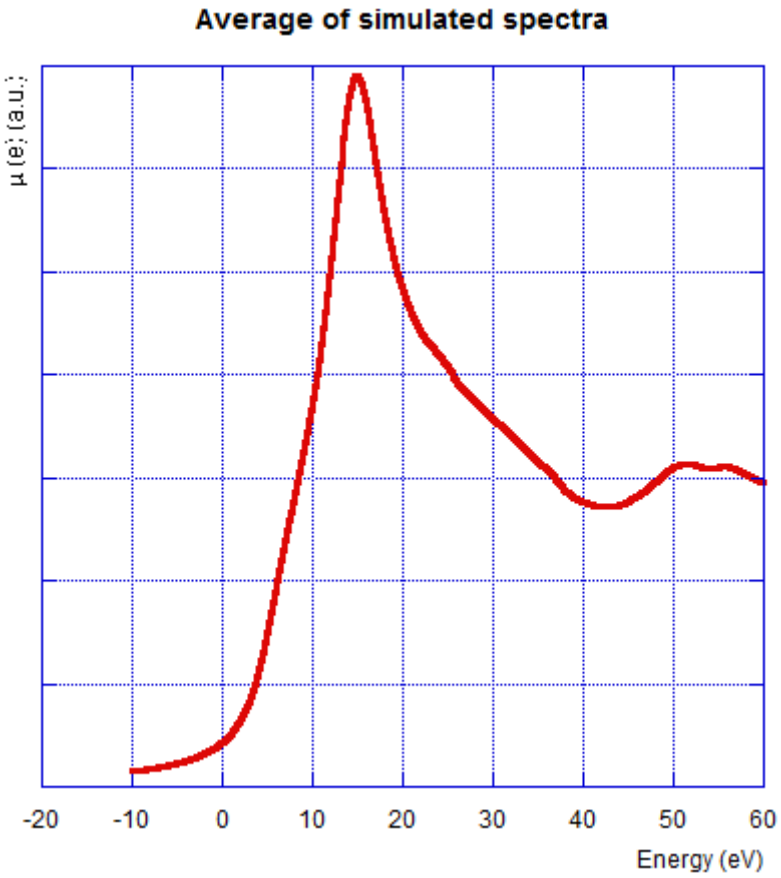
QuantumEspresso
pw.x – self consistent field calculation

XSPECTRA
xspectra.x – dipole calculation

Simulated XANES spectra

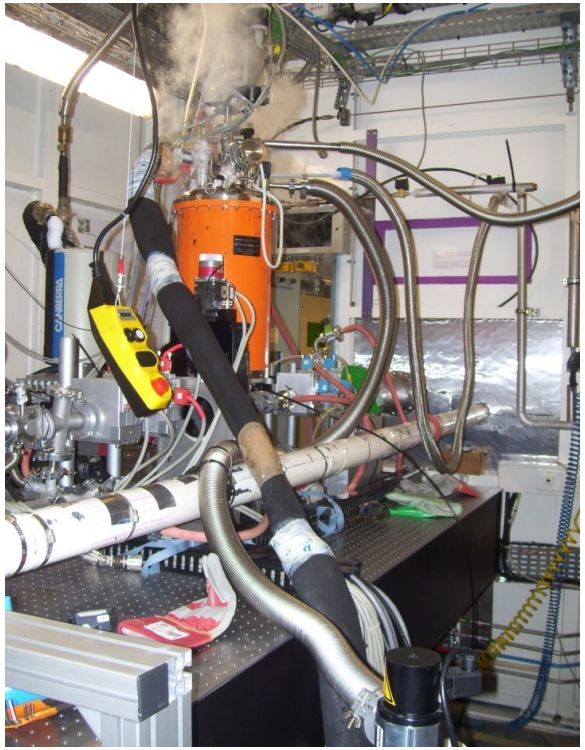


Simulated spectra of 8 configurations of Cu(II) in water

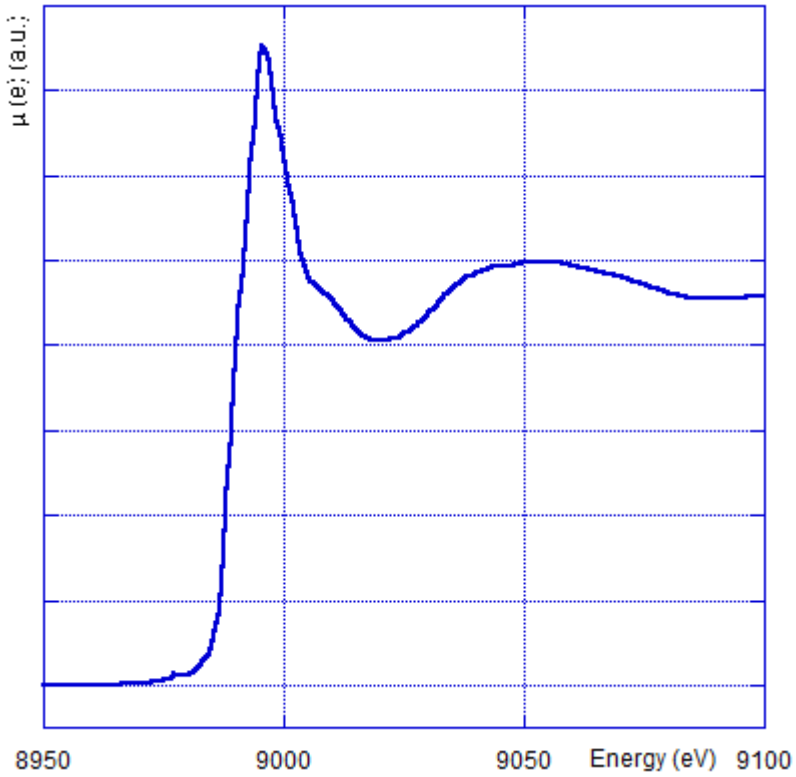


Comparison with Experimental data

The XAS spectrum of Cu_2SO_4 in water at 13 K was acquired at the ESRF synchrotron - Grenoble



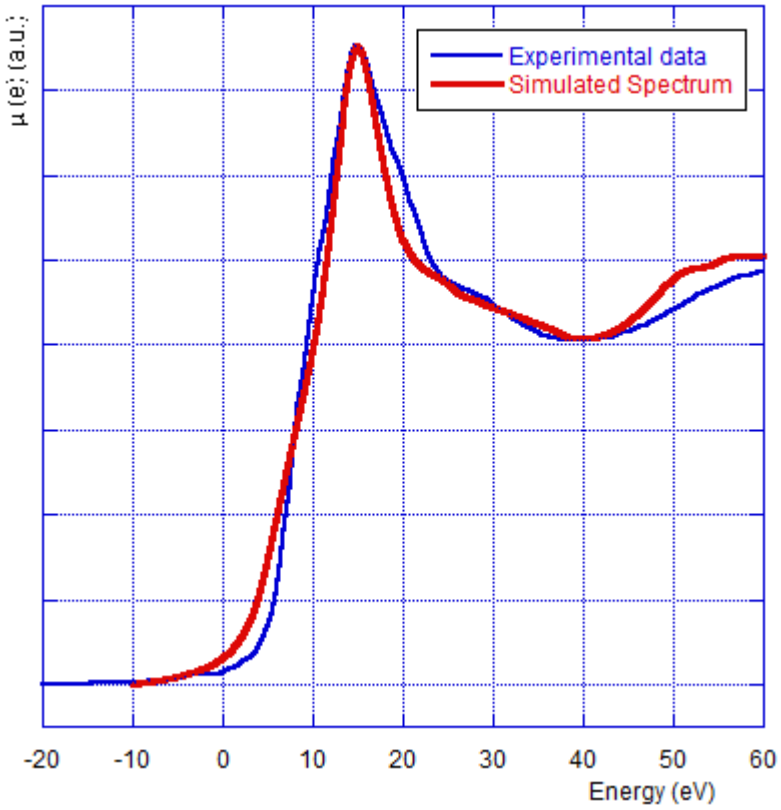
BM30B beamline



Comparison with Experimental data

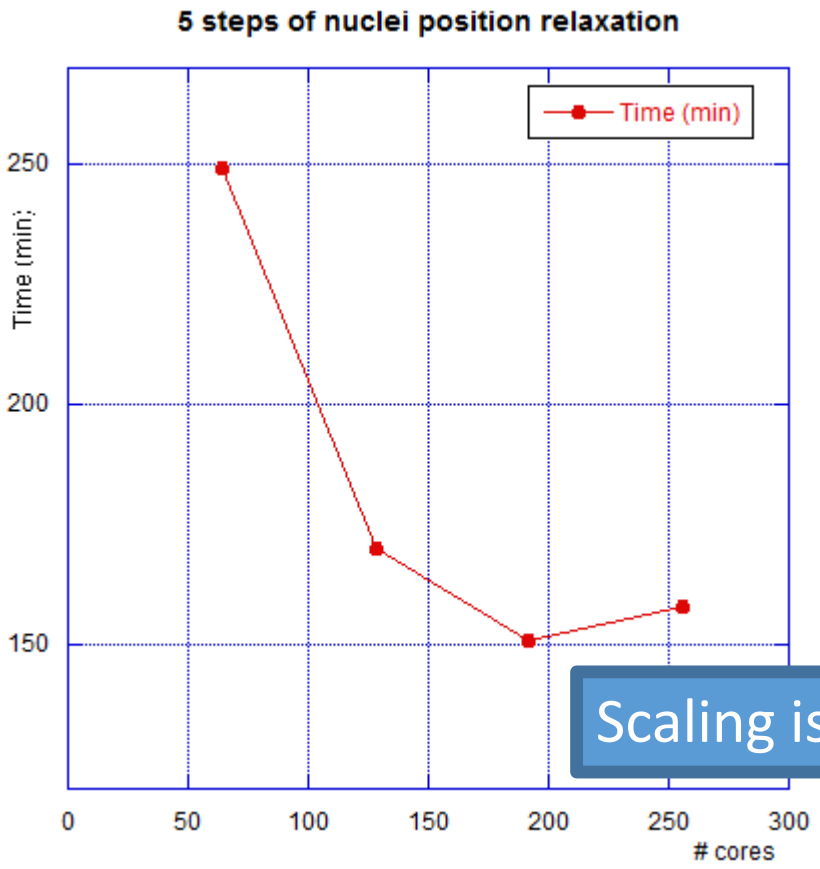
Simulation results are in good agreement with the experimental data

(even using just 8 configurations and not including the quadrupole contribution)

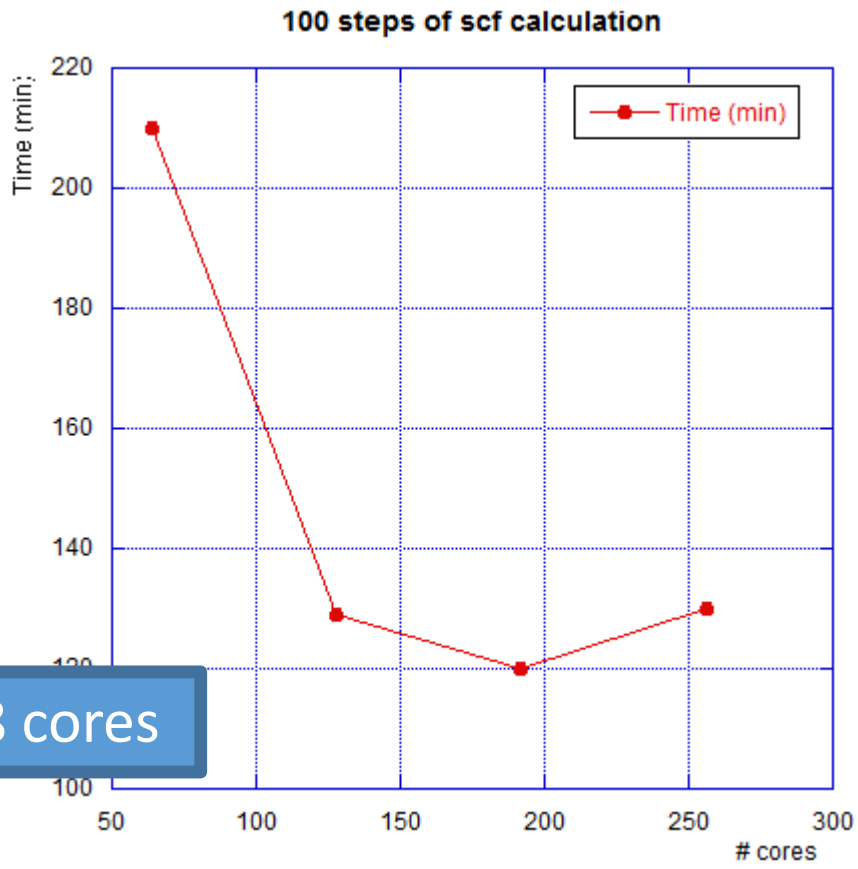


Computational Workload

Time required for 5 iterations of nuclei position relaxation on the Zefiro Theocluster



Time required for 100 iterations of scf on the Zefiro Theocluster



Scaling is good up to 128 cores

Computational Workload

Total CPU time required for the project (~100 configurations) is given by

relax calculation: ~ 500 corehours/configuration
scf calculation: ~ 500 corehours/configuration
XANES calculation: ~ 100 corehours/configuration

~ 110 kcorehours

Conclusions

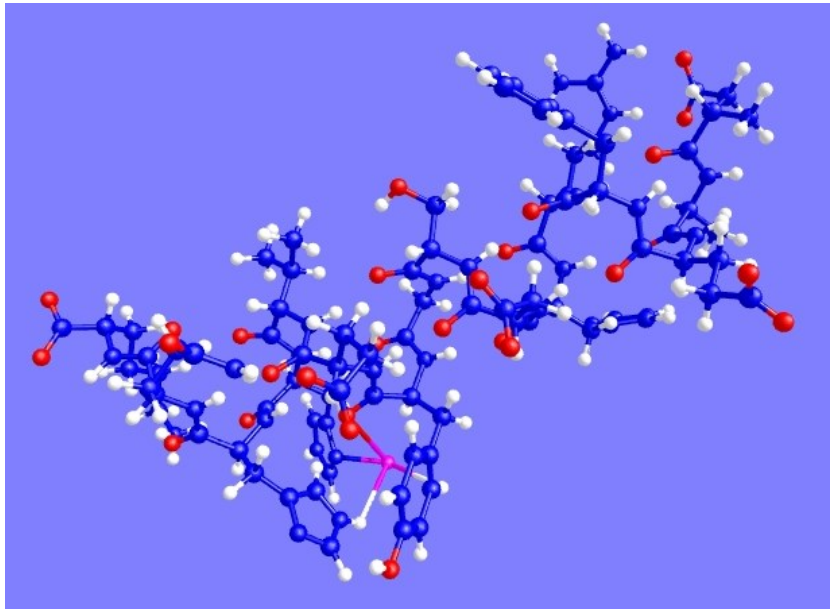
- *Ab initio* simulation of XANES spectra of metal ions in solution is feasible
- Good agreement between simulated and experimental data
- The effect of second order corrections due to the quadrupole contribution should be analyzed
- …

Outlook

Only ~10^5 core hours are needed to simulate XANES spectra from 100 configurations of the small system shown here but…

For a biologically realistic and interesting system, e.g. a few $A\beta_{1\text{-}40}$ peptides (400 atoms, ~ 1200 electrons) in complex with Cu(II) in a water (explicit and implicit) environment*

$>10^8$ → 10^{10} core hours



* to avoid periodic images interaction

People

- Prof. Silvia Morante
- Prof. Giancarlo Rossi
- Dr. Velia Minicozzi
- Dr. Giovanni La Penna

[The Biophysics Group in Tor Vergata
http://biophys.roma2.infn.it/](http://biophys.roma2.infn.it/)

Thank you for the attention!

¿¿¿ Questions ???