First-principle calculation of X-ray absorption spectra

Emiliano De Santis[1], Giovanni La Penna[2], Velia Minicozzi[1], Gian Carlo Rossi[1], Silvia Morante[1], Francesco Stellato[1]

[1]*Dipartimento di Fisica & I.N.F.N. – Roma Tor Vergata*

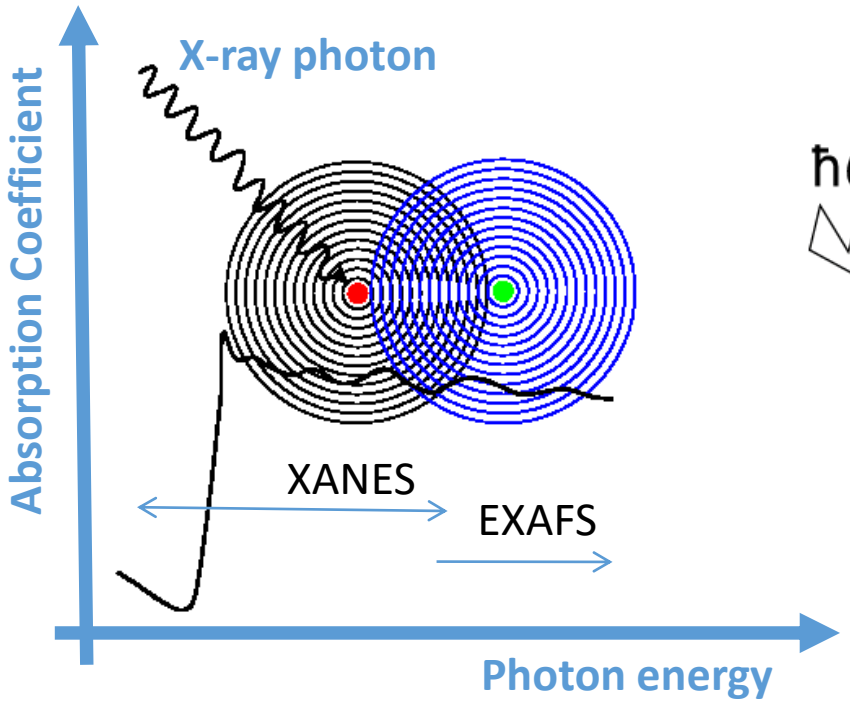
[2] ICCOM-CNR – Sesto Fiorentino

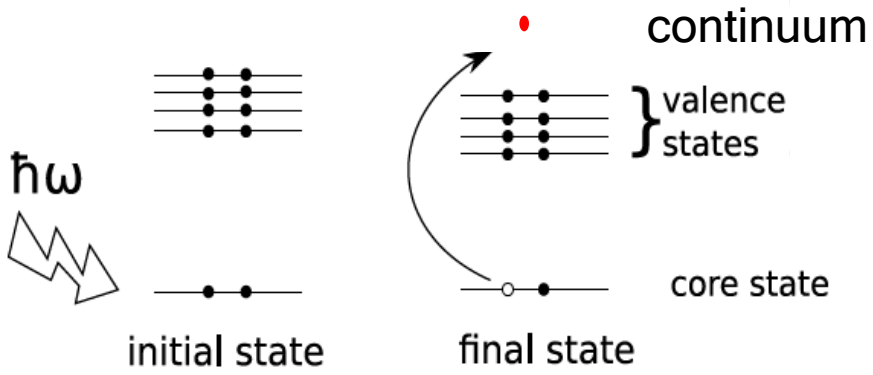
Outline

- X-ray Absorption Spectroscopy
  - *Ab initio* calculations of XAS spectra
    - Cu(II) & Zn(II) in water:
      Theoretical simulations *vs* experimental data
      - Conclusions and Outlook

X-ray Absorption Spectroscopy

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





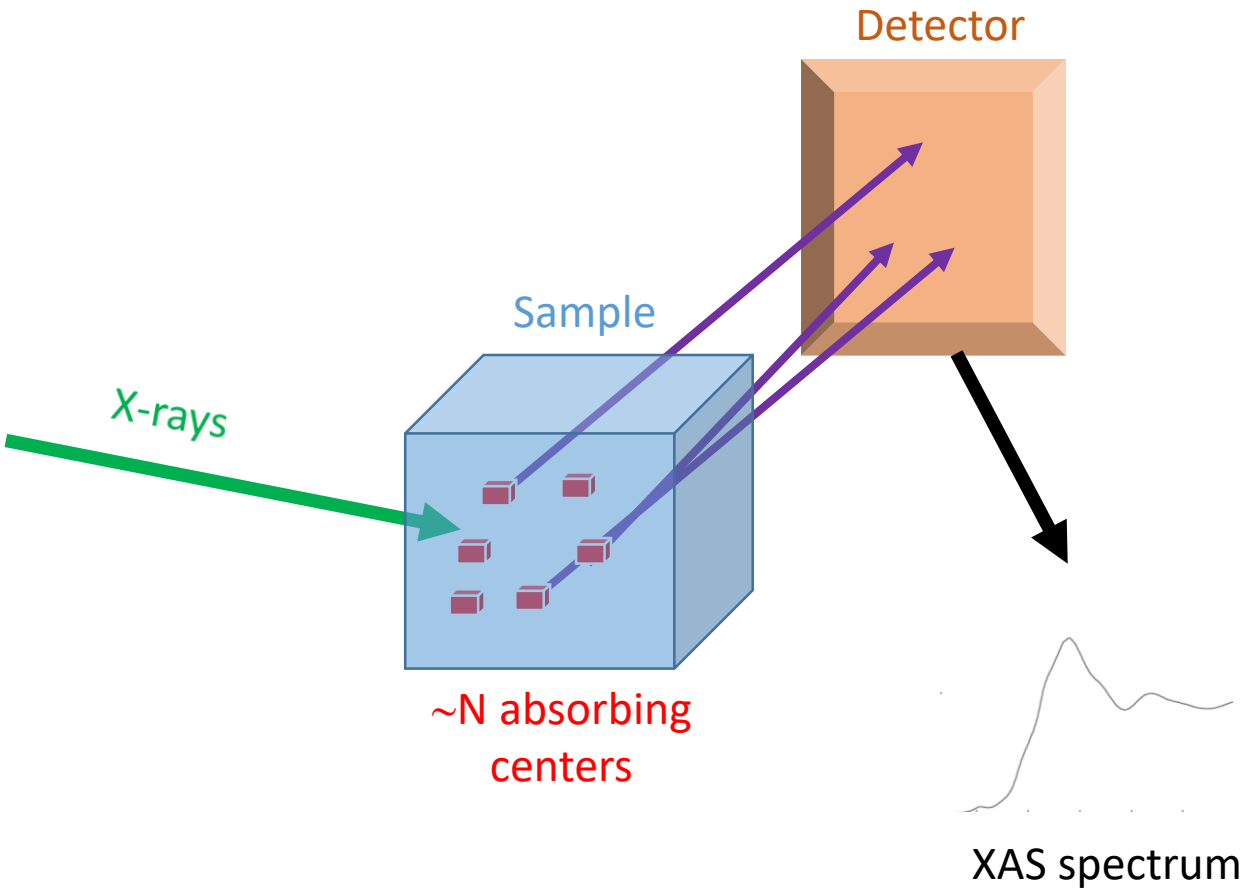
XAS features

✓Selective for the absorber

✓Local probe (~5 Å) (no crystals needed)

X-ray Absorption Spectroscopy

A typical XAS experiment

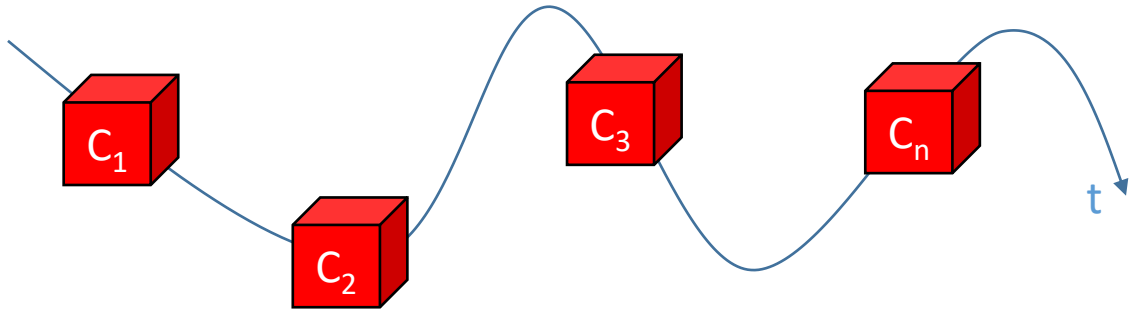


The XAS spectrum is the average of a large number, N, of absorption events from N absorbing centers, each one living in a potentially slightly different configuration

Ab initio XAS spectra calculation

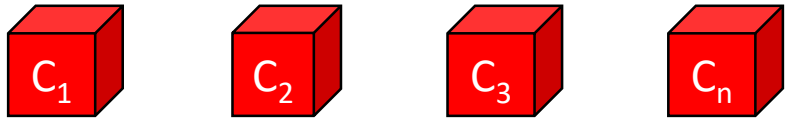
Under the ergodic hypothesis, the ensemble of configurations "seen" by the X-rays could be substituted by the single configurations along a molecular dynamics trajectory

Molecular dynamics trajectory



Different classical starting models are built to explore the configurations space

Classical starting models



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

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

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

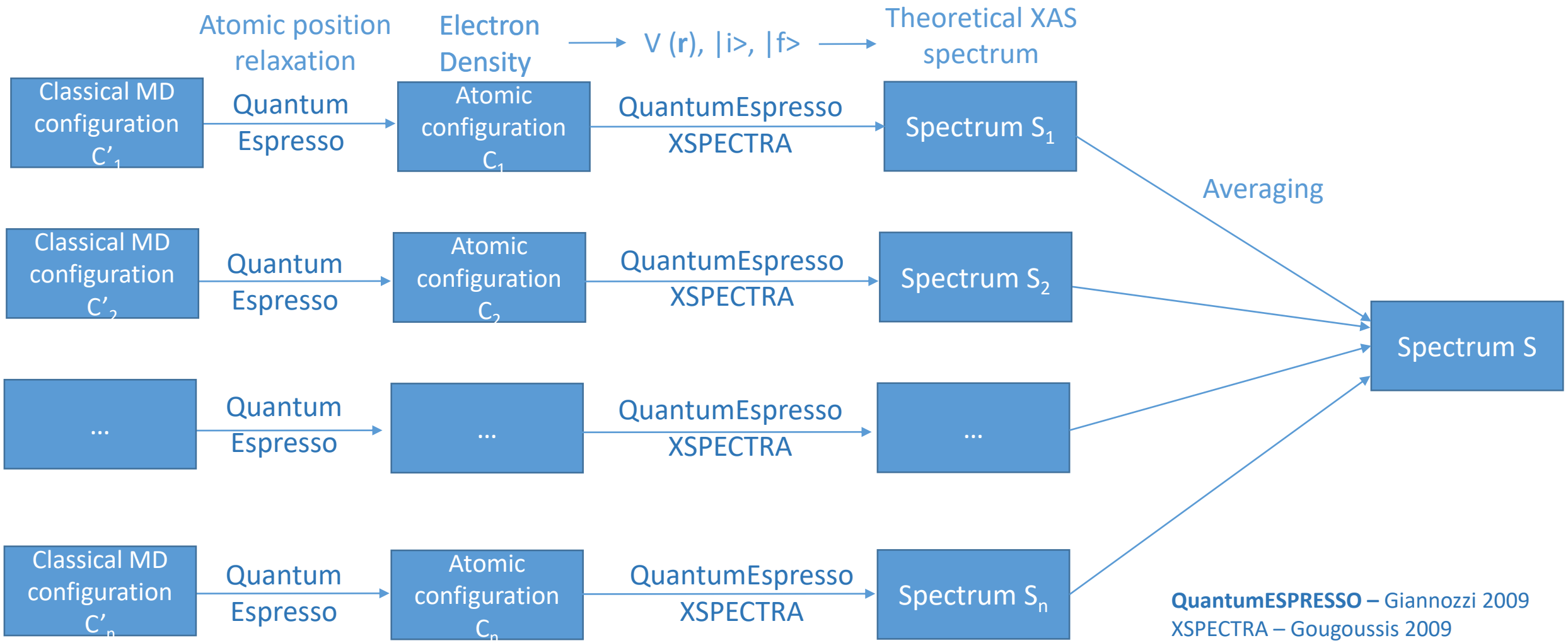
Dipole

Quadrupole

Final State

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

Ab initio XAS calculations



QuantumESPRESSO – Giannozzi 2009
XSPECTRA – Gougoussis 2009

Divalent Cations in water – Cu(II) & Zn(II)

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

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

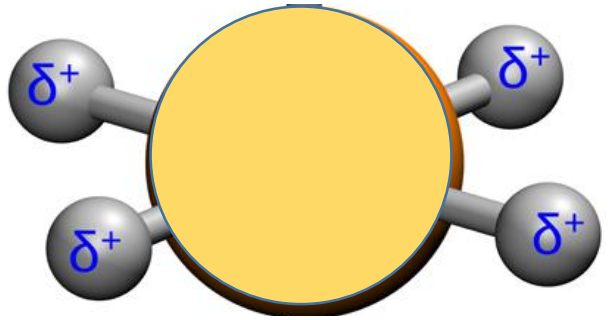
Different Cu(II)/Zn(II) – water coordination geometries have been proposed

Classical modeling of metal ions

A classical approach to metal binding

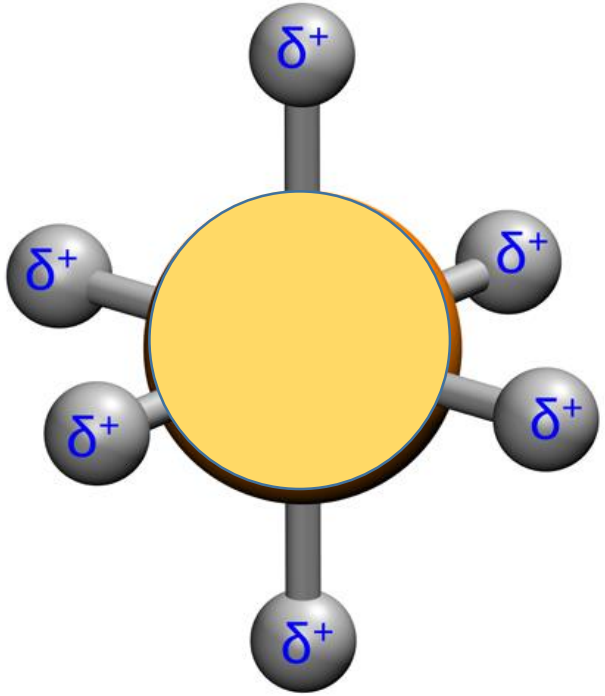
The metal ion is represented by the *dummy atoms* method.
Dummy charges δ are located in given geometries around the central metal ion

This allows building metal complexes without explicitly creating bonds between the metal and the surrounding atoms

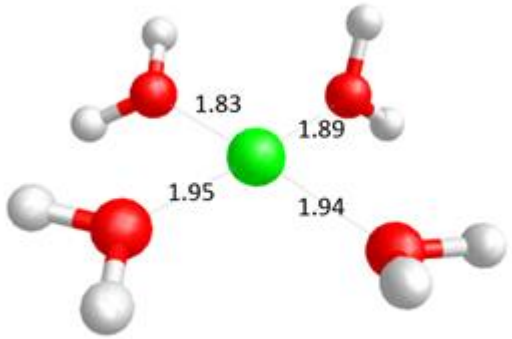


Square-planar
Coordination mode

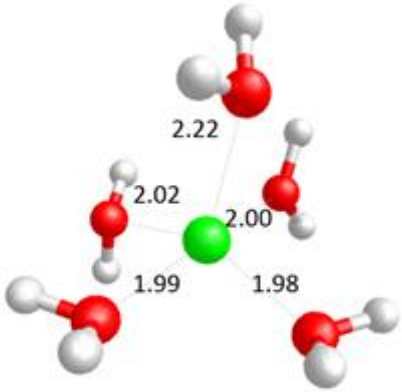
Octahedral
Coordination mode



Cu(II) Configurations

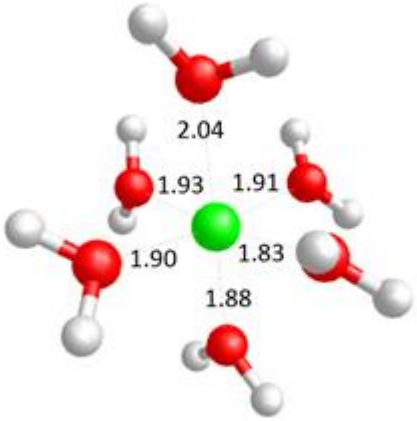


20 configurations with 4 water molecules bound to the Cu(II) along a classical MD trajectory



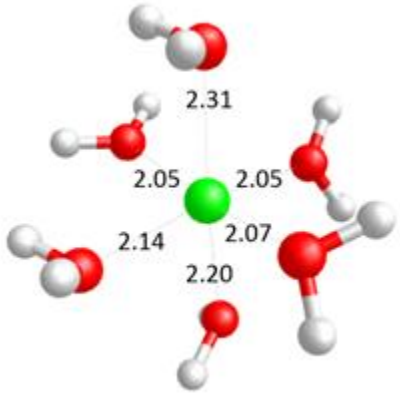
Tetra-coordinated structures relax into penta-coordinated ones

Atomic positions have then been quantum-mechanically refined

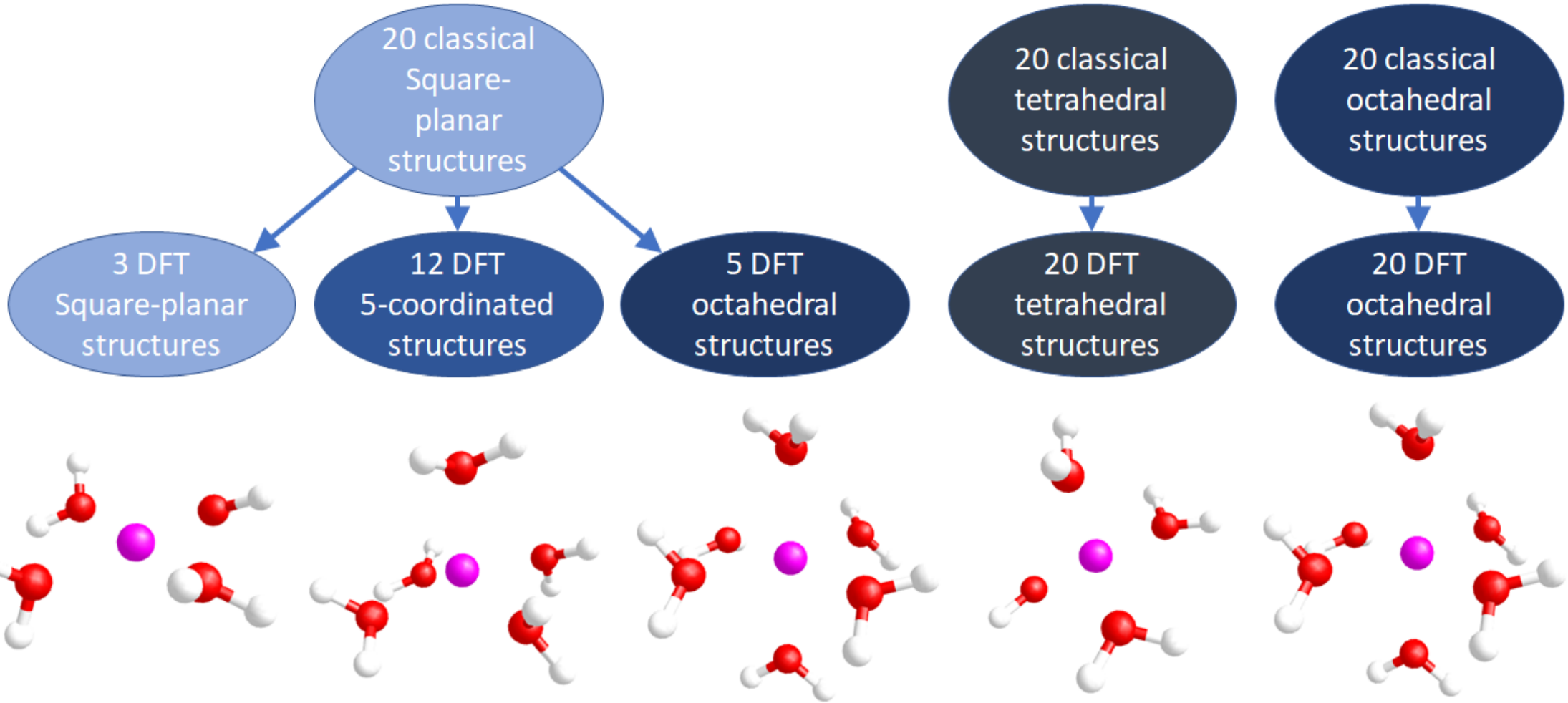


Hexa-coordinated structures remain hexa-coordinated

20 configurations with 6 water molecules bound to the Cu(II) along a classical MD trajectory

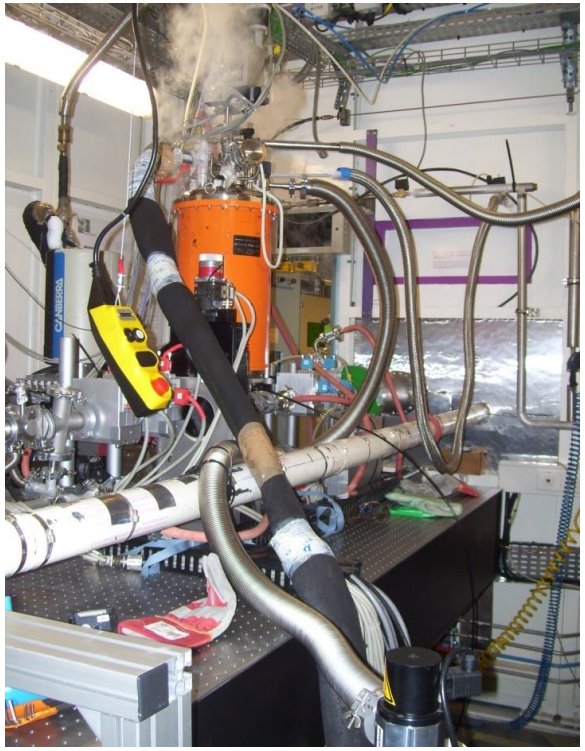


Zn(II) Configurations



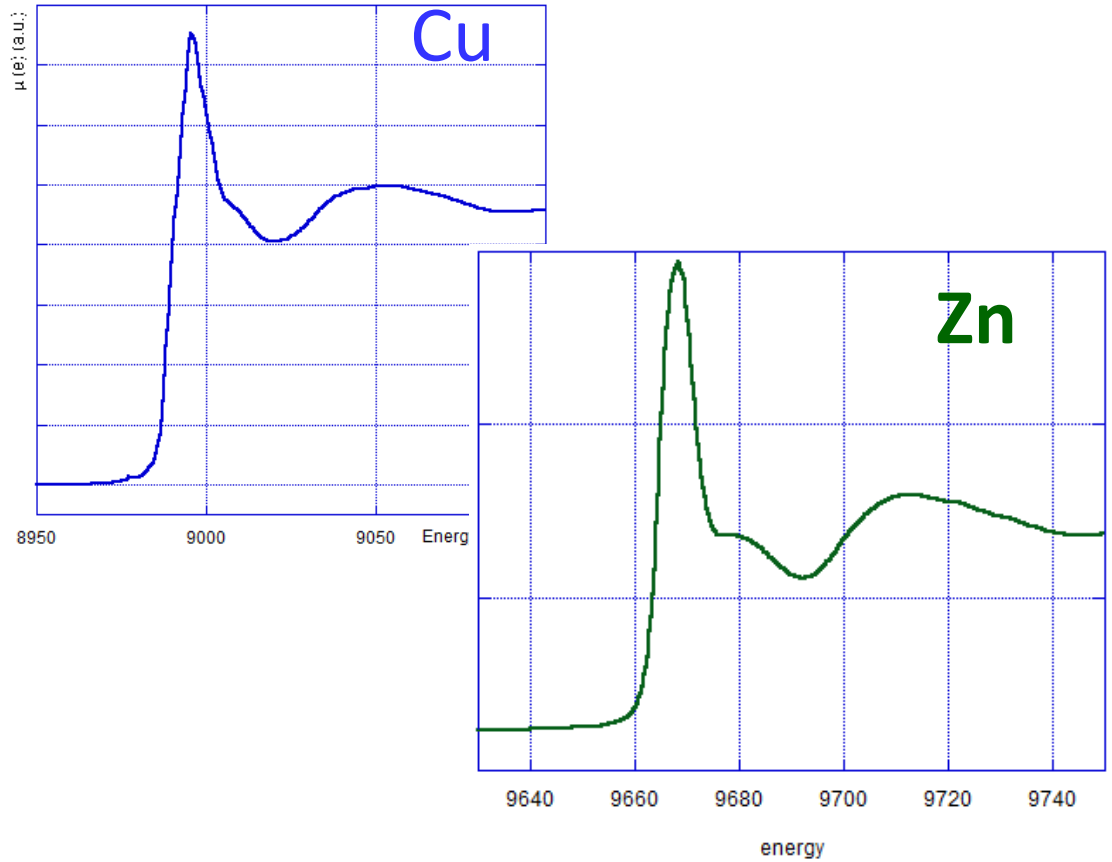
Comparison with Experimental data

XAS spectra of Cu_2SO_4 in water and of $ZnCl_2$ in water acquired at ESRF



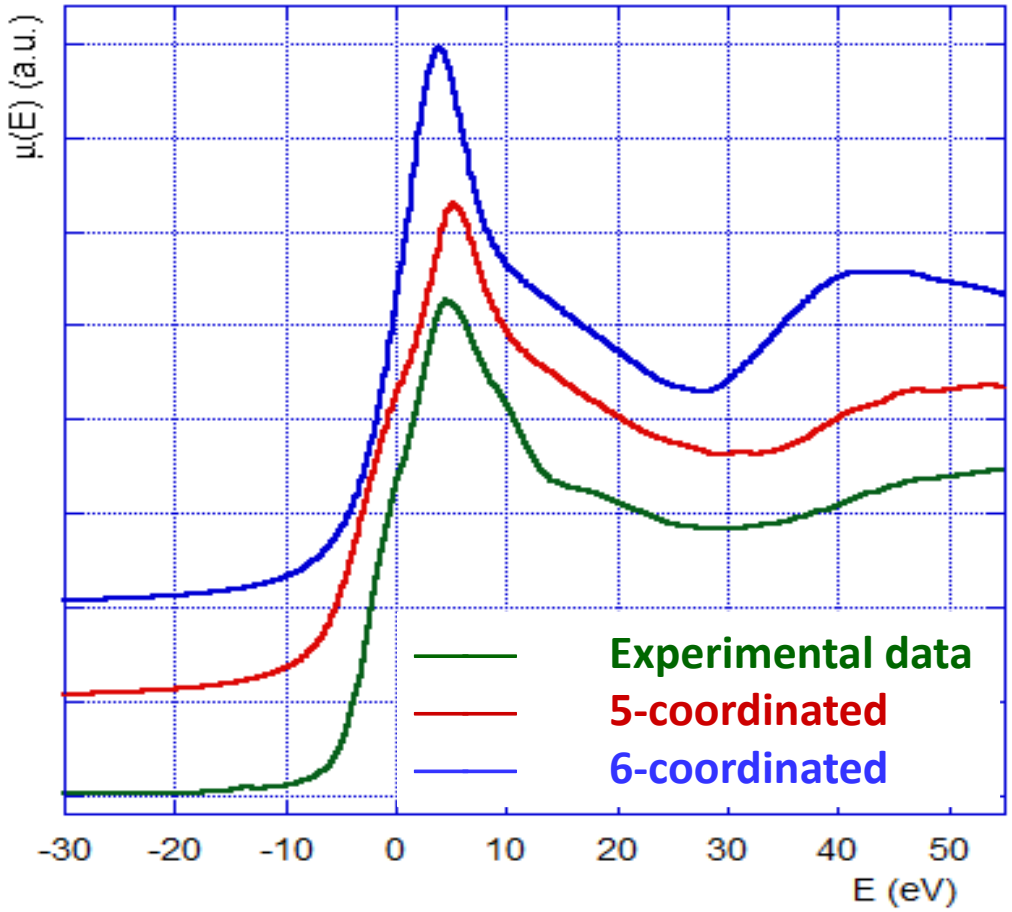
FAME

ESRF
The European Synchrotron



Cu(II) - Comparison with Experimental data

The experimental spectrum is better simulated by a penta-coordinated Cu(II)



Simulations performed on
Zefiro (INFN) & Galileo (CINECA) clusters

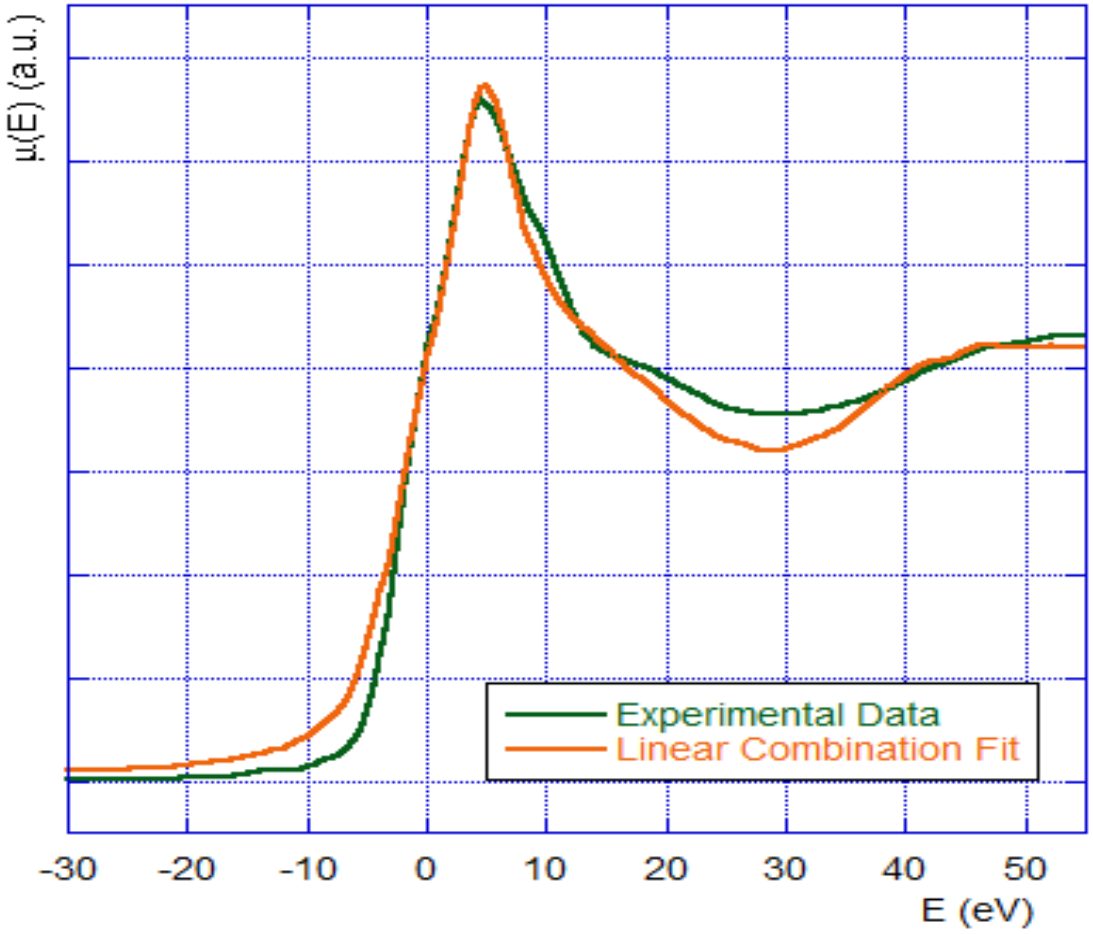
Cu(II) - Comparison with Experimental data

A linear combination analysis shows that the best agreement with the experimental data is obtained when assuming the presence of

78 % penta-coordinated Cu(II)

+

22% hexa-coordinated Cu(II)



G. La Penna, V. Minicozzi, S. Morante, G.C. Rossi, F. Stellato
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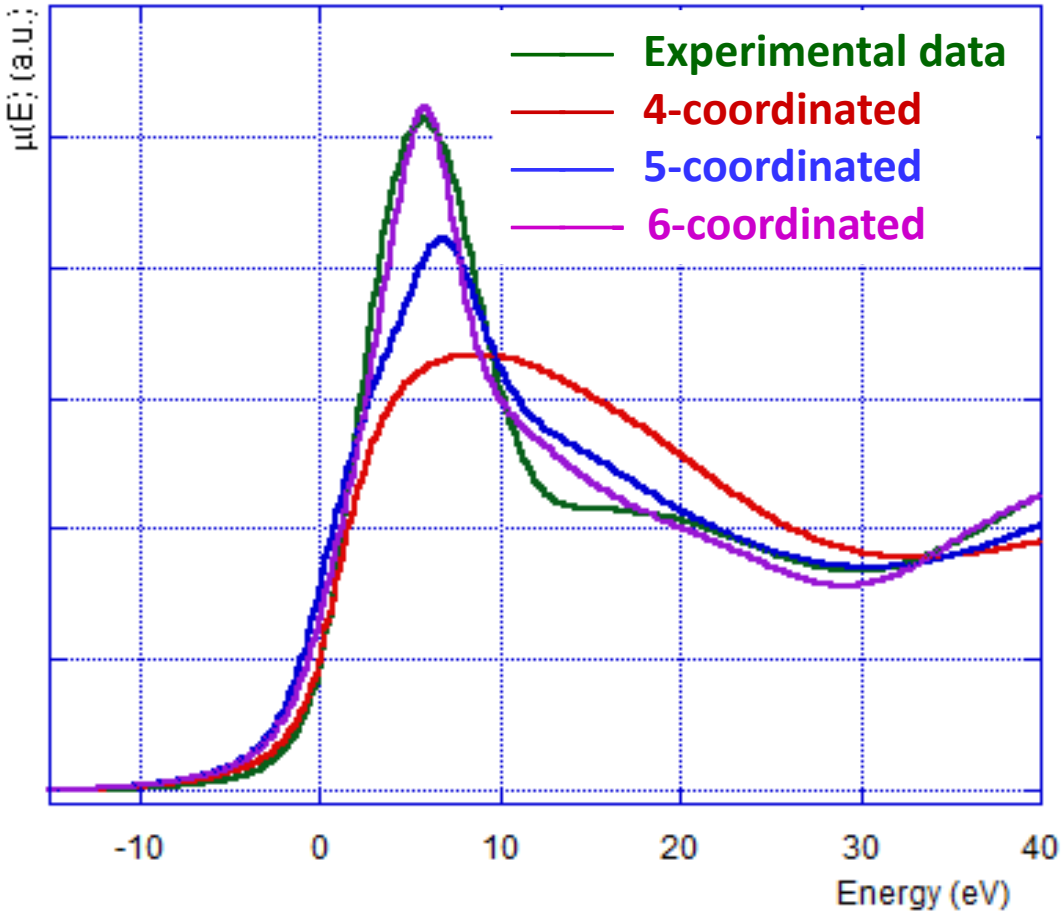
Zn(II) - Comparison with Experimental data

The experimental spectrum is
Well reproduced assuming a
hexa-coordinated Zn(II)



Simulations performed on
Galileo & Marconi (CINECA) clusters

Conclusions

- A multi-scale approach for the MD simulation of metal ions
- A scheme for the *ab initio* calculation of experimental observables

- Good agreement between simulated and experimental data:

  Cu(II) is mainly penta-coordinated, Zn(II) is hexa-coordinated

- Our method builds a bridge connecting

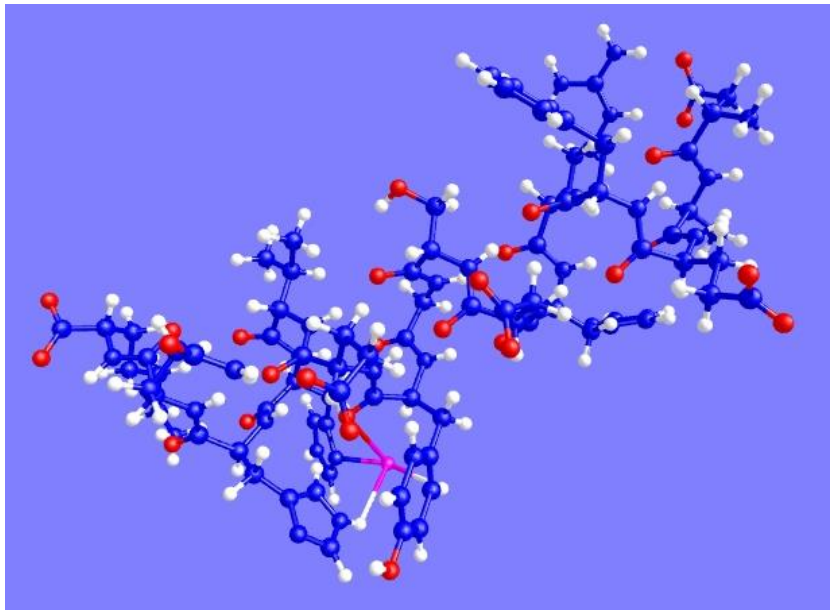
numerical simulations & experimental data

Outlook
Running on a long bridge…

~10^6 core hours on CPU clusters were needed to perform
MD simulations & XANES calculations
of the small systems I talked about here
but…

Biologically realistic and interesting systems,

e.g. a few $A\beta_{1\text{-}40}$ peptides (400 atoms, ~ 1200 electrons)
in complex with Cu(II) in a water environment



>10^8 Core Hours

People

- Prof. Silvia Morante
- Prof. Giancarlo Rossi
- Dr. Velia Minicozzi
- Dr. Giovanni La Penna
- Dr. Francesco Stellato
- Dr. Emiliano De Santis

The Biophysics Group in Tor Vergata
http://biophys.roma2.infn.it/