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

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The possibilities offered by high performance parallel computing forfirst principle simulations of systems composed by a large number of atoms are opening up the way to new approaches not only for ab initio molecular dynamics simulations, but also for providing improved models for the interpretation of experimental data.
In this context, we are developing a strategy to compute the electron density of biologically relevant systems to simulate ab initio X-ray Absorption Spectroscopy (XAS) spectra. The XAS signal is originated by the scattering of the photoelectron with the surrounding atoms and therefore strongly depends on the potential seen by it. The structure of the XAS spectrum is usually computed starting from an approximated potential. Here we develop a strategy to evaluate the potential directly from the knowledge of the exact electron density calculated from first principles.
After producing a number of atomic configurations (via classical or first principle MD), our approach consists in calculating the electron density in correspondence of each of these configurations from which the photoelectron potential and the simulated XAS spectrum are computed. Under the ergodicity hypothesis, the average over the computed spectra over many configurations will represent the experimental spectrum as the latter results from the sum of XAS signals from the many thermodynamically accessible configurations of the measured system.
We report in this talk the results of an ab initio simulation of the XAS spectra of a system consisting of Cu(II) ions in water (see Figure 1(a)). This system is a good starting point to pave the way to the much more complicated case of computing the XAS spectrum of realistic and biologically relevant systems, such as biomolecules in water in complex with transition metals recently studied in [1].
For the system in Figure 1(a), consisting of one Cu(II) ion dissolved in 29 water molecules, we selected a number of equilibrated configurations along a classical MD trajectory. On these we performed single-point (i.e. fixed nuclei positions) electron density calculations with the help of the QuantumESPRESSO suite [2]. The XAS spectra were finally computed making use of the Xspectra code [3].
In Figure 1(b) we show a comparison between the experimental XAS data of a Cu(II) sulfate water solution (blue line), acquired at the ESRF BM30B beamline, and the theoretical spectrum (red line)resulting from averaging over the simulated spectra of eight system configurations taken along a classical MD trajectory. Our preliminary analysis shows that the ab initio strategy for simulating XAS spectra we have described is quite effective in providing a good description of XAS experimental data.

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