First principle calculation of X-ray absorption spectra

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Keywords: metal ions, X-ray absorption spectroscopy, density functional theory

The unprecedented progress of high performance computing we are witnessing today offers the possibility of accurate electron density calculations of atomic systems in realistic physico-chemical conditions. Detailed information of this kind is instrumental not only for *ab initio* molecular dynamics simulations, but also for a model-independent interpretation of experimental data.
We present here a strategy aimed at performing a first-principle calculation of the very informative low energy part of the X-ray Absorption Spectroscopy spectrum based on the density functional theory determination of the electronic potential [1].
To test the effectiveness of the approach we have applied the method to the computation of the characteristic features of the X-ray Absorption Near Edge Structure (XANES) part of the XAS spectrum in the paradigmatic case of metal cations, namely Cu(II) and Zn(II), in water solution. In order to keep into account the effect of the metal site structure thermodynamic fluctuations in determining the experimental signal, the theoretical spectrum is evaluated as the average over the computed spectra of a statistically significant number of equilibrated metal site configurations. The agreement of the theoretical spectrum obtained with experimental XAS data is quite good [2].
The remarkable success of this approach in the interpretation of XAS data makes us optimistic about the possibility of extending the computational strategy we have outlined to the more interesting case of molecules of biological relevance bound to transition metal ions. This will be particularly relevant in the study of the metal coordination modes in cases where the metal-protein complex cannot be crystallized, as it happens for the amylogenic proteins involved in the pathogenesis of Alzheimer's disease and transmissible spongiform encephalopathies [3}[4].

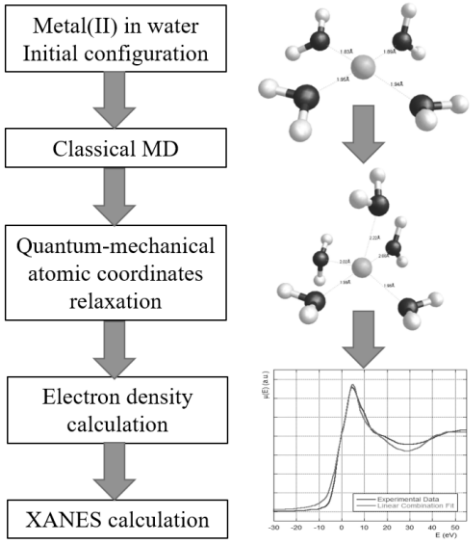

Figure 1. Left panel: the low-chart illustrating the XANES calculation procedure. Right panel: the case of Cu(II) ions in water (right side).

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