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X-ray absorption spectral shapes

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I will discuss some aspects of the theory and simulation of x-ray absorption spectral shapes. Concerning machine learning approaches, a complication is that the most accurate methods take too much time, so they ideally should be approximated in a reliable fashion. We can distinguish 3 different starting points for the interpretation of XAS spectral shapes:

(1) Closed shell systems can be described with Bethe-Saltpeter (BSE) or time-dependent DFT models that can be approximated with DFT based approaches
(2) 3d and 4d XAS of f-systems and 2p XAS of 3d systems can be described with local models dominated by the intra-atomic electron-electron interactions in the atomic multiplet and crystal field multiplet models
(3) Covalent 3d systems need the inclusion of charge fluctuations (charge transfer Δ and Hubbard U) in impurity multiplet or Dynamical Mean-Field (DMFT) methods.

There are a number of additional issues:
(a) In the DFT approximation to BSE/TDDFT, one has to choose an exchange-correlation potential, determine its U value and choose a core-hole treatment.
This leads to a variety of methods/choices and it is likely that the best choice is material and XAS edge dependent.
(b) The interpretation of transition metal K edges adds some additional challenges. The main dipole edge can be interpreted from DFT. However, the 1s XPS spectra of (for example) transition metal oxides show multiple peaks, implying that one photon energy gives rise to electrons with multiple kinetic energies. This means that the 1s XAS spectral shape must be described as the convolution of the empty states as calculated with DFT with the 1s XPS spectral shape [Ghiasi et al., Phys. Rev. B. 100, 075146 (2019)]. In addition, the quadrupole peaks are excitonic and have an extra core hole shift of ˜3 eV and need to be described with multiplets.
(c) The complication for machine learning based multiplet methods (atomic, crystal field, impurity, DMFT) is that these are real space localised model Hamitonians. There exist no uniform first-principle method to derive the parameters in these model Hamiltonians from geometric structures. A nice example is the Hubbard U that is large in impurity multiplet calculations, but approaches zero in DFT with accurate XC potentials such as r2SCAN.

These issues together imply that we are still far from a general first-principle route of accurate XAS spectral shape simulations.

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