

# The 2p X-ray absorption spectra of transition metal systems: New developments and ab-initio routes.

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## Introduction

In this paper I will give my view on the status of our understanding of the 2p ( $L_{2,3}$ ) x-ray absorption spectra of transition metal systems. I will mainly focus on solid transition metal oxides and on coordination complexes of transition metal ions. This contribution was written at the CECAM workshop on X-ray spectroscopy, 13-15 July 2011. Some of the latest results as presented at the workshop have been included, in particular from the contributions by Frank Neese, Peter Blaha, John Rehr and George Sawatzky.

I will first describe the main interactions arising with the creation of a 2p core hole. In section 3 I briefly introduce the charge transfer multiplet model. Section 4 deals with recent ab-initio routes towards the description of  $3d^0$  systems. Section 5 treats the recent advances in the ab-initio description of systems with partly occupied 3d states.

## The main interactions involved in 2p XAS excitations

In 2p x-ray absorption a system with partly filled 3d states is dominated by the transitions to the empty 3d states. I approximate the ground state as  $3d^N$  and due to the self-screened 2p3d excitation the main final state contribution will be  $2p^5 3d^{N+1}$ . The consequence is that if the ground state can be described well with one  $3d^N$  configuration (for example for most divalent compounds and complexes) the whole 2p XAS spectrum can be explained from a transition  $3d^N \rightarrow 2p^5 3d^{N+1}$ . Note that this behaviour is completely different from 2p XPS where the direct excitations leads to a poorly screened  $2p^5 3d^N$  state that will transfer most of its intensity to the well screened  $2p^5 3d^{N+1} \underline{L}$  state. This implies that 2p XPS will be dominated by charge transfer effects [1-3]

An ab-initio description of the 2p XAS spectrum would need to describe the main ground state and final state interactions. This includes for the ground state:

- G1 Hybridization and translation symmetry, the adequate description of the chemical bonds for molecules and band structure for solids.
- G2 Local exchange interactions including spin- and orbital polarization i.e. the intra-atomic 3d3d multipole interactions
- G3 Interatomic exchange interactions
- G4 3d spin-orbit coupling, with a strength between 10 and 100 meV, often (but not always) quenched by translation symmetry or crystal field symmetry.
- G5 In case of strong correlations specific interactions, for example the interatomic 3d3d interaction is explicitly included with a correlation energy ( $U$ ), taking into account the effects due to charge fluctuations in the 3d occupation.

Most present day DFT codes do not describe all these ground state effects adequately. For example DFT (in the local density approximation) does not treat the local spin correctly and it cannot handle the intra-atomic 3d3d multipole interactions. DFT works well in non-magnetic systems such as CaO and SrTiO<sub>3</sub>. Quantum chemistry calculations can have spin as a good quantum number and include the correct multiplet structure, but such calculations are limited to small clusters and do not contain the effects due to translational symmetry.

The additional final state effects of the 2p core hole include:

- F1. The core hole potential.
- F2. The core hole spin-orbit coupling, yielding a distinction between the L<sub>3</sub> and L<sub>2</sub> edge. Without the effects mentioned in F4 and F5 and without the inclusion of the ground state spin-orbit coupling (G3), the L<sub>3</sub> and L<sub>2</sub> spectra are identical with a ratio of 2:1.
- F3. The core hole induced charge transfer effects, including shake states. This effect includes the transitions to orbitals that are higher in energy in the ground state and are coupled into combined states. Due to the core hole potential and the different localization of orbitals, the final state ordering of orbitals is strongly modified with the 3d orbitals shifted down.
- F4. The core hole – valence hole exchange interaction, the direct spin-spin coupling of the core spin and the valence spins, within the CTM model described with the G<sub>1</sub> Slater integral.
- F5. The higher order term of the Core hole – valence hole exchange interaction, within the CTM model described with the G<sub>3</sub> Slater integral.
- F6. The core hole – valence hole multipole interactions. The 2p and 3p core holes have a dipole-dipole interaction with the 3d holes, described with the F<sub>2</sub> Slater integral.

### **The charge transfer multiplet calculations**

The basis for the ligand field multiplet and charge transfer multiplet calculations is the observation that the 2p XAS spectra of many transition metal systems are quasi-atomic spectra that can be described well with atomic  $3d^N \rightarrow 2p^5 3d^{N+1}$ , where all other effects are included into an effective electric field. Concerning the ground state this implies that the translation symmetry is neglected and the hybridization described with an effective field (G1). The local interactions G2 and G4 are treated explicitly and the interatomic exchange is again described with an effective magnetic or exchange field. Strong interatomic correlations (G5) are included with empirical parameters for 3d3d correlation (U) and 3d-ligand correlation ( $\Delta$ ).

All final state effects of the 2p core hole are treated explicitly. The core hole spin-orbit coupling (F2) and the atomic multiplet interactions (F4,F5,F6) are calculated for an isolated atom or ion and transferred to a molecule or solid. The core hole potential (F1) does not affect the spectral shape and the core hole induced charge transfer effects (F3) are treated with empirical parameters.

The CTM model has been initially developed by Theo Thole, partly in collaboration with Kozo Okada, Hirohiko Ogasawara, Akio Kotani, Gerrit van der Laan and George Sawatzky [3, references therein]. Recently we have incorporated Theo Thole's program into a user friendly interface CTM4XAS that can calculate the XAS, XPS, XES and RIXS spectra of transition metal systems and rare earths [4]. Figure 1 shows the graphical interface for the calculations. The CTM4XAS program can be downloaded from the website <http://www.anorg.chem.uu.nl/CTM4XAS/>.

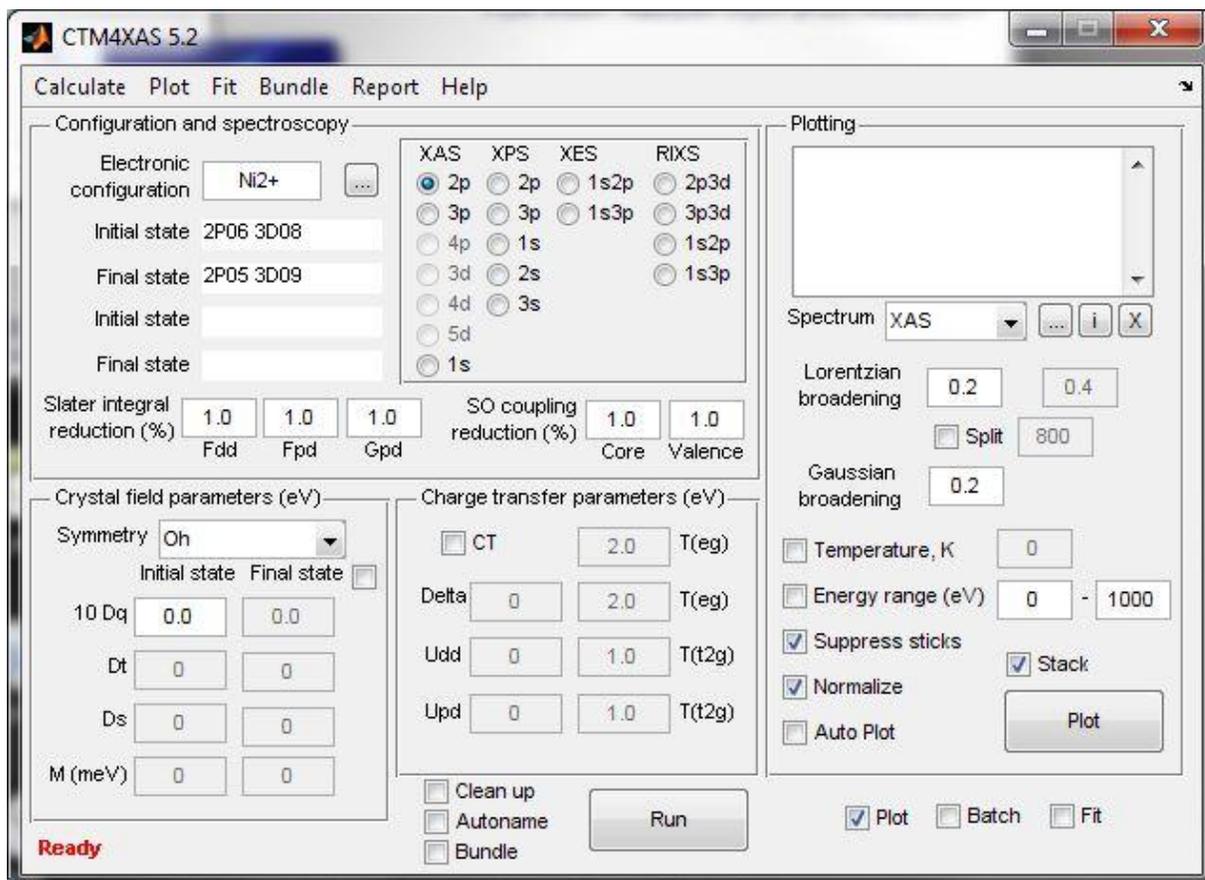


Figure 1: The CTM4XAS interface for the charge transfer multiplet calculations of XAS, XPS, XES and RIXS spectra.

### Ab-initio calculations of $3d^0$ systems

Transition metal systems where the ground state has no occupied 3d states allow some important approximations. First this implies that these systems are insulators due to the gap between the highest occupied states and the empty (3d) states. Note that 3d states are here defined as electrons in the '3d band or 3d orbitals', for example as appearing in a DFT calculation. This does not identify with the occupation of 3d character in a calculation because, for example, in a transition metal oxide such as  $\text{SrTiO}_3$ , the oxygen 2p valence band contains significant 3d character due to hybridization.

Because of the absence of 3d states in the ground state, the intra-atomic 3d3d multipole interactions (G2), interatomic exchange interactions (G3), 3d spin-orbit coupling (G4) and interatomic 3d3d correlations (G5) can be neglected, creating a ground state calculation that can adequately be solved in a mean field approximation. In addition the final state has only a single 2p hole and a single 3d electron, allowing the use of the Bethe-Salpeter (BSE) and TD-DFT approaches that explicitly describe single-hole single-electron excitations.

Detailed BSE calculations of TiO<sub>2</sub> have been described by Eric Shirley [5]. They have been improved and incorporated into the OCEAN program recently [6]. Laskovski and Blaha have added 2p XAS BSE calculations into the WIEN2K code [7]. At the CECAM workshop Peter Blaha explained that the BSE calculations allow for a detailed analysis of the nature of the 2p<sup>5</sup>3d<sup>1</sup> final states, such as their division into spin-orbit character and crystal-field character.

Peter Kruger has used multi-channel multiple scattering (MCMS) to calculate the 2p XAS spectrum of TiO<sub>2</sub>. He has shown that it is important to use a large cluster to correctly describe the long range effects in the rutile and anatase crystal structure [8]. TDDFT calculations have also been applied to 3d<sup>0</sup> transition metal systems. The group in Trieste calculated both molecules such as TiCl<sub>4</sub> and solids such as TiO<sub>2</sub> using ADF based TDDFT calculations. The absence of the small triplet peaks in TiO<sub>2</sub> and the unexpected branching ratio suggests that the combined effect of multiplet effects and spin-orbit couplings is not yet treated correctly in the results as published [9-11].

Frank Neese presented at the CECAM workshop new calculations, based on the ORCA code [12]. These calculations start out from a single electron transition to 2p<sup>5</sup>3d<sup>1</sup> singlet states and subsequently allow the mixing of selected triplet states. This procedure also allows the treatment of systems with partly occupied 3d states discussed below. Hidekazu Ikeno and co-workers have developed an ab-initio multiplet code based on DFT-CI within the jj-coupling limit. This procedure allows the accurate calculation of the 2p XAS spectrum of 3d<sup>0</sup> (and 3d<sup>N</sup>) systems [13-15], starting from a ground state geometry as determined a normal DFT calculation.

In order to obtain some quantitative insights into the differences between the results reached, we recently compared the ab-initio MCMS and DFT-CI results with CTM calculations for CaO [16]. Both ab-initio models described this system well and the main discrepancy seems to be the calculation of the core hole spin-orbit coupling. It would be very interesting to define a set of reference systems and calculate them with all the newly available models. 3d<sup>0</sup> model systems could include a rocksalt ionic oxide such as CaO, a high-valent high-symmetry oxide such as SrTiO<sub>3</sub> and a heavily distorted high-valent oxide such as V<sub>2</sub>O<sub>5</sub>.

### **Ab-initio calculations of 3d<sup>N</sup> systems**

The ab-initio calculation of 3d<sup>N</sup> systems is far more challenging because (1) the ground state is affected by intra-atomic 3d3d multipole interactions (G2), interatomic exchange

interactions and magnetic order (G3), 3d spin-orbit coupling (G4) and interatomic 3d3d correlations (G5). Figures 2 and 3 show the results of CTM4XAS calculations on two 3d5 systems, respectively the solid state system MnO in Figure 2 and the coordination compound  $\text{Fe}^{3+}(\text{tacn})_2$  in figure 3 [17].

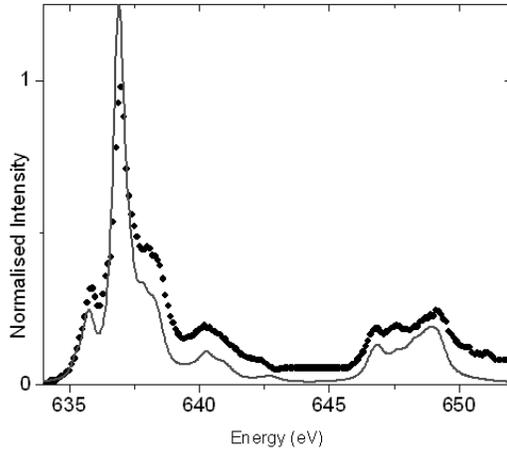


Figure 2: 2p XAS spectrum of MnO compared with a CTM4XAS calculation [2]

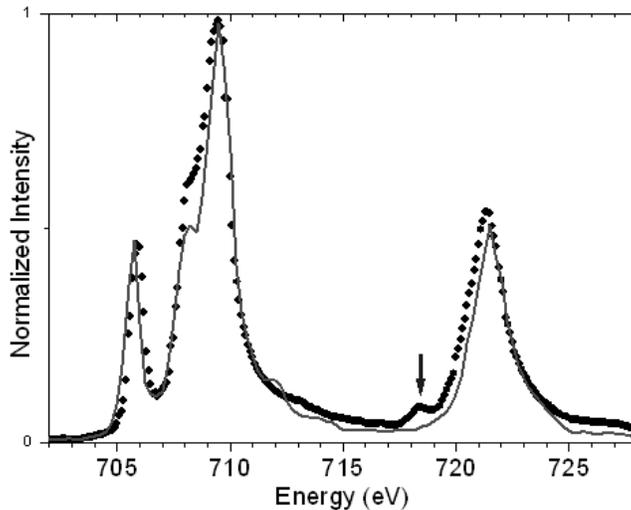


Figure 3: 2p XAS spectrum of  $\text{Fe}^{3+}(\text{tacn})_2$  compared with a CTM4XAS calculation. [17]

The  $2p^5 3d^{N+1}$  final state can not be (exactly) described by a single-hole single-electron excitation model such as BSE and TDDFT. BSE is well defined only for the case that one has two particles and it actually is equivalent to the two particle greens function method [18,19] For example, if one would have to deal with  $\text{LaTiO}_3$  rather than  $\text{SrTiO}_3$  which are both large gap insulators but La has  $\text{Ti}^{3+}$  and has an unpaired 3d electron, implying that LDA will not work correctly. However also important is that we now have (even if we neglect the neighboring Ti atoms) a 3 particle problem i.e. a 2p core hole and two 3d electrons. In a local cluster calculation this can be handled but this is not feasible by

including only the interaction between the core hole and the excited electron in the two particle problem as is the case in BSE. This three particle problem (or many particles in case of more 3d electrons) is a very difficult problem for ab-initio band theory.

Some of the models described above have been attempted for systems with partly occupied 3d states. At the CECAM workshop Frank Neese explained that normal TDDFT will capture only a fraction of the 2p excited states in case of a  $3d^5$  Mn<sup>2+</sup> system, essentially due to the fixation of the total spin to 5/2. By adding additional configurations, including the 3/2 states, the 2p XAS spectrum of a Mn<sup>2+</sup> system could be reproduced with the exception of some minor peaks in between the L<sub>3</sub> and L<sub>2</sub> edge. Peter Blaha did show preliminary BSE results for MnO and CoO. The general shapes seemed reproduced but further work is needed for a more detailed description. Note that CoO has the additional complication that the <sup>4</sup>T<sub>1</sub> ground state is split by the 3d spin-orbit splitting to 4 states separated by less than 100 meV [3, 20].

The DFT-CI model of Ikeno et al has been routinely applied to transition metal oxides with, in general, good agreement [13-15]. The multiplet effects are treated correctly but the method still has some limitations with regard to the treatment of charge transfer effects. Alternative methods to calculate the 2p XAS spectra of transition metal oxides are being developed by Takayuki Uozumi [21] and Maurits Haverkort [22]. These methods start from a LDA+U calculation and project the resulting wave function to a small cluster containing 1 to 4 metal ions. For the cluster the complete multiplet calculation is performed. This procedure has been applied to study Fe-Ti inter-element excitations in the RIXS spectrum of FeTiO<sub>3</sub> [21]. In his talk at the CECAM workshop, George Sawatzky pointed out that mixed valent systems are governed with different charge transfer energetics, which can make it necessary to treat the two metal mixed valent system coherently as one object, for example Mn<sup>3+</sup>-O-Mn<sup>4+</sup> [23].

### **Concluding remarks**

With the constant improvements of the methods as described above, in my opinion we are close to the point that ab-initio methods can explain the 2p XAS spectra of transition metal systems, both for solids and for coordination complexes. This would be a great achievement and would significantly enhance the impact of 2p XAS spectra. In the near future we will remain in a situation where we will have to make choices regarding the most suitable method which will be system and spectroscopy dependent, which makes it important to develop all of the methods further. This also includes the application of cluster calculations to larger systems and finding ways of imbedding them in, for example the cluster DMFT method.

As a final remark I quote the statement from George Sawatzky that some 2p XAS spectra are 'rather boring'. I agree with this statement in the sense that some 2p XAS spectra, in particular the spectra of covalent systems (including high-valent oxides and metals) contain few clear features. Fortunately the 2p XAS experiment is only the initial excitation of the system and one can use this excitation in a range of information-rich spectra and features. This includes resonant (inelastic) x-ray scattering and diffraction

[24-25] for which the spectroscopy involving the same atoms and actually the same excitations becomes very rich and full of detailed fine structure and long range order dependencies not visible in the XAS spectra ~~themselves-themselves~~.

This also implies that if a method does correctly simulate a 2p XAS spectrum this does not mean that the same method can also explain the resonant (inelastic) scattering and reflection spectra. For example in case where the 2p XAS spectrum yields a broad featureless spectral shape, these resonant experiments could reveal much fine details that are not resolved in 2p XAS. This will give new information that can be used for the further development of the theory, but this will be an additional and difficult task to solve for the ab-initio methods.

### Acknowledgements

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