

# New Developments in Charge Transfer Multiplet Calculations: Projection Operators, Mixed-Spin States and $\pi$ -Bonding

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**Abstract.** This paper presents a number of new additions to the charge transfer multiplet calculations as used in the calculation of L edge X-ray absorption spectra of 3d and 4d transition metal systems, both oxides and coordination compounds. The focus of the paper is on the consequences of the optimized spectral simulations for the ground state, where we make use of a recently developed projection technique. This method is also used to develop the concept of a mixed-spin ground state, i.e. a state that is a mixture of a high-spin and low-spin state due to spin-orbit coupling combined with strong covalency. The charge transfer mechanism to describe  $\pi$ -bonding uses the mixing of the metal-to-ligand charge transfer (MLCT) channel in addition to the normal CT channel and allows for the accurate simulation of  $\pi$ -bonding systems, for example cyanides.

**Keywords:** X-ray absorption,  $\pi$ -bonding, charge transfer multiplet theory

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## INTRODUCTION

The present understanding of the shapes of X-ray absorption spectra of transition metal systems is based on two distinctive models, (1) the single-particle excitation model for the metal and ligand K edges and (2) the charge transfer multiplet model for the metal L and M edges. In the X-ray absorption process an electron is excited from a core state to an empty state. In the single-particle excitation model it is, implicitly, assumed that all other electrons do not participate in the X-ray induced transition. This makes it possible to rewrite the Fermi Golden rule into a simple equation that identifies the X-ray absorption cross section with the empty density of states, modified by the transition matrix element. The most popular codes to calculate the density of states of both molecules and solids are based on Density Functional Theory.

The main approximation made in this approach is that many body effects are not important. This includes both valence band many body effects and many body effects that involve the core electron, or better the core hole in the final state. The wave function of the core hole interacts with the valence

electrons (holes), which is a standard result from the quantum description of atomic structure. These atomic interactions turned out to be essentially unscreened in the solid state and need to be treated explicitly for all core states except K edges. In case of 1s core holes, their overlap with valence electrons has energy effects in the meV range, whereas the 2p, 3s and 3p core holes in 3d metals have energy effects in the order of 10 eV, where in case of the 3s core hole this interaction is simplified to an exchange interaction. In addition to these multiplet effects, core spectra are subject to screening effects that involve localized electron states. These charge transfer effects can be treated with the charge transfer model and the combination of both effects has led to the development of the charge transfer multiplet (CTM) model. The advantage of the CTM model is that the calculations are fast and apply to all core level spectroscopies using the same ground state. In this paper, three recent additions of the CTM model will be discussed: (1) a projection method to determine the nature of the ground state that is used in the CTM model, also in order to compare it to the ground states used in DFT calculations, (2) the description of mixed spin ground states in orbital-

ordered transition metal oxides, and (3) the special role of  $\pi$ -bonding.

## GROUND STATE PROJECTION

In transition metal systems with only  $\sigma$ -bonding, including all bulk oxides, only ligand to metal charge transfer plays a role. This implies that it is sufficient to describe the initial state as  $3d^n + 3d^{n+1}\underline{L}$ . For example,  $\text{Fe}^{\text{III}}$  has a  $3d^5$  ground state and only mixing with  $3d^6\underline{L}$  turned out to be crucial for the description of the 2p XAS and 2p XPS spectral shapes, where in case of 2p XPS additional improvements are seen with the inclusion of the double ligand to metal charge transfer to  $3d^7\underline{L}^2$ .

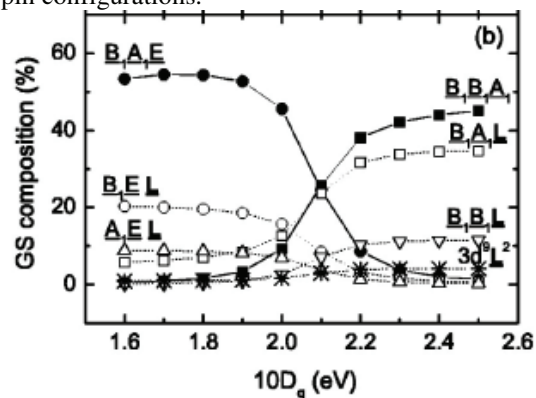
A high-spin  $3d^5$  ground state in octahedral symmetry has a  ${}^6A_1$  ground state with the electrons essentially in a  $t_{2g}^3e_g^2$  configuration, where all electrons are spin-up. There are two important  $3d^6\underline{L}$  configurations, one with  $t_{2g}$ -mixing to  $t_{2g}^4e_g^2$  and one with  $e_g$ -mixing to  $t_{2g}^3e_g^3$ . The difference is that the added 3d electron is spin-down  $t_{2g}$  respectively  $e_g$ . In octahedral symmetry there is the approximate rule that  $e_g$  mixing is twice as important as  $t_{2g}$  mixing and this rule is confirmed for the actual results for  $\text{Fe}^{\text{III}}(\text{acac})_2$ , where one finds 90% metal character (10% transfer) to  $t_{2g}$  and 75% (24% transfer) to  $e_g$  [1].

Another interesting case is a  $3d^5$  low-spin ground state that has five  $t_{2g}$  states filled (one empty) and all  $e_g$  states empty.  $T_{2g}$ -mixing leads to a  $t_{2g}^6\underline{L}$ -configuration, which has one multiplet state, whereas  $e_g$ -mixing leads to  $t_{2g}^5e_g^1\underline{L}$ , which can have a large range of multiplet states. It turns out that in case of  $\text{Fe}^{\text{III}}(\text{tacn})_2$  the contribution of  $t_{2g}$ -mixing is only a few percent, versus 37% for  $e_g$ -mixing. This means that in a good first approximation, there is only  $e_g$ -mixing in these systems. An interesting feature of low-spin  $3d^5$  systems is that in octahedral symmetry the leading edge is only visible in the  $L_3$  edge. The leading edge is due to a  $2p^5t_{2g}^6$  final state and this state has pure  $2p_{3/2}$  respectively  $2p_{1/2}$  character because the  $3d$ -manifold has no moments. The ground state is  ${}^2T_2$  and the dipole selection rule dictates that only the  $L_3$  peak is visible, as confirmed by data on  $\text{Ru}^{\text{III}}(\text{NH}_3)_6$  [2]. In contrast a diverse range of systems shows a small leading peak at the  $L_2$  edge, which can be explained from the combined action of  $3d(4d)$  spin-orbit coupling and a trigonal distortion. Systems that show this effect include  $\text{Fe}^{\text{III}}(\text{tacn})_2$ ,  $\text{Fe}^{\text{III}}(\text{CN})_6$  [3],  $\text{Ru}^{\text{III}}(\text{bpy})_2$  [4], but also oxides including the low spin  $\text{Co}^{\text{IV}}$  system  $\text{Na}_x\text{CoO}_2$  [5].

## MIXED-SPIN GROUND STATES

In general transition metal (oxide) systems are divided into high-spin and low-spin. In some cases, there is the possibility of intermediate spin, for example for  $3d^5$  systems, that can be high-spin  $S=5/2$ , intermediate spin  $S=3/2$  and low-spin  $S=1/2$ .

We discuss the  $\text{Ni}^{\text{III}}$  ground state in more detail.  $\text{Ni}^{\text{III}}$  is a  $3d^7$  system and its octahedral high-spin ground state is  ${}^4T_1$ . This ground state has a  $t_{2g}^5e_g^2$  configuration, where it is noticed that this one-electron configuration is only approximate due to the effects of the  $3d3d$  interactions. Calculations show that the ground state has a  $\sim 90\%$   $t_{2g}^5e_g^2$  configuration, with the remaining  $\sim 10\%$  other configurations. If  $3d$  spin-orbit coupling is included, the spin state deviates slightly from  $S=3/2$  due to admixture of, mainly,  $S=1/2$  low-spin configurations.



**FIGURE 1.** The contributions of the various 3-hole orbital states are given for a  $\text{Ni}^{\text{III}}$  ion in  $D_{4h}$  symmetry.  $A_1$  identifies with a  $z^2$  orbital;  $B_1$  is  $x^2-y^2$ ;  $B_2$  is  $xy$  and  $E$  is  $xz$  and  $yz$ . The ground state changes from high-spin  ${}^4E$  at low crystal field values to low-spin  ${}^2A_1$ .

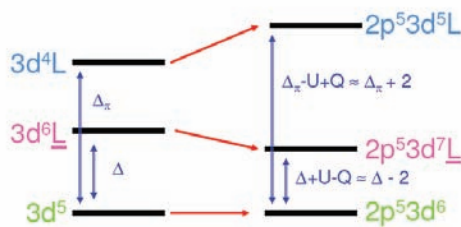
Next we introduce charge transfer with  $3d^8\underline{L}$  states, and in addition lower the symmetry to tetragonal. Because  $\text{Ni}^{\text{III}}$  is rather covalent, the high-spin ground state is only 60% pure in  $t_{2g}^5e_g^2$ , as indicated in Figure 1 with its three holes in  $x^2-y^2$ ,  $z^2$  and  $xz/yz$  orbitals. Figure 1 gives the six largest contributions to the ground state, with  $\sim 15\%$  a  $3d^8\underline{L}$  configuration with holes in  $x^2-y^2$ ,  $xz/yz$  and a ligand hole of  $z^2$  character, [6]. At large crystal fields, the ground state is  ${}^2E$  low-spin with a  $\sim 50\%$  contribution from two coupled holes in  $x^2-y^2$  and a hole in  $z^2$ . The experimental spectrum of  $\text{EuNiO}_3$  at room temperature can best be simulated with  $10Dq_{\text{eff}}=2.0$  eV, which indicates a ground state that is a mixture of  $\sim 45\%$  high-spin  $A_1B_1E$ ,  $\sim 15\%$  low-spin  $B_1B_1A_1$  and  $\sim 40\%$  charge transfer states. This state is neither high-spin nor low-spin and can best be named a mixed spin ground state.

Mixed spin ground states need a number of ingredients (1) the possibility of high-spin and low-

spin states, (2) a non-zero effect of the 3d spin-orbit coupling, (3) large charge transfer effects, and (4) most importantly, a crystal field that makes HS and LS states near degenerate. Systems where these conditions could be fulfilled include the oxides containing Ni<sup>III</sup>, Co<sup>III</sup> and Mn<sup>III</sup> ions.

## $\pi$ -BONDING

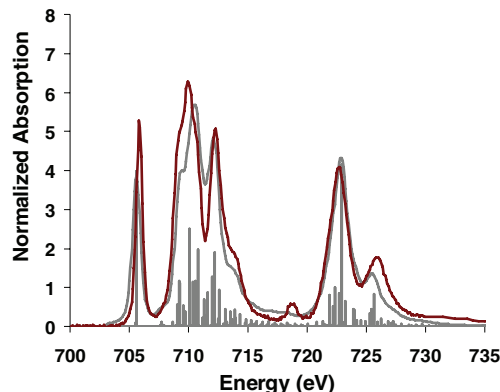
In systems that contain significant  $\pi$ -bonding an additional charge transfer channel becomes dominant. In addition to ligand metal charge transfer (CT) that mixes  $3d^n + 3d^{n+1}\underline{L}$ , metal ligand charge transfer (MLCT) is important. This can be described as  $3d^n + 3d^{n-1}\underline{L}$ . Figure 2 shows the mixing of  $3d^5+3d^6\underline{L}+ 3d^4\underline{L}$ . The creation of a 2p core hole transfers the extra electron to the 3d-band, which is essentially a charge conserving optical transition. This implies that the ordering of states remains similar to the ground state, where it is noticed that each  $3d^n$  configuration consists of the full crystal field multiplet manifold. In addition, the final state  $2p^53d^n$  configurations contain the effects of the 2p spin-orbit coupling and the  $2p3d$  multiplet effects.



**FIGURE 2.** The mixing of a  $3d^5$  ground state with  $3d^6\underline{L}$  at energy  $\Delta$  and with  $3d^4\underline{L}$  at energy  $\Delta_x$ . The final state energies shift down for CT and up for MLCT by a small energy, given as the difference between the core hole potential  $Q$  and the Hubbard  $U$ .

This methodology to describe  $\pi$ -bonding has been used to describe the L edge spectra of  $\text{Fe}^{\text{III}}(\text{CN})_6$  and  $\text{Fe}^{\text{II}}(\text{CN})_6$  [3]. The tacn-complex only allows  $\sigma$ -bonding and the cyanide complex both  $\sigma$ - and  $\pi$ -bonding. The  $\text{Fe}^{\text{III}}(\text{tacn})_2$  spectrum shows essentially the structure of the  $2p^53d^6$  final state multiplet, where the fine details can be simulated after inclusion of charge transfer effects, using the different orbital covalency (DOC) effect with much larger  $e_g$  mixing [1]. Figure 3 shows the  $\text{Fe}^{\text{III}}(\text{CN})_6$  spectrum that shows a similar structure as the  $\text{Fe}^{\text{III}}(\text{tacn})_2$  spectrum, with one major difference, which is the extra large peak at 712 eV. CTM calculations using the configurations  $3d^5+3d^6\underline{L}+ 3d^4\underline{L}$  do exactly reproduce the  $\text{Fe}^{\text{III}}(\text{CN})_6$  spectrum as can be seen in Figure 3. The fact that the peak induced by mixing with  $3d^4\underline{L}$  is this large, implies that the (lowest energy)  $3d^5$  and the  $3d^4\underline{L}$

configurations are near degenerate, i.e.  $\Delta_x \sim 0$  eV. In the final state the  $2p^53d^6$  and  $2p^53d^5\underline{L}$  configurations form bonding and anti-bonding states that are visible at  $\sim 710$  eV and at  $\sim 712$  eV, where in Figure 2 we have seen that this energy difference increases by  $\sim 2.0$  eV in the final state. In addition to the energy difference, also the hopping is modified in the final state, and all evidence to date suggests that all hopping terms are a bit reduced in the final state [7], which will help in the creation of a large satellite for MLCT, where it always makes normal CT satellites smaller [8].



**FIGURE 3.** The experimental L edge spectra of  $\text{Fe}^{\text{III}}(\text{CN})_6$  (thick line) compared with CTM calculations (sticks and broadened to thin line).

These results show that the improvements in CTM simulations allow for a detailed simulation of systems with both  $\sigma$ - and  $\pi$ -bonding. With regard to the mixed-spin ground states, it remains to be seen how often they occur in actual systems. The analysis shows they could be present in covalent Mn, Co and Ni (oxide) systems and the ordering properties of many of these oxides suggest a complex local spin- and orbital moment situation.

## REFERENCES

1. E.C. Wasinger, F.M.F. de Groot, B. Hedman, K.O. Hodgson and E.I. Solomon E. I. *J. Am. Chem. Soc.* **125**, 12894 (2003).
2. T.K. Sham, *J. Am. Chem. Soc.* **105**, 2269-2273 (1983).
3. R.K. Hocking, E.C. Wasinger, F.M.F. de Groot, K.O. Hodgson, B. Hedman, and E.I. Solomon E. I. *J. Am. Chem. Soc.* **128**, 10442 (2006).
4. W. Gawelda, M. Johnson, F. M. F. de Groot, R. Abela, C. Bressler, and M. Chergui, *J. Am. Chem. Soc.* **128**, 5001 (2006).
5. T. Kroll *et al. Cond-Mat.* 0606518 (2006)
6. C. Piamonteze, F.M.F. de Groot, H.C.N. Tolentino, A.Y. Ramos, N.E. Massa, J.A. Alonso, and M.J. Martínez-Lope, *Phys. Rev. B.* **71**, 020406 (2005)
7. S.M. Butorin, *J. Elec. Spec.* **110**, 213 (2000).
8. F.M.F. de Groot, *Coord. Chem. Rev.* **249**, 31 (2005).