Multiplet coupling and band structure in L$_{2,3}$-edge XAS through multi-channel multiple scattering theory

Peter Krüger
ICB, UMR 5209 Université de Bourgogne - CNRS, BP 47870, F-21078 Dijon, France
E-mail: pkruger@u-bourgogne.fr

Abstract. Using the recently developed multi-channel multiple scattering (MCMS) method we have calculated the x-ray absorption spectra (XAS) at the L$_{2,3}$-edge of transition metal compounds. The MCMS method is an ab initio scheme which combines an accurate description of the band structure of the material with a correlated many-electron wave function on the absorber atom. Thereby configuration interaction in the XAS final state, in particular multiplet effects, can be taken into account. In the present implementation, we use an electron-hole wave function and treat the interaction with all other electrons on a mean-field level. The calculated spectra agree well with experiment for the early transition metals (Ti,V), where the L2-L3 configuration mixing is particularly strong. We present a detailed study of titanium oxides with nominal Ti$^{4+}$ ground state, namely rutile and anatase TiO$_2$ and perovskite SrTiO$_3$. The XAS spectra display a rich fine structure with marked differences between the three systems despite the almost identical octahedral coordination of the Ti atom. The calculated spectra are in excellent agreement with the experimental data of all three compounds. As an example for a late 3d-metal we have studied the L$_{2,3}$-XAS and the x-ray magnetic circular dichroism (XMCD) of iron. In agreement with recent time-dependent density functional studies, we find that also for the late 3d elements, the particle-hole description can yield satisfactory L3/L2 branching ratios and lineshapes of the isotropic XAS spectrum if the screened monopole term of particle-hole Coulomb interaction is properly taken account for. The XMCD spectra of the same calculation are, however, less good than both atomic multiplet and one-electron spectra indicating clear limitations for the application of particle-hole theories to late 3d elements.

1. Introduction
The rich physics of transition metal compounds is strongly related to the particular nature of their 3d-valence states. On the one hand the 3d-states are partly localised and thus retain some electron correlation effects of the free atom, e.g. Hund’s rule coupling responsible for the formation of magnetic moments. On the other hand the 3d-states are considerably hybridised (i.e. delocalised) and thus strongly participate in solid state phenomena such as bonding, electronic transport and magnetic ordering. X-ray absorption spectra (XAS) recorded at the transition metal L$_{2,3}$ edges probe the (unoccupied) 3d-states in a most direct way due to the chemical and orbital selectivity of the XAS process. L$_{2,3}$-edge XAS is therefore a major tool for the analysis of the structural, electronic and magnetic properties of transition metal compounds. For the theoretical description of XAS, two opposite approaches have been developed, one starting from a localised and the other one from a delocalised description of the 3d-states.
The first one is based on atomic multiplet theory. It is a configuration interaction method and thus accounts well for (local) electron correlation effects. Solid state effects are treated by adding to the atomic hamiltonian either an effective crystal field or the hybridisation with a few near-neighbour ligand orbitals, in which case one arrives at the charge transfer cluster model. The atomic multiplet and charge transfer cluster model approaches have been extremely successful in describing and understanding the XAS and related spectroscopies of transition metal compounds [1]. However, all extra-atomic terms (crystal field and hybridisation) are usually introduced through empirical parameters, which limits considerably the predictive power of this scheme. Some years ago Ogasawara et al. [2] have presented cluster calculations for L$_2$/L$_3$-edge XAS of transition metal oxides using a full \textit{ab initio} quantum chemistry method. They could achieve good agreement with experiment without introducing any empirical parameters. While this approach marks a significant progress in the field, it is clear that quantum chemistry methods are limited to very small systems. Consequently, there is little hope that long range band structure effects and metallic systems can be handled in this framework.

The second approach starts from the electronic structure of the solid as described by density functional theory. In the simplest scheme, the independent particle approximation (IPA), the many-electron XAS matrix element is replaced by its one-electron counterpart and the XAS spectrum becomes essentially proportional to a partial density of unoccupied states on the absorber atom ($d$-states in the case of the L$_2$ and L$_3$-edges). The IPA is quite successful for K-edge XAS, but it performs very poorly at the L$_{2,3}$-edges of many transition metal systems. Especially for the early 3$d$-elements, the IPA fails completely and does not even reproduce the observed L$_3$/L$_2$ branching (i.e. intensity) ratio. While the IPA yields the statistical value of 2 the observed value is about 1 for the early transition elements Ca–V. This highly non-statistical value is due to the 2$p$-3$d$ Coulomb and exchange coupling in the XAS final state which results in a strong L$_2$-L$_3$ channel mixing. It is a case of strong configuration interaction, which explains why the IPA completely fails. At least a particle-hole theory is needed to account for this configuration interaction, or “multiplet” effect. Zaanen et al. [3] were the first to present such a particle-hole theory for the solid state and achieved good results for the early transition metals Ca–V. Their theory was, however, not fully \textit{ab initio} as they used rescaled atomic data for the particle-hole coupling. Later, Schwitalla and Ebert [4] treated the problem in time-dependent density functional theory (TD-DFT) using the random-phase approximation (RPA) for the particle-hole interaction. The L$_3$/L$_2$ branching ratio was found in good agreement with experiment for the beginning of the 3$d$ series but the calculated values were much too small at the end of the series. Ankudinov et al. [5] have extended the TD-DFT approach of Ref. [4] by adding a diagonal exchange-correlation (XC) part to the RPA kernel. A diagonal XC kernel corresponds essentially to the monopole term of the particle-hole Coulomb interaction (and to the F$_0$(2p,3d) Slater integral in Zaanen’s method [3]). This term shifts spectral weight to lower energies and may thus reduce or even cancel the spectral weight transfer from L$_3$ to L$_2$ coming from the 2$p$-3$d$ multiplet coupling (which corresponds to the RPA part of the kernel). With their improved kernel, Ankudinov et al. could obtain branching ratios in good agreement with experiment for the whole 3$d$ series. Some years ago, we have developed a multichannel multiple scattering (MCMS) theory for the L$_{2,3}$-edge XAS using a particle-hole wave function [6]. We have applied the theory to several Ca compounds and obtained lineshapes in good agreement with experiment. More recently E. Shirley has extended the Bethe-Salpeter approach for XAS to the L$_{2,3}$-edge including the particle-hole multiplet coupling [7]. He applied the method to nominal $d^0$ compounds and obtained good results for CaF$_2$ and SrTiO$_3$ but somewhat poorer results for TiO$_2$. In the present paper we employ use the MCMS method [6] with a few extensions which are described in the next section. In the result section we report XAS calculations on titanium oxides, as well as the bulk transition metals titanium, vanadium and iron. For iron we also discuss the x-ray magnetic circular dichroism (XMCD) spectra.
2. Theory

Multichannel multiple scattering theory was developed by Natoli et al. [8] as a generalisation of the multiple scattering method to correlated N-electron wave functions. Krüger and Natoli [6] provided the first implementation of MCMS theory for L\textsubscript{2,3}-edge absorption spectra using a particle-hole wave function. The same method is applied in the present work with a few new features, such as the introduction of the Fermi level and the use of LDA+U potentials. Only a sketch of the general formalism is given here with emphasis on the new features. A complete description of the method can be found in Ref. [6].

The absorption cross section for x-rays with energy $\omega$ and polarisation $q = 0, \pm 1$ is given by

$$
\sigma(\omega, q) \propto \omega \text{Im} \left\{ \sum_{\Gamma \Gamma'} M^\alpha_\Gamma(q) \tau^{00}_{\Gamma \Gamma'}(E_g + \omega) M^{\alpha'}_{\Gamma'}(q) \right\}.
$$

(1)

Here $M^\alpha_\Gamma(q) = \langle \Psi^\alpha_\Gamma | D_q | \Psi_g \rangle$ are the transition matrix elements. $D_q$ is the transition operator for which we use the electric dipole approximation in length form. $\Psi_g$ is the ground state wave function with energy $E_g$ and $\Psi^{\alpha}_\Gamma$ denotes the final state wave function in channel $\Gamma$ inside the absorber atomic sphere with proper matching conditions at the sphere boundary [6]. For the ground state we take the filled 2p shell. For the final state we take a $(2p^5, \epsilon^1)$ configuration, where $\epsilon$ denotes a scattering state with energy $\epsilon$. We thus use a particle-hole picture and treat all valence electrons of the ground state as spectators. Further, $\tau^{ii'}_{\Gamma \Gamma'}$ denotes the multichannel scattering path operator, which is the central quantity of MCMS theory. Here, $i, j$ are site indices with $i = 0$ being the absorber site. Finally $\Gamma = \alpha L s$ is the combined channel index, with $\alpha$ collecting the 2p-hole quantum numbers and $L = (l, m)$ the orbital and $s$ the spin quantum numbers of the photoexcited electron.

We assume that correlation effects are limited to the absorber site. Then the elements of $\tau$ for this site can be calculated as [6]

$$
\tau^{00}_{\Gamma \Gamma'} = \left[ T^{-1}_{\Gamma \Gamma'} - \delta_{aa'} \rho_{LL'}(k_s, s) \delta_{ss'} \right]^{-1}.
$$

(2)

Here $T^{-1}_{\Gamma \Gamma'}$ is the inverse of the multichannel scattering matrix of the absorber and $\rho$ is the reflectivity of the “environment”, i.e. the cluster without absorber atom. In this work we shall apply the formalism also to spin-polarised ground states and therefore the reflectivity has an explicit spin-dependence. $[\ldots]^{-1}$ denotes the matrix inverse. In Ref. [6] we did not need a Fermi cut-off since we focussed on Ca compounds, where the 3d-band is empty in the ground state. Here we shall apply the method to systems with strong hybridisation of the 3d-states (TiO\textsubscript{2}) and to transition metals (Ti, V, Fe) where the Fermi level is obviously needed to ensure the Pauli principle.

In the independent particle picture, the absorption spectrum is proportional to $\tau^{(1)}(\epsilon)(1 - f_\mu(\epsilon))$. Here $\tau^{(1)}$ is the single particle scattering path operator on the absorber site, which is given by $(t^{-1} - \rho)^{-1}$, where $t$ is the single particle t-matrix of the absorber. Further, $\epsilon$ is the energy of the electron in the final state, $\mu = E_F$ the Fermi energy and $f_\mu(x) = 1/(1 + \exp((x - \mu)/(k_BT))$ the Fermi function. In order to obtain the correct independent particle limit in the case of vanishing correlation, we extend Eq. (2) as follows

$$
\tau^{00}_{\Gamma \Gamma'} = \left[ T^{-1}_{\Gamma \Gamma'} - \delta_{aa'} t^{-1} + \delta_{aa'} (t^{-1} - \rho)/(1 - f_\mu) \right]^{-1}
$$

(3)

where the term $(t^{-1} - \rho)/(1 - f_\mu)$ is evaluated for $\epsilon = k^2_s$ and we have suppressed the quantum numbers $Ls$ of the excited electron. For vanishing particle-hole interaction, we have $T^{-1} = \delta_{aa'} t^{-1}$ and so the independent particle result is recovered. In a many-body Green’s function language, the multichannel scattering path operator corresponds to matrix elements of
the particle-hole Green’s function. Since the free solution is \( \delta_{\alpha \alpha'} (1 - f_\mu) \times [t^{-1} - \rho]^{-1} \), the term \( \delta_{\alpha \alpha'} t^{-1} - T^{-1} \) can be identified with the interaction kernel.

The local density approximation (LDA) is known to underestimate the band gap in insulators. Therefore we have used a (simplified) LDA+U scheme for the Ti oxides. The self-consistent LDA-potentials as calculated with the LMTO code [9] yield band gaps of 1.7, 1.6 and 1.4 eV in TiO\(_2\) rutile, anatase and SrTiO\(_3\), respectively, while the experimental values are 3.05, 3.2 and 3.2 eV. In order to fix this shortcoming of the LDA, we have added a constant shift \( \Delta E_d \) to the potential when the Ti-d partial waves are calculated. This is essentially equivalent to the most simple LDA+U scheme where a term of the form \( U \langle n_d \rangle n_d \) is added to the hamiltonian.

The only difference is that our correction is not self-consistent. We have used the same value \( \Delta E_d = 2 \) eV for all Ti oxides (TiO\(_2\) and SrTiO\(_3\)), which brings the band gap very close to the experimental values.

3. Results and discussion

Titanium oxides.

Before discussing the Ti-L\(_{2,3}\)-edge absorption spectra of the titanium oxides, we have a look at the density of states (DOS). The relevant partial DOS for the Ti-L\(_{2,3}\)-XAS is Ti-d, since the dipole operator selects Ti-d and Ti-s waves as final states, and the latter have negligible weight. In Fig. 1 a we show the Ti-d partial DOS of SrTiO\(_3\) as calculated through the k-space band structure code LMTO in the LDA. The band gap is indicated by an arrow. Its value (1.4 eV) is much smaller than in experiment (3.2 eV), which is a well-known shortcoming of the LDA.

Figure 1 b shows the Ti-d DOS as calculated with our multiple scattering program for a cluster of 293 atoms and the self-consistent LMTO potentials. This “MS-LDA” DOS agrees well with the LMTO DOS, which shows that the Ti-3d band structure can be well reproduced with the real-space MS method for a cluster size of about 300 atoms. Figure 1 c shows the same calculation as Fig. 1 b but with our LDA+U correction. The shape of the Ti-d DOS is hardly changed but the value of the band gap is increased to 3.0 eV and thereby agrees well with experiment (3.2 eV). Also for rutile and anatase TiO\(_2\), we have carried out such comparisons between the Ti-d DOS calculated in LMTO, MS-LDA, and MS-LDA+U. The conclusions are the same as for SrTiO\(_3\): a multiple scattering calculation with a cluster of about 300 atoms reproduces well the LMTO DOS and our LDA+U scheme with the same parameter value \( \Delta E_d = 2 \) eV corrects well the underestimated LDA band gap in all three compounds.

For all XAS calculations of the Ti oxides, we have used the LDA+U corrected LMTO potentials. Figure 2 shows the calculated spectra along with the experimental data taken from Ref. [10] for SrTiO\(_3\) and from Ref. [11] for TiO\(_2\). The experimental spectra have been shifted to match the theoretical energy scale, but the theoretical curves have been neither energy-shifted nor normalised. So the changes in peak positions and intensities between the different theoretical spectra are meaningful. In order to simulate core-hole lifetime broadening we have convoluted the spectra using a Lorentzian with an energy dependent HWHM of the form \( \Gamma(\omega) = \Gamma_0 + a \times (\omega - \omega_0) \), where \( \omega_0 \) is the \( L_3 \) threshold energy. We have taken the values \( \Gamma_0 = 0.1 \) eV and \( a = 0.05 \) for all spectra in Fig. 2. This is a simple way to take into account the fact that the 2p\(_{3/2}\)-hole (L2-edge) has a much shorter lifetime than the 2p\(_{1/2}\)-hole (L3-edge) due to the \( L_2 \rightarrow L_3 \) Coster-Kronig decay.

The uppermost curves in each panel (IPA-GS) were obtained by completely neglecting the particle-hole interaction, that is, we have used the independent particle approximation (IPA) together with the ground state (GS) potential. The unbroadened IPA-GS spectra (not shown) are simply given by the sum of the Ti-d DOS at the L3 and L2-edge in the statistical branching ratio (2:1). The IPA-GS calculations do not agree at all with the data, which shows that in these systems, the core-hole effect can by no means be neglected. The spectra denoted IPA-CH are obtained in the IPA but with a partially screened core-hole (CH) potential. The latter is a
Figure 1. Ti-d partial density of states (DOS) of SrTiO$_3$ calculated using the LMTO code (a) and the multiple scattering (MS) method for a 297 atom cluster (b,c). The band gaps are indicated by arrows.

A linear mixture between a fully screened and a bare 2p-core-hole potential. The relative weight of the unscreened part was set to 10%. The fully screened core-hole potential corresponds to the final state rule and was obtained through a constrained self-consistent LDA calculation with a spherical symmetric 2p-hole on the Ti absorber atom in a supercell of four formula units. This is exactly the same screening model with the same mixing parameter value that we have used for Ca compounds [6]. It is seen that XAS line-shape strongly changes when the core-hole potential is added. The spectral features become much sharper and, in this respect, the agreement with experiment improves. Some of the peaks positions can now be related to the experimental ones. The overall agreement is, however, still very bad. Many features are missing and the peak intensities are completely wrong. These results indicate that it is impossible to reproduce the spectra in the IPA whatever final state potential is used. The IPA fails because of the 2p-3d Coulomb and exchange interaction which causes strong final state configuration mixing between 2p$_{3/2}$ and 2p$_{1/2}$ core hole states, i.e. strong L3-L2 channel mixing. The spectra labelled “MC” in Fig. 2 are calculated using the MCMS method with the 2p-3d Coulomb and exchange interaction included and the partially screened single particle potential (same potential as IPA-
Figure 2. X-ray absorption spectra of Ti oxides calculated within the independent particle approximation (IPA) with ground state (GS) or core-hole (CH) potential, as well as with the multichannel (MC) scheme which includes the particle-hole Coulomb and exchange coupling. The experimental spectra (Exp.) are taken from Refs. [10] (SrTiO$_3$) and [11] (TiO$_2$).

CH). The “MC” spectra are in excellent agreement with experiment for all three compounds. In TiO$_2$ rutile and anatase, all the peaks A-G agree well in position, intensity and width. The most prominent difference between the spectra of the three Ti oxides is the fine structure of the (nominal) L$_3$-E$_g$ band (peaks labelled D,E in TiO$_2$). While there is a single peak in SrTiO$_3$, the peak splits asymmetrically in TiO$_2$ with the shoulder on opposite sides for rutile and anatase. In the crystal field multiplet model these differences are attributed to the different point symmetry at the Ti site, related to the distortion of TiO$_6$ octahedra [12]. This interpretation was, however, questioned by Crocombette and Jollet [13] who showed that the non-cubic ligand field due to the distortion of the oxygen octahedra is much too small to produce an observable splitting of the L$_3$-E$_g$ peak. As we shall show in detail in a forthcoming paper [14], the present results obtained in MCMS theory fully confirm the analysis by Crocombette and Jollet. Indeed, the L$_3$-E$_g$ peak
is not split when we carry out the TiO$_2$ calculations using TiO$_6$ clusters with the exact atomic positions. Only for clusters bigger than 30 atoms an extra peak appears between the L$_2$-T$_2$g and the L$_3$-E$_g$, and it requires cluster sizes over 60 atoms to obtain a D-E peak splitting in agreement with experiment. This analysis clearly shows that the L$_3$-E$_g$ peak splitting is not a local effect. Therefore it can neither be explained with atomic crystal field nor TiO$_6$ charge transfer models. Instead it is a non-local effect that requires a quite precise description of the Ti-3d band structure which is possible only using k-space band structure or large cluster calculations.

**XAS of the early transition metals Ti and V.**

In Fig. 3 we show the L$_{2,3}$-edge spectra of bulk titanium and vanadium. The experimental data (“Exp.”) was taken from Ref. [3]. The upper four curves in each panel are the calculated spectra obtained with different approximations. The calculated spectra have been Lorentzian broadened (Exp.) was taken from Ref. [3]. The upper four curves in each panel are the calculated spectra

The experimental L$_3$/L$_2$ branching ratio is about 1 for Ti and slightly larger for V. In the IPA, the branching ratio has the statistical value of 2, as seen in the IPA-GS spectra. The inclusion of particle-hole coupling provided by the multichannel approach (spectra MC) leads to a spectra weight transfer from L$_3$ to L$_2$, and thus brings the branching ratio much closer to the experimental value. Comparing the different final state potentials within the set of MC spectra, it can be seen that the GS and CH0 potentials yield very similar spectra (especially in V) which are in good agreement with experiment. The potential with 10% unscreened core-hole (MC-CH) however, compares badly with the data. So we observe that the difference between the ground state and the fully screened core-hole potential is very small, and that introduction of some unscreened core-hole worsens the agreement with experiment. Both findings are in contrast to the early 3d oxides (TiO$_2$, CaO [6]).

The experimental L$_3$/L$_2$ branching ratio is about 1 for Ti and slightly larger for V. In the IPA, the branching ratio has the statistical value of 2, as seen in the IPA-GS spectra. The inclusion of particle-hole coupling provided by the multichannel approach (spectra MC) leads to a spectra weight transfer from L$_3$ to L$_2$, and thus brings the branching ratio much closer to the experimental value. Comparing the different final state potentials within the set of MC spectra, it can be seen that the GS and CH0 potentials yield very similar spectra (especially in V) which are in good agreement with experiment. The potential with 10% unscreened core-hole (MC-CH) however, compares badly with the data. So we observe that the difference between the ground state and the fully screened core-hole potential is very small, and that introduction of some unscreened core-hole worsens the agreement with experiment. Both findings are in contrast to the early 3d oxides (TiO$_2$, CaO [6]).

The experimental L$_3$/L$_2$ branching ratio is about 1 for Ti and slightly larger for V. In the IPA, the branching ratio has the statistical value of 2, as seen in the IPA-GS spectra. The inclusion of particle-hole coupling provided by the multichannel approach (spectra MC) leads to a spectra weight transfer from L$_3$ to L$_2$, and thus brings the branching ratio much closer to the experimental value. Comparing the different final state potentials within the set of MC spectra, it can be seen that the GS and CH0 potentials yield very similar spectra (especially in V) which are in good agreement with experiment. The potential with 10% unscreened core-hole (MC-CH) however, compares badly with the data. So we observe that the difference between the ground state and the fully screened core-hole potential is very small, and that introduction of some unscreened core-hole worsens the agreement with experiment. Both findings are in contrast to the early 3d oxides (TiO$_2$, CaO [6]).

The experimental L$_3$/L$_2$ branching ratio is about 1 for Ti and slightly larger for V. In the IPA, the branching ratio has the statistical value of 2, as seen in the IPA-GS spectra. The inclusion of particle-hole coupling provided by the multichannel approach (spectra MC) leads to a spectra weight transfer from L$_3$ to L$_2$, and thus brings the branching ratio much closer to the experimental value. Comparing the different final state potentials within the set of MC spectra, it can be seen that the GS and CH0 potentials yield very similar spectra (especially in V) which are in good agreement with experiment. The potential with 10% unscreened core-hole (MC-CH) however, compares badly with the data. So we observe that the difference between the ground state and the fully screened core-hole potential is very small, and that introduction of some unscreened core-hole worsens the agreement with experiment. Both findings are in contrast to the early 3d oxides (TiO$_2$, CaO [6]).
Figure 3. X-ray absorption spectra of Ti and V bulk metals calculated within the independent particle approximation (IPA) or the multichannel approach (MC). The single particle final state potential was either the ground state (GS), the partially screened (CH) or the fully screened (CH0) core-hole potential. Exp. are experimental spectra.

state potential, either alone, or with a small fraction of unscreened core-hole added to it. We did not employ the fully screened core-hole potential because the latter generally yields worse results than the ground state potential for L_{2,3}-XAS and XMCD of late transition metals. One reason for this is that the screening charge fills mainly minority spin states and thus leads to a reduced final state magnetic moment. XMCD of late transition metal measures, however, the ground state moments, as the success of the XMCD sum rules [17] shows.

For comparison, we have also calculated the Fe XAS and XMCD spectra in atomic multiplet theory for a (3d^7) ground state and (2p^53d^8) final state configuration. The spin-orbit and Slater integrals were calculated using Cowan’s code [18]. The Slater integrals were rescaled to 80% and the weak 3d spin-orbit coupling was neglected. The ground state multiplet is the Hund’s rule 4F state. We have added a small exchange field (0.01 eV) in order to lift the M_S degeneracy and have averaged the spectra over M_L-degenerate ground states. The line spectra were Lorentzian broadened with $\Gamma_0 = 0.7$ eV and $a = 0.02$. They are shown as “Atom” in Fig. 4.

First we discuss the XAS spectra. The IPA spectrum is in good agreement with experiment. Both the branching ratio and the asymmetric line shape are well reproduced. When the particle-hole coupling is included (MC0) with the same (ground state) potential, the L3/L2 branching
Figure 4. XAS and XMCD of bulk Fe calculated in the independent particle approximation (IPA), in the multichannel scheme (MC0, MC1) and with atomic multiplet theory (Atom), along with the experimental spectra taken from Ref [15] (Exp.) and [16] (Exp2). For IPA and MC0 the ground state potential was used while in MC1, 6% of unscreened core-hole was added to it. Here all spectra have been normalised to equal L3 XAS peak height.

...
neglect the monopole term (MC0) we obtain identical results to the RPA in Ref. [4]. When we take into account the monopole term by adding a fraction $\alpha$ of unscreened core-hole potential, then spectral weight is transferred (back) from L2 to L3, as we have already noticed for Ti, V (Fig. 3, curves MC-CH). For Fe, we have achieved best agreement with experiment by using $\alpha = 0.06$, shown as curve MC1 in Fig. 4. The MC1 spectrum is almost identical to the IPA, which confirms the observation of Ankudinov [5] that the monopole term can completely cancel the branching ratio reduction due to the particle-hole multiplet coupling. From the foregoing, one may get the impression that a properly screened particle-hole interaction reduces to the IPA for the late 3d-elements. This is not true, however, since clear differences remain between IPA and MC1 for the polarisation dependent spectra as can be seen from our XMCD results.

The experimental XMCD displays a negative peak at L3 and positive peak at L2 of somewhat lower intensity. These main features are quite well reproduced in the IPA and in the atomic multiplet calculation. The particle-hole spectrum MC0 compares very badly with experiment. The addition of small fraction of the bare core-hole potential in MC1 improves considerably the XMCD spectrum, but the overall agreement with experiment is still much less good than for IPA and multiplet calculations. One interesting feature in the experimental spectrum is the weak positive peak at the high energy side of L3 which we have marked by an arrow in Fig. 4. This feature is clearly seen in the Exp2 data [16] but smeared out in the Exp. data [15], probably due to limited resolution. In analogy to XMCD at the Ni-L3 edge in FeNi$_2$O$_4$ [19] this feature can be attributed to a spin-flip final state, where the 2p$_{3/2}$ core-hole spin is coupled antiparallel to the spin of the 3d valence holes. In the IPA spectrum the spin-flip peak is missing, but it is present in the multichannel (MC0, MC1) spectra, which reflects the electron-hole multiplet coupling in this scheme. The position and amplitude of the this peak is however, in bad agreement with experiment. Although far from perfect, the agreement with experiment is much better in the atomic multiplet calculation. The fact that the particle-hole multichannel theory performs so poorly on XMCD indicates that the exchange between the excited electron and the “spectator” d-electrons is not correctly taken account for in particle-hole theories.

4. Conclusions
We have presented calculations of L$_{2,3}$-edge XAS for several transition metal systems using the multichannel multiple scattering method with a particle-hole wave function. We find excellent agreement with experiment for SrTiO$_3$, as well as rutile and anatase TiO$_2$ with the same core-hole charge screening model which was found appropriate for Ca compounds [6]. The differences in lineshape between the three Ti oxides are due to differences in the long range band structure, rather than to short range ligand field or charge transfer effects. The XAS of the early transition metals Ti and V are also well reproduced in the particle-hole calculations, but the charge screening mechanism is distinctly different from the oxides. The core-hole is efficiently screened by the itinerant d-electrons and the ground state potential can be used for the XAS calculation. For the late transition metal Fe, the particle-hole approach performs less well than the IPA. The particle-hole multiplet coupling reduces the L3/L2 branching ratio from the IPA value of 2, in contradiction to experiment. Although this problem can be “repaired” in the isotropic XAS by adding a properly screened monopole part of the particle-hole Coulomb interaction, the XMCD lineshapes are in less good agreement with experiment than both IPA and atomic multiplet calculations.

The author thanks Calogero R. Natoli and Frank M. F. de Groot for stimulating discussions. Financial support from the European Union through the FP6 project Light Source Theory Network is gratefully acknowledged.
References

[1] De Groot F and Kotani A 2008, *Core Level Spectroscopy of Solids*, CRC Taylor & Francis, London.
[2] Ogasawara K, Iwata T, Koyama Y, Ishii T, Tanaka I and Adachi H, 2001 *Phys. Rev. B* **64** 115413.
[3] Zaanen J, Sawatzky G A, Fink J, Speier W and Fuggle J C 1985, *Phys. Rev. B* **32** 4905.
[4] Schwitalla J and Ebert H 1998, *Phys. Rev. Lett.* **80** 4586.
[5] Ankudinov A L, Nesvizhskii A I and Rehr J J 2003, *Phys. Rev. B* **67** 115120.
[6] Krieger P and Natoli C R 2004, *Phys. Rev. B* **70** 245120.
[7] Shirley E L 2005, *J. Electron Spectrosc. Relat. Phenom.* **144** 1187.
[8] Natoli C R, Benfatto M, Bruder C, Ruiz Lopez M F and Foulis D L 1990, *Phys. Rev. B* **42**, 1944.
[9] Andersen O K and Jepsen O 1984, *Phys. Rev. Lett.* **53** 2571.
[10] Woicik J C, Shirley E L, Hellberg C S, Andersen K E, Sambasivan S, Fischer D A, Chapman B D, Stern E A, Ryan P, Ederer D L and Li H 2007, *Phys. Rev. B* **75** 140103.
[11] Kucheyev S O, van Buuren T, Baumann T F, Satcher J H Jr, Willey T M, Meulenberg R W, Felter T E, Poco J F, Gammon S A and Terminello L J 2004, *Phys. Rev. B* **69** 245102.
[12] De Groot F M F, Fuggle J C, Thole B T and Sawatzky G A 1990, *Phys. Rev. B* **41** 928.
[13] Crocombette J P and Jollet F 1994, *J. Phys. Condens. Matter* **6** 10811.
[14] Krüger P, to be submitted.
[15] Chen C T, Idzerda Y U, Lin H-J, Smith N V, Meigs G, Chaban E, Ho G H, Pellegrin E, and Sette F 1995, *Phys. Rev. Lett.* **75** 152.
[16] Le Cann X, Boeglin C, Carriere B and Hricovini K 1996, *Phys. Rev. B* **54** 373.
[17] Thole B T, Carra P, Sette F and van der Laan G 1992, *Phys. Rev. Lett.* **68** 1943.
[18] Carra P, Thole B T, Altarelli M and Wang X 1993, *Phys. Rev. Lett.* **70** 694.
[19] Cowan R D 1981, *The Theory of Atomic Structure and Spectra*, University of California Press, Berkeley.
[20] van der Laan G, Henderson C M, Pattrick R A, Dhesi S S, Schofield P F, Dudzik E and Vaughan D J 1999, *Phys. Rev. B* **59** 4314.