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## Sum rule practice

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We discuss the theoretical limitations and experimental restrictions of the sum rules for x-ray magnetic dichroism, which relate the integrated signals of the spin-orbit split core levels to ground state properties, such as spin and orbital magnetic moments. A special choice of geometry, such as a transverse magnetic field, makes it possible to separate ground state moments which cannot be distinguished in a collinear geometry.

**Keywords:** magnetic circular dichroism; orbital magnetization; spin polarization; x-ray absorption spectroscopy.

### 1. Introduction

Thole *et al.* (1992) and Carra *et al.* (1993a) derived sum rules which relate the integrated signals over the spin-orbit split core edges of the x-ray magnetic circular dichroism (XMCD) to ground state orbital and spin magnetic moments. These rules were extended by Carra *et al.* (1993b) to include electric quadrupole transitions and magnetic linear dichroism. A generalization to x-ray magnetic scattering was given by Luo *et al.* (1993) and to photoemission by Thole and van der Laan (1993). Ankudinov and Rehr (1995) rederived the sum rules using the independent electron approximation. Ebert (1996) used first-principles spin-polarized relativistic multiple-scattering calculations for metallic magnets. Van der Laan (1998a) derived sum rules for *jj*-coupled operators by including cross terms between the  $j = l \pm 1/2$  levels, so that these sum rules are no longer restricted to *jj*-coupling but valid in intermediate coupling.

### 2. Theoretical limitations

The derivation of the sum rules requires a separation of the transition probability into a physical and geometric part. To perform the angular momentum recoupling, it is assumed that the radial matrix elements are constant over the absorption edge. Although each *j* edge extends only over a narrow energy range of a few eV, transitions from different parts of the valence band can have different cross-sections. Wu *et al.* (1994) showed that the radial matrix integrals at the Ni  $L_{2,3}$  in the metal vary linearly with photon energy from the bottom to the top of the band due to a change in spin-orbit interaction. Since this change is proportional to the expectation value of the orbital moment,  $L_z$ , the effect on the orbital sum rule is not dramatic, however, the effect on the spin sum rule can be larger. Such effects are usually absent in the strongly localized *f* shell of the rare earths, which have narrow band widths, but can be present in actinides.

The sum rules are based on the assumption that it is possible to integrate the signal of a core level assigned by a good quantum numbers, such as the total angular momentum *j*. However, core-valence interactions can induce a transfer of spectral weight between the *j* edges, invalidating both the spin-orbit sum rule (Thole & van der Laan, 1988; van der Laan, & Thole 1988a) and the spin sum rule. Alternatively, the sum rules can be used indirectly, by

scaling the calculated absorption curve to the measured spectrum. For localized calculations this eliminates the effect of *jj* mixing. However, band structure calculations can display a different line shape when the core-valence interaction is not properly included. Band theory can also have difficulties to calculate the correct number of holes and branching ratio of the isotropic spectrum (Ebert, 1996). Anderson impurity model calculations give usually a good result for localized materials including transition metal oxides and rare earths (van der Laan & Thole, 1992).

To explain the x-ray absorption spectrum (XAS) it is often sufficient to consider only electric dipole transitions, certainly in the soft x-ray range. Carra and Altarelli (1990) pointed out the importance of the electric quadrupole transitions  $2p \rightarrow 4f$  at the  $L_{2,3}$  edges of the rare earths. These excitations can be strong due to the large magnetic moment of the *4f* compared to the *5d* shell. Electric dipole and quadrupole transitions have a different angular and temperature dependence, so they can be separated as demonstrated by Lang *et al.* (1995) and Giorgetti *et al.* (1995). It is more difficult to separate the  $c + 1$  and  $c - 1$  channels in the dipole excitation. Fortunately, for the  $2p$  excitation in  $3d$  transition metals the *s* channel can be neglected since its cross-section is less than 1 % of the total. Overall, the consensus seems to be that the uncertainty in the orbital and spin moment for  $3d$  transition metals is within 10 %. For the  $L_z/S_z$  ratio the accuracy appears to be even better, around 5 %, mainly because the number of holes drops out.

### 3. Experimental complications

Saturation effects occur in both electron yield and fluorescence. The electron escape depth is of the order of tens of Å, which makes the electron yield signal extremely surface sensitive, necessitating surface science preparation. The orbital moment at the surface can be different from the bulk due to symmetry breaking. For thickness dependent studies the electron escape depth must be taken explicitly into account. The yield electrons can undergo spin dependent scattering, resulting in an imbalance between the spin majority and minority electrons. Evidence for this effect seems to come from spin scattering through thin ferromagnetic films (Oberli *et al.*, 1998).

Saturation effects occur because the electron escape depth cannot be neglected with respect to the x-ray attenuation length (van der Laan & Thole 1988b), especially at grazing incidence. Measurements in transmission are preferred, but unfortunately the x-ray attenuation length is very short; only a few hundreds Å. Chen *et al.* (1995) measured 50–70 Å thick films of Fe and Co on 1 mm thick parylene. However, strain deformation in thin films induced by the substrate can lead to changes in the crystalline structure, which changes the orbital moment.

The total electron yield sensitivity is dependent on the type of detector and its precise location with respect to the sample. Since electrons of lower kinetic energy originate on average from deeper in the sample, different detectors might probe different sample depths. This complicates the comparison between measurements carried out by various research groups.

To obtain absolute moments we need to know precisely the degree of circular polarization of the x-rays. Difficulties can arise when the polarization is different at each edge. For instance, the Pd  $L_{2,3}$  edges are well separated (3173 and 3330 eV) so that the change in the degree of circular polarization can be large, especially when the monochromator crystals are operating near the Brewster angle ( $\sim 45^\circ$ ). Furthermore, it is often forgotten that the

measured intensity is given by the product of line strength and photon energy, while the sum rule applies to the line strength. This requires a correction, e. g. for Pd  $L_{2,3}$  edges. A reliable  $I_0$  monitor is essential, because the photon flux is not constant as a function of energy. Undulator devices often show strong flux variations over a short energy range. When the  $I_0$  normalization is incorrect, the two  $j$  edges are weighted with different factors resulting in wrong spin dependent moments.

Also the anisotropy of the crystal lattice can give variations in the observed spin to orbital moment ratio. For instance, when the magnetization is not along a high-symmetry direction, the orbital moment is no longer parallel to the spin direction. Since we measure only the projection of moments, a too small orbital moment is obtained when the light polarization is parallel to the magnetization direction (Dürr *et al.*, 1996).

The arbitrariness in the choice of the integration limits is another source of errors. In principle, the signal must be integrated over the entire absorption edge. This works often nicely for the dichroic signal which goes rapidly to zero above the edge where the continuum states are non-magnetic. However, to obtain moments *per hole* also the isotropic spectrum has to be integrated. The *background* below and above the edge has usually not the same height so that it is not straightforward to separate discrete and continuum states. Furthermore, the application of the spin sum rule requires the choice of a specific energy point to separate the two edges. Such a choice is ambiguous when the dichroic signal is not entirely zero in between the two edges, as is often the case in e. g.  $3d$  transition metals.

The isotropic spectrum is rarely measured. Since the light can only be polarized transversally, three measurements with orthogonal linear polarization need to be added. Instead, the sum of the two spectra with opposite helicities is usually taken. However, this is only correct when the linear dichroism vanishes. Some research groups prefer to use, instead of XMCD, the asymmetry. However, the latter depends also on the linear dichroism, so that orbital and quadrupole moments are entangled.

The spin sum rule contains also the magnetic dipole term,  $T_z$ , which is usually small in  $3d$  transition metal systems with cubic symmetry but which is large in actinides due to the strong  $5f$  spin-orbit coupling (Collins *et al.*, 1995). Several ways have been proposed to separate  $S_z$  and  $T_z$ . Since in  $3d$  transition metals,  $T_z \approx S_z Q_{zz}$ , where the quadrupole moment,  $Q$ , is a traceless tensor, Stöhr and König (1995) proposed to take the sum of three mutually orthogonal XMCD measurements, in which case  $T_z$  vanishes and only  $S_z$  remains. In practise, obscuration effects make it difficult to perform this procedure. Alternatively, one can measure the dichroism under different angles (Weller *et al.*, 1995). However, the magnetocrystalline anisotropy of the sample requires measurements along the principal axes of the crystal (Dürr *et al.*, 1996; Dürr & van der Laan, 1996). Alternatively, it is possible to measure the transverse x-ray magnetic circular dichroism (TXMCD), where one exploits the competition between the crystal field and spin-orbit interaction to measure the anisotropy in the moments (Dürr & van der Laan, 1996; van der Laan, 1998b). When the spins are forcefully aligned along a non-symmetry direction by a satu-

rating external magnetic field, the spin-orbit coupling tries to align the orbital moment parallel to the spin moment, whereas the crystal field prefers an alignment of the orbital moment along the easy-direction of magnetization. Consequently, the orbital moment is no longer collinear with the spin moment, and has a component perpendicular to the spin moment which serves as a direct measure for the orbital anisotropy. This transverse orbital component is obtained by applying the sum rules to the TXMCD spectrum. Likewise, the transverse geometry enables us to separate the magnetic dipole term, describing the spin anisotropy, from the isotropic spin moment (van der Laan, 1998b).

Summarizing we can say that although it has become clear that there are many theoretical and experimental complications attached to the application of the sum rules, it provides still the only *direct* tool to separate the orbital and spin contribution to the total magnetic moments. This method is element specific, sensitive to submonolayer coverages and buried interfaces, non-destructive and generally applicable to all classes of magnetic materials, such as  $3d$ ,  $4d$  and  $5d$  transition metals, lanthanides and actinides.

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