

X-Ray Circular Dichroism and Local Magnetic Fields

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Sum rules are derived for the circular dichroic response of a core line (CMXD). They relate the intensity of the CMXD signal to the ground-state expectation value of the magnetic field operators (orbital, spin, and magnetic dipole) of the valence electrons. The results obtained are discussed and tested for transition metals and rare earths.

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For circular dichroism in the x-ray region (CMXD), Thole *et al.* [1] have recently derived a new magneto-optical sum rule. It shows that, to a good approximation, the intensity of the CMXD signal, integrated over a complete core-level edge of a ferromagnet (or ferrimagnet), is proportional to the ground-state expectation value of the orbital angular momentum operator L_z . The derivation was carried out for electric dipole transitions in a localized model, considering a single ion in an arbitrary crystal-field symmetry and including hybridization effects.

In this Letter we show that, within the same framework, another sum rule can be obtained. It relates the CMXD signal, integrated over a single partner of a spin-orbit-split core-level edge, to the ground-state expectation value of the operators (L_z , total spin S_z , and magnetic di-

pole $[\sum_i \mathbf{s}_i - 3\hat{\mathbf{r}}_i(\hat{\mathbf{r}}_i \cdot \mathbf{s}_i)]_z$) that describe the magnetic field generated by the valence electrons. Our results indicate that, besides $\langle L_z \rangle$, as described in Ref. [1], CMXD spectroscopy can provide an independent determination of the ground-state expectation value of S_z [2]; this has been tested using CMXD data, taken at the $L_{2,3}$ edges of the ferromagnetic metals Fe, Co, and Ni [3]. Furthermore, valuable, site-specific information on the magnetic anisotropy of the sample can be obtained, as discussed below.

We consider the electric dipole transitions of a single partner of spin-orbit-split edge, in an ion with the valence shell only partly filled. Let $|\Psi\rangle$ denote any state of the ground configuration l^n of the ion. The final-state configuration is represented by $|\Psi'jm\rangle = |\underline{c}_{jm}l^{n+1}(\Psi')\rangle$; here Ψ' denotes any state of the outer shell l^{n+1} and $\underline{c}_{jm}$ stands for a hole in a core level. The dipole matrix element is given by

$$\begin{aligned} \langle \Psi | r C_q^{(1)} | \Psi' jm \rangle &= \sum_{\lambda\sigma} \langle \Psi | c_{jm}^\dagger l_{\lambda\sigma} | \Psi' jm \rangle \langle c_{jm} | C_q^{(1)} | l_{\lambda\sigma} \rangle R_{cl} \\ &= \sum_{\lambda\sigma} \langle \Psi | c_{jm}^\dagger l_{\lambda\sigma} c_{jm} | \Psi' \rangle \\ &\quad \times \sum_{\gamma} (-)^{m-\gamma-1/2} \begin{pmatrix} 1/2 & c & j \\ \sigma & \gamma & -m \end{pmatrix} \begin{pmatrix} c & 1 & l \\ -\gamma & q & \lambda \end{pmatrix} [j]^{1/2} P_{cl}. \end{aligned} \quad (1)$$

The notation is as follows: $c_{jm}^\dagger$ and $l_{\lambda\sigma}^\dagger$ represent creation operators for core and valence electrons, respectively; $C_q^{(1)}$ denotes a normalized spherical harmonic; $[j] = 2j+1$, R_{cl} stands for the radial matrix element of the $c \rightarrow l$ dipole transition; and $P_{cl} = \langle c || C^{(1)} || l \rangle R_{cl}$. The total intensity of the j edge is expressed by

$$I^j = \sum_{\Psi' m \lambda \sigma \lambda' \sigma'} \langle \Psi | c_{jm}^\dagger l_{\lambda\sigma} c_{jm} | \Psi' \rangle \langle \Psi' | c_{jm}^\dagger l_{\lambda'\sigma'} c_{jm} | \Psi \rangle [j] \sum_{\gamma\gamma'} \begin{pmatrix} 1/2 & c & j \\ \sigma & \gamma & m \end{pmatrix} \begin{pmatrix} c & 1 & l \\ \gamma & q & \lambda \end{pmatrix} \begin{pmatrix} c & 1 & l \\ \gamma' & q & \lambda' \end{pmatrix} \begin{pmatrix} 1/2 & c & j \\ \sigma' & \gamma' & m \end{pmatrix} P_{cl}^2. \quad (2)$$

In this expression, the final states can be removed by extending the set $|\Psi'\rangle$ to the whole Hilbert space and using the closure relation. The added states give no contribution to I^j . Then, using a standard graphical notation for the angular factor [4], we have

$$I^j = \sum_{m \lambda \sigma \lambda' \sigma'} \langle \Psi | c_{jm}^\dagger l_{\lambda\sigma} c_{jm} c_{jm}^\dagger l_{\lambda'\sigma'} c_{jm} | \Psi \rangle [j] \quad \begin{array}{c} \begin{array}{ccccc} \ell & & j & & \ell \\ & \diagdown & & \diagup & \\ & c & & c & \\ & \diagup & & \diagdown & \\ 1 & & 1/2 & & 1/2 \end{array} & \begin{array}{ccccc} j & & \ell & & j \\ & \diagdown & & \diagup & \\ & c & & c & \\ & \diagup & & \diagdown & \\ 1/2 & & 1 & & 1 \end{array} \end{array} P_{cl}^2. \quad (3)$$

Transforming the diagonal matrix element by means of $\{c_{jm}^\dagger, c_{jm}\} = 1$ and recoupling the angular part to obtain coupled tensor operators, one has the following:

$$I^j = \sum_{\lambda\sigma\lambda'\sigma'} \langle \Psi | 1 - l_{\sigma\sigma'}^\dagger l_{\lambda'\sigma'} | \Psi \rangle [j] \sum_{xyz} [xyz] \quad (4)$$

$$= \left\{ \frac{[j]}{[1c]} + [j] \sum_{xyz} [xyz]^{1/2} \langle \Psi | W_0^{(xy)z} | \Psi \rangle \right\} P_{cl}^2,$$

with $[a \cdots b] = (2a+1) \cdots (2b+1)$. On the basis of expression (4) one can see that the total intensity I^j of the j edge is given by the ground-state expectation value of a linear combination of double tensors $W^{(xy)z}$, as defined by Judd [5]. The variables x , y , and z are limited to $x=0, \dots, 2l$, $y=0, 1$, and $z=0, 1, 2$, because of the triads $(l \times l)$, $(1/2 \times 1/2)$, and (1×1) ; the $9j$ symbol is zero unless $x+y+z$ is even. For $z=0$ and 2 , the $3j$ symbol

$$\begin{pmatrix} 1 & z & 1 \\ -q & 0 & q \end{pmatrix}$$

is an even function of q ; for $z=1$, it is odd. Therefore, only $z=1$ terms appear in the circular dichroism and the CMXD signal, integrated over a single partner of a spin-orbit-split edge, can be written as

$$\int_{j_{\pm}} d\omega (\mu^+ - \mu^-) \propto I_{q^{\pm}1}^j - I_{q^{\pm}-1}^j$$

$$= \left\{ \frac{[j_{\pm}]}{2c+1} \frac{l(l+1)+2-c(c+1)}{4l(l+1)(2l+1)} \langle \Psi | L_z | \Psi \rangle \pm \frac{c}{2c+1} \frac{l(l+1)-c(c+1)-2}{3c(2l+1)} \langle \Psi | S_z | \Psi \rangle \right. \\ \left. \pm \frac{c}{2c+1} \frac{l(l+1)[l(l+1)+2c(c+1)+4]-3(c-1)^2(c+2)^2}{6l(l+1)(2l+1)c} \langle \Psi | T_z | \Psi \rangle \right\} (P_{cl}^{\pm})^2, \quad (5)$$

in units of $\hbar$. Here, $\mathbf{T} = \sum_i \mathbf{s}_i - 3\mathbf{r}_i(\mathbf{r}_i \cdot \mathbf{s}_i)/r_i^2$ and $j_{\pm} = c \pm 1/2$; μ denotes the absorption coefficient.

It can be shown that expression (5) is still valid in the presence of an additional, partly filled spectator shell [1]; it can also be generalized to the case of a hybridized ground state, as discussed in Ref. [1]. In both cases only the l shell contributes to $\langle L_z \rangle$, $\langle S_z \rangle$, and $\langle T_z \rangle$ (shell selectivity).

On the basis of our findings, one can view CMXD spectroscopy as a probe of the magnetic field of the valence electrons. The probe is *shell specific*; furthermore, the orbital and spin contributions can be separated: (i) Adding the two partners of a spin-orbit-split edge and normalizing to the unpolarized x-ray-absorption spectroscopy spectrum, one has

$$\rho = \int_{j_+ + j_-} d\omega (\mu^+ - \mu^-) / \int_{j_+ + j_-} d\omega (\mu^+ + \mu^- + \mu^0) = \frac{1}{2} \frac{l(l+1)+2-c(c+1)}{l(l+1)(4l+2-n)} \langle L_z \rangle, \quad (6)$$

yielding the ground-state expectation value of the orbital angular momentum per hole [1,6]. (ii) The ground-state expectation value of the spin-dependent part of the local magnetic field per hole is given by

$$\delta = \frac{\int_{j_+} d\omega (\mu^+ - \mu^-) - [(c+1)/c] \int_{j_-} d\omega (\mu^+ - \mu^-)}{\int_{j_+ + j_-} d\omega (\mu^+ + \mu^- + \mu^0)}$$

$$= \frac{l(l+1)-2-c(c+1)}{3c(4l+2-n)} \langle S_z \rangle + \frac{l(l+1)[l(l+1)+2c(c+1)+4]-3(c-1)^2(c+2)^2}{6lc(l+1)(4l+2-n)} \langle T_z \rangle. \quad (7)$$

To obtain expressions (6) and (7) we neglected relativistic corrections to the radial part and set $P_{cl}^+ = P_{cl}^-$; this approxi-

TABLE I. Numerical evaluation of $\Delta = [(I^+ - I^-)_{L_3} - 2(I^+ - I^-)_{L_2}]/P_d^2$ and $\bar{\Delta} = [\Delta - \frac{2}{15}\langle S_z \rangle]/\Delta$, in an octahedral crystal field, for (a) 3d and (b) 4d and 5d ions, in an exchange field of 0.01 eV.

	10 Dq (eV)	Δ	$\langle S_z \rangle$	$\bar{\Delta}$
(a)				
$\text{Ni}^{2+}(d^8)$	1	-0.124	-0.994	4%
	1.5	-0.123	-0.997	5%
$\text{Co}^{2+}(d^7)$	1	-0.127	-1.043	9%
	1.5	-0.130	-1.047	8%
$\text{Fe}^{2+}(d^6)$	1	-0.210	-1.720	9%
	1.5	-0.211	-1.731	9%
(b)				
$\text{Pd}^{2+}(d^8)$	1	-0.137	-0.968	6%
$\text{Rh}^{2+}(d^7)$	1	-0.125	-0.934	1%
$\text{Pt}^{2+}(d^8)^a$	3	-0.1609	-0.800	34%
$\text{Ir}^{2+}(d^7)^a$	3	-0.076	-0.554	31%

^aCalculation performed at the $M_{2,3}$ edges.

mation introduces errors which are generally small [1].

The expectation value of the magnetic dipole operator $\langle T_z \rangle$ provides a measure of the anisotropy of the field of the spins when the atomic cloud is distorted, either by the spin-orbit interaction or by crystal-field effects [7].

Specific cases will now be discussed in detail.

(i) *The $L_{2,3}$ edges of the 3d transition metals.* It has to be pointed out first that, in 3d series, the spin-orbit splitting of the $L_{2,3}$ edges is not large enough to prevent their mixing, caused by Coulomb interactions in the final state. This makes an exact separation of the two partners impossible; however, the effect becomes small ($\leq 5\%$) on approaching the end of the series.

In the cubic phase of Fe, Co, and Ni, the magnetic dipole contribution is expected to be small. [The Hartree-Fock (HF) values of the spin-orbit parameters fall in the

TABLE II. Orbital to spin moment ratio in Fe, Co, and Ni (3d electrons).

	Ni	Co	Fe
$\langle L_z \rangle / \langle S_z \rangle$	0.19 ^a 0.17 ^b	0.13 ^a 0.14 ^b	0.133 ^a 0.124 ^b

^aThis work and the CMXD data of Ref. [3].

^bStearns, Ref. [10].

range $0.05 \lesssim \zeta_d \lesssim 0.08$ eV [8].] This is confirmed by numerical calculations, performed with Cowan-Butler's atomic programs [8,9] (full multiplet structure in a crystal field, with the exchange interaction simulated by an applied magnetic field, coupled to $\mathbf{S}$ only). They are reported in Table I(a).

Given an ion in a cubic field, a nonzero value of $\langle T_z \rangle$ can only be obtained via spin-orbit coupling. (O_h symmetry cannot induce a quadrupole moment.) In Ni^{2+} , $\langle T_z \rangle$ has a small value, as the 3A_2 term is not spin-orbit split. In Co^{2+} and Fe^{2+} , with the 4T_1 and the 5T_2 terms both split by a few hundred K, the effect of spin-orbit coupling depends on the strength of the exchange field. However, $\langle T_z \rangle$ appears to be sufficiently quenched ($\bar{\Delta} \leq 15\%$, for exchange fields up to 0.05 eV) and can be neglected with respect to $\langle S_z \rangle$. Therefore, in these systems, a measurement of δ should provide a fairly accurate determination of the ground-state expectation value per hole of the spin operator S_z .

Alternatively, one can consider the CMXD spectrum only and determine the ratio $\langle L_z \rangle / \langle S_z \rangle$. We have evaluated this quantity using CMXD data obtained at the $L_{2,3}$ edges of Fe, Co, and Ni [3]; the results, reported in Table II, are in good agreement with the corresponding neutron-scattering data [10].

(ii) *The $M_{4,5}$ edges of rare earths.* These systems are characterized by an almost pure LSJ coupling Hund's-rule ground state. In this case $\langle T_z \rangle$ can be evaluated analytically [11]. One has

$$\langle T_z \rangle = \langle M \rangle (l - n + 1/2) \frac{3(S - J)^2(S + J + 1)^2 - L(L + 1)[L(L + 1) + 2S(S + 1) + 2J(J + 1)]}{2(2l + 3)(2l - 1)(2L - 1)SJ(J + 1)}, \quad (8)$$

for $n \leq 2l + 1$. The case $n \geq 2l + 1$ is accounted for by $n \rightarrow 4l + 2 - n$. For $l = 0$ configurations ($n = 0, 2l + 1$, and $4l + 2$): $\langle T_z \rangle = 0$, as $S = J$. Also (Landé)

$$\langle S_z \rangle = \langle M \rangle \frac{J(J + 1) + S(S + 1) - L(L + 1)}{2J(J + 1)}. \quad (9)$$

Within an LSJ term, the ratio $\langle S_z \rangle$ to $\langle T_z \rangle$ is constant and the two contributions can be separated.

We have also estimated $\langle T_z \rangle$ in 4d and 5d ions. The numerical results are displayed in Table I(b). In the 5d ions, a strong spin-orbit coupling ($\zeta_d \cong 2$ eV, HF) makes $\langle T_z \rangle$ rather large. In this case, further experimental information and/or calculation are required to separate $\langle S_z \rangle$ and $\langle T_z \rangle$.

It is worthwhile to compare our CMXD sum rules to the analysis of magnetic circular dichroism in the optical region. We use the properties of core holes to obtain ground-state expectation values of L_z , S_z , and T_z , from a measurement at one temperature in ferromagnetic and paramagnetic d and f systems. In the optical region on the other hand, the ground-state expectation value of the total magnetic moment is determined from the temperature dependence of the dichroic spectra [12].

To summarize, for electric dipole transitions in a single ion model, we have derived a new magneto-optical sum rule for the circular dichroism in the x-ray region. It relates the CMXD response of a single partner of a spin-orbit-split core level to the "shell-resolved" operators of

the magnetic field of the valence electrons, thus providing valuable insight into the nature of CMXD spectroscopy. Applications of the sum rule to the determination of $\langle L_z \rangle / \langle S_z \rangle$ in Fe, Co, and Ni metals provide a good agreement with existing experimental data.

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