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 dipole $[\sum_i \mathbf{s}_i - 3\hat{\mathbf{r}}_i(\hat{\mathbf{r}}_i\cdot\mathbf{s}_i)]_z$) 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

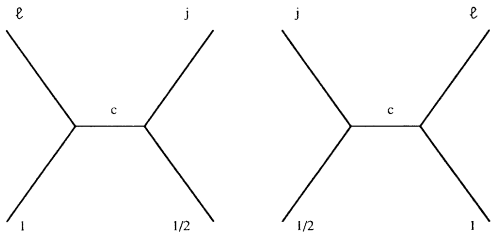
$$\begin{aligned}\langle\Psi|rC_q^{(1)}|\Psi' jm\rangle &= \sum_{\lambda\sigma}\langle\Psi|c^\dagger_{jm}l_{\lambda\sigma}|\Psi' jm\rangle\langle cjm|C_q^{(1)}|l_{\lambda\sigma}\rangle R_{cl}\\ &= \sum_{\lambda\sigma}\langle\Psi|c^\dagger_{jm}l_{\lambda\sigma}c_{jm}|\Psi'\rangle\\ &\quad\times\sum_\gamma(-)^{m-\gamma-1/2}\begin{pmatrix}1/2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

The notation is as follows: $c^\dagger_{jm}$ and $l^\dagger_{\lambda\sigma}$ 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

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

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

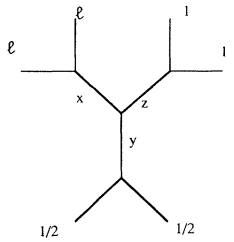
$$I^j = \sum_{m\lambda\sigma\lambda'\sigma'}\langle\Psi|c^\dagger_{jm}l_{\lambda\sigma}c_{jm}c^\dagger_{jm}l^\dagger_{\lambda'\sigma'}c_{jm}|\Psi\rangle[j]$$

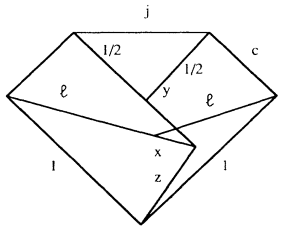


$$P_{cl}^2\,. \tag{3}$$

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

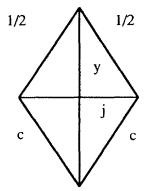
$$I^{j}=\sum_{\lambda\sigma\lambda'\sigma'}\langle\Psi|1-l^{\dagger}_{\lambda\sigma}l_{\lambda'\sigma'}|\Psi\rangle[j]\sum_{xyz}[xyz]$$

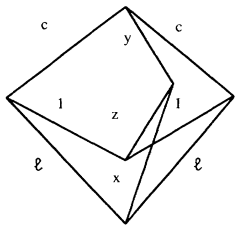


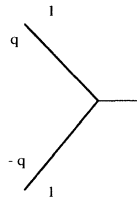


P^{2}_{cl}

$$=\left\{\frac{[j]}{[1c]}+[j]\sum_{xyz}[xyz]^{1/2}\langle\Psi|W_{0}^{(xy)z}|\Psi\rangle\right.$$







$$\left.\right\}P^{2}_{cl}\,, \qquad (4)$$

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 $x=0,\ldots,2l$, $y=0,1$, and $z=0,1,2$, because of the triads $(l\times l)$, $(1/2\ y\ 1/2)$, and $(1\ z\ 1)$; 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

$$\int_{j_{\pm}}d\omega(\mu^{+}-\mu^{-})\propto I^{j_{\pm}}_{q=1}-I^{j_{\pm}}_{q=-1}$$
$$=\left\{\frac{[j_{\pm}]}{2c+1}\frac{l(l+1)+2-c(c+1)}{4l(l+1)(2l+1)}\langle\Psi|L_{z}|\Psi\rangle\pm\frac{c}{2c+1}\frac{l(l+1)-c(c+1)-2}{3c(2l+1)}\langle\Psi|S_{z}|\Psi\rangle\right.$$
$$\left.\pm\frac{c}{2c+1}\frac{l(l+1)[l(l+1)+2c(c+1)+4]-3(c-1)^{2}(c+2)^{2}}{6l(l+1)(2l+1)c}\langle\Psi|T_{z}|\Psi\rangle\right\}(P^{\pm}_{cl})^{2}\,, \qquad (5)$$

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 $j_{\pm}=c\pm1/2$; 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

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

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

$$\delta=\frac{\int_{j_{+}}d\omega(\mu^{+}-\mu^{-})-[(c+1)/c]\int_{j_{-}}d\omega(\mu^{+}-\mu^{-})}{\int_{j_{+}+j_{-}}d\omega(\mu^{+}+\mu^{-}+\mu^{0})}$$
$$=\frac{l(l+1)-2-c(c+1)}{3c(4l+2-n)}\langle S_{z}\rangle+\frac{l(l+1)[l(l+1)+2c(c+1)+4]-3(c-1)^{2}(c+2)^{2}}{6lc(l+1)(4l+2-n)}\langle T_{z}\rangle\,. \qquad (7)$$

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 $\Delta=[(I^+-I^-)_{L_3}-2(I^+-I^-)_{L_2}]/P_{cl}^2$ and $\tilde{\Delta}=[\Delta-\frac{2}{15}\langle S_z\rangle]/\Delta$, 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	$\langle S_z\rangle$	$\tilde{\Delta}$
(a)				
$Ni^{2+}(d^8)$	1	−0.124	−0.994	4%
	1.5	−0.123	−0.997	5%
$Co^{2+}(d^7)$	1	−0.127	−1.043	9%
	1.5	−0.130	−1.047	8%
$Fe^{2+}(d^6)$	1	−0.210	−1.720	9%
	1.5	−0.211	−1.731	9%
(b)				
$Pd^{2+}(d^8)$	1	−0.137	−0.968	6%
$Rh^{2+}(d^7)$	1	−0.125	−0.934	1%
$Pt^{2+}(d^8)$ [a]	3	−0.1609	−0.800	34%
$Ir^{2+}(d^7)$ [a]	3	−0.076	−0.554	31%

[a]Calculation 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 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 **S** only). They are reported in Table I(a).

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]	0.13 [a]	0.133 [a]
	0.17 [b]	0.14 [b]	0.124 [b]

[a]This work and the CMXD data of Ref. [3].
[b]Stearns, Ref. [10].

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 ($\tilde{\Delta}\leq 15\%$, 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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