X-Ray Circular Dichroism as a Probe of Orbital Magnetization

B. T. Thole,[1] Paolo Carra,[2] F. Sette,[2] and G. van der Laan[3]

[1]*Department of Chemical Physics, Materials Science Centre, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands*

[2]*European Synchrotron Radiation Facility, BP 220, F-38043 Grenoble CEDEX, France*

[3]*Daresbury Laboratory, Science and Engineering Research Council, Warrington, WA4 4AD, United Kingdom*

(Received 2 December 1991)

A new magneto-optical sum rule is derived for circular magnetic dichroism in the x-ray region (CMXD). The integral of the CMXD signal over a given edge allows one to determine the ground-state expectation value of the orbital angular momentum. Applications are discussed to transition-metal and rare-earth magnetic systems.

PACS numbers: 78.70.Dm, 78.20.Ls

The orbital part of the magnetic moment, μ_L, in magnetic materials is determined by the interplay among several effects: Coulomb and spin-orbit interactions, hybridization, and crystal fields. To study these effects, the independent determination of μ_L and μ_S (the spin part) is of prime importance.

In neutron scattering, the two contributions can be separated by fitting the measured form factors with a suitable model [1]. In nonresonant x-ray diffraction, as shown by a theoretical analysis [2,3], different polarization responses directly separate spin and orbital densities; however, all attempts to implement a quantitative separation experimentally have been, so far, inconclusive [4].

In this Letter we show that, to a good approximation, it is possible to measure directly the ground-state expectation value of the orbital angular momentum operator L_z by core-level absorption spectroscopy. This is achieved by considering the difference between the integrated absorption intensity for right and left circularly polarized light. This integral of the circular magnetic x-ray dichroism (CMXD) has to be taken over a complete core-level edge of magnetically oriented ferromagnetic or ferrimagnetic materials. If the edge is spin-orbit split, the integration must be over the two components. Our results agree well with the available experimental data, such as those obtained at the $L_{2,3}$ edges of ferromagnetic Ni [5], and the $M_{4,5}$ edges of Gd^{3+} in the gadolinium iron garnet [6].

The strong final-state interactions of the valence shell with the core hole normally allow one to draw only indirect conclusions about the ground state from core-level spectra. However, the importance of the integrated CMXD is that it directly measures a ground-state property.

The importance of sum rules is well known in optical spectroscopy, and has often been used to derive nontrivial ground-state properties, such as the number of electrons participating in a band of optical transitions, the plasma frequency, etc. In magneto-optics, the following sum rule was derived by Smith for zero external magnetic field [7]:

$$\sum_{\beta}(f_{\alpha\beta}^{+}-f_{\alpha\beta}^{-})=\frac{2}{\hbar}\left[\langle\alpha|L_z|\alpha\rangle+\frac{1}{2mc^2}\langle\alpha|S_z(X\nabla_x V+Y\nabla_y V)|\alpha\rangle\right], \tag{1}$$

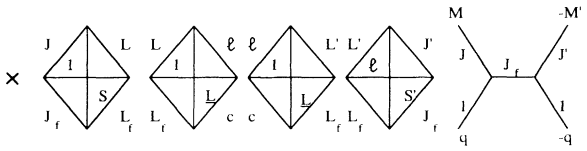
with $f_{\alpha\beta}^{\pm}$ the oscillator strengths for left and right circularly polarized light. The second term in the right-hand side arises from the spin-orbit interaction in the valence shell; order-of-magnitude estimates, based on hydrogenic wave functions, show that it gives a very small correction to the first term. Expression (1), derived by considering $E1$ transitions only, is formally exact; nevertheless, it has a limited degree of application, as it implies a sum over an infinite number of transitions.

To derive a more useful formulation, in which *only E1 transitions in a finite interval of energy (one edge) appear*, we first consider a model system consisting of a single ion with the valence shell only partly filled. Any state of the ground configuration l^n of the ion, in an arbitrary symmetry crystal field, can be expressed in terms of a complete basis set: $|\psi\rangle=\sum_\mu a_\mu|\mu\rangle$. Any basis can be chosen; for convenience we use the basis $|\mu\rangle=|l^n\alpha LSJM\rangle$. In the same way, any state of the final configuration cl^{n+1} (c denotes a core hole) can be expanded in the basis $|\lambda\rangle=|l^{n+1}(\underline{\alpha L}\,\underline{S J})(c\,\frac{1}{2}\,j)J_f M_f\rangle$ [8]. Given the ground state $|\psi\rangle$, transition probabilities to a dipole-allowed final state can be written as

$$P_q(\psi)=\sum_{\mu,\mu',\lambda}a_\mu a_{\mu'}\langle\mu|C_q^1|\lambda\rangle\langle\lambda|C_{-q}^1|\mu'\rangle \equiv\langle\psi|P_q|\psi\rangle,$$

where C_q^1 is the normalized spherical harmonic operator. Our aim is to find a simple expression for an arbitrary matrix element of P_q, for the l^n configuration. Applying the Wigner-Eckart theorem and using standard graphical methods [9,10], one has

$$\langle\mu|P_q|\mu'\rangle=\sum_{\underline{a}\underline{L}\underline{S}L_fS_fJ_f}\delta_{SS_f}\delta_{S'S_f}(n+1)[\underline{L},\underline{S},L_f,J_f]([J,J']/[S,S'])^{1/2}$$

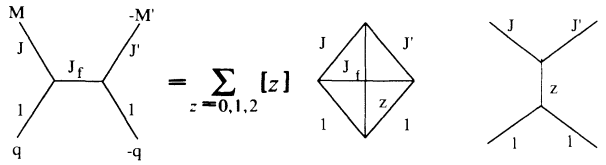


$$\times\{cfp\}P_{cl}^{(1)2},$$

with

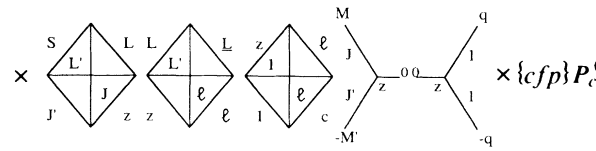
$$\{cfp\}=(l^n\alpha LS|\}l^{n+1}\underline{a}\underline{L}\underline{S})(l^{n+1}\underline{a}\underline{L}\underline{S}\{|l^n\alpha'L'S'),$$

$P_{cl}^{(1)}$ the radial part, and $[a,\ldots,b]=(2a+1)\cdots(2b+1)$. This expression can be conveniently transformed by applying Theorems 3 and 4 (YLV 3 and 4) of Yutsis, Levinson, and Vanagas [10]. First, we use the relation



and sum over J_f using YLV 4; then we rearrange the resulting expression, by applying YLV 3 to L, L', and z, and sum over L_f (YLV 4). Finally, we apply YLV 3 to z, 1, and 1 to obtain

$$\langle\mu|P_q|\mu'\rangle=\sum_{\underline{a}\underline{L}\underline{S}z}[z](n+1)\frac{[\underline{L},\underline{S}]}{[S]}[J,J']^{1/2}$$



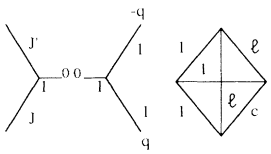
$$\times\{cfp\}P_{cl}^{(1)2}.$$

As $z=(0,1,2)$, because of the triad $(z,1,1)$, P_q consists of a sum of three terms, each with a different q dependence. The $z=2$ term describes linear dichroism; it will not be discussed here. The $z=0$ term can be written as [11]

$$\sum_{\underline{a}\underline{L}\underline{S}}(n+1)\frac{[\underline{L},\underline{S}]}{[S]}[J,J']^{1/2}\delta_{LL'}\delta_{JJ'}([LJlL'l1])^{-1/2}[1]^{-1}\{cfp\}P_{cl}^{(1)2}=\frac{4l+2-n}{[1,l]}P_{cl}^{(1)2},\tag{2}$$

where $4l+2-n$ denotes the number of holes in the valence shell. Expression (2) is q independent; it describes the unpolarized absorption spectrum and provides a useful normalization (see below). For the $z=1$ term, we find

$$[1]\langle\alpha LSJ||U^1||a'L'S'J'\rangle\times$$



$$P_{cl}^{(1)2}=q\frac{c(c+1)-l(l+1)-2}{4l(l+1)(2l+1)}\langle\mu|L_z|\mu'\rangle P_{cl}^{(1)2},\tag{3}$$

in units of $\hbar$ [12]. This is our main result [13].

In deriving expressions (2) and (3), we neglected the differences between the radial parts if the edge is spin-orbit split. They arise from relativistic corrections, which scale with the ratio of the core level spin-orbit splitting to the average excitation energy. This approximation introduces errors of the order of 1% for the $L_{2,3}$ edges of $3d$ transition metals and the $M_{4,5}$ edges of rare earths [14].

Now, we briefly discuss the connection between our single-edge results and the sum rule of Eq. (1) with the small spin-orbit corrections omitted. Once again, we consider a single ion with the valence shell only partly filled. Then, Eqs. (1) and (3) are consistent if

$$A_{l-1,l}\sum_{n'}P_{nl,n'l-1}^{(1)2}E_{nl,n'l-1}+A_{l+1,l}\sum_{n'}P_{nl,n'l-1}^{(1)2}E_{nl,n'l+1}=1,\tag{4}$$

with $E_{nl,n'l'}$ the average transition energy and

$$A_{l'l}=[l'(l'+1)-l(l+1)-2]/4l(l+1)(2l+1);$$

the sums are extended to all $E1$-allowed transitions with nonzero CMXD, including the continuum. This equation holds exactly for one-electron spherical systems because

of the Wigner-Kirkwood sum rules [8]. A Hartree-Fock evaluation of (4) for Gd^{1+} ($4f^7 6s^2$) shows agreement within 8%. The discrepancy is due to configuration interaction, which makes an exact separation into single-shell contributions impossible, especially for transitions to the continuum [8,14].

To obtain an expression which directly compares to experiments, we normalize expression (3) to the unpolarized absorption spectrum [expression (2)]. We have

$$\rho \equiv \frac{\int_{\text{edge}} d\omega(\mu^+ - \mu^-)}{\int_{\text{edge}} d\omega(\mu^+ + \mu^- + \mu^0)} = \frac{1}{2}\frac{c(c+1) - l(l+1) - 2}{l(l+1)(4l+2-n)}\langle L_z\rangle , \quad (5)$$

independent of $P_{cl}^{(1)}$. Here μ denotes the absorption coefficient. As ρ is a quantity directly measurable from polarization-dependent core-level spectra, expression (5) allows the determination of the ground-state expectation value $\langle L_z\rangle$ per hole.

It can be shown that our results for the integrated CMXD still hold in the case of a larger basis set. Consider the addition of an extra (partly filled) shell X to the l^n configuration, for which $c \rightarrow X$ transitions can be neglected; with Θ and Θ' denoting arbitrary states of l^n and cl^{n+1} we have

$$\langle l^n\Theta, X|C_q^1|cl^{n+1}\Theta', X'\rangle = \delta_{XX'}\langle l^n\Theta|C_q^1|cl^{n+1}\Theta'\rangle ,$$

indicating that the presence of the extra shell has no effect on the integrated CMXD (although it may change the shape of the spectrum). The orbital momentum of the spectator state X is not measured; in other words, the integrated CMXD provides a *shell-selective* measure of $\langle L_z\rangle$. Similar considerations apply when there is hybridization. Take an arbitrary ground state, given as a mixture of two configurations, $|g\rangle = \alpha_1|l^n\Theta_1\rangle + \alpha_2|l^{n+1}\underline{L}\Theta_2\rangle$, and consider transitions to the $E1$-allowed final state, $|f\rangle = \beta_1|cl^{n+1}\Theta_1'\rangle + \beta_2|cl^{n+2}\underline{L}\Theta_2'\rangle$. Neglecting the weak $c \rightarrow \underline{L}$ transitions, we have

$$\langle P_q\rangle_{z=1} = qA_{cl}P_{cl}^{(1)2}(\alpha_1^2\langle l^n\Theta_1|L_z|l^n\Theta_1\rangle + \alpha_2^2\langle l^{n+1}\underline{L}\Theta_2|L_z|l^{n+1}\underline{L}\Theta_2\rangle) ,$$

showing that $\langle P_q\rangle_{z=1}$ provides the total $\langle L_z\rangle$ of the configuration.

Using the particle-hole symmetry, it can also be shown that expression (4) holds for transitions from the l^n configuration to any $E1$-allowed empty shell.

Experimentally, the determination of $\langle L_z\rangle$ requires the measurement of the absorption spectra, on a ferromagnetic sample, with the **B** field parallel (μ^+), antiparallel (μ^-), and perpendicular (μ^0) to the photon angular momentum vector. At the $L_{2,3}$ edges of Ni, μ^+ and μ^- have been accurately measured [15] and the integrated intensities determined; they give $\rho = 0.025 \pm 0.003$ assuming $\mu^0 = (\mu^+ + \mu^-)/2$. Using this value in Eq. (5), for $c=1$ ($2p$) and $l=2$ ($3d$), we obtain $\langle L_z\rangle = 0.050 \pm 0.006$ per hole, in agreement with calculations [16] and neutron scattering data [1], indicating a $0.05\mu_B$ orbital magnetic moment per Ni atom. We also apply Eq. (5) to CMXD data obtained at the $M_{4,5}$ edges of $Fe_5Gd_3O_{12}$. In this system the $4f^7$ ground-state configuration of Gd^{3+} (an almost pure $^8S_{7/2}$ state) implies $\langle L_z\rangle = 0$. This is confirmed by the integrated CMXD data [6] which yield $\langle L_z\rangle = 0.00 \pm 0.06$. It is important to notice that even values of ρ of 0.01 can be measured with a (5–10)% precision, allowing determination of orbital moments as small as $0.01\mu_B$.

To summarize, we have shown how to derive an approximate magneto-optical sum rule, which relates the integrated CMXD response of a core level to the ground-state expectation value of a "shell-specific" orbital magnetization. Expression (5), derived in the electric dipole approximation, with a few assumptions introducing generally small errors, agrees with existing data for Ni and Gd.

The experimental relevance of our work stems from the fact that CMXD, yielding a direct measure of $\langle L_z\rangle$, provides a suitable method to independently measure the orbital contribution to the magnetic moment. These findings should motivate further CMXD experimental investigations on magnetic materials; in the case of transition metals and actinides, our sum rule can be used in the study of the quenching of the orbital momentum and its relation to the localized or itinerant nature of the total magnetic moment.

We are grateful to M. Altarelli, F. de Bergevin, J. P. Desclaux, P. M. Platzman, and G. A. Sawatzky for stimulating discussions.

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$$\langle l^n \alpha LS||U^K||l^n \alpha' L'S'\rangle = \delta_{SS'}(4l+2-n)(-1)^{l+L+K}[L,L']^{1/2}$$

$$\times \sum_{\underline{\alpha}\underline{L}\underline{S}} (-1)^{\underline{L}} \begin{Bmatrix} l & K & l \\ L & \underline{L} & L' \end{Bmatrix} (l^{4l+2-n}\alpha LS\{|l^{4l+2-n-1}\underline{\alpha}\,\underline{L}\,\underline{S}\rangle(l^{4l+2-n-1}\underline{\alpha}\,\underline{L}\,\underline{S}|\}l^{4l+2-n}\alpha LS)$$

$$= \delta_{SS'}(4l+2-n)[L,L']^{1/2}\left(\frac{n+1}{4l+2-n}\right)\frac{[\underline{L},\underline{S}]}{[L,S,L',S']^{1/2}}(l^{4l+2-n}\cdots)(\cdots)$$

$$= \delta_{SS'}\frac{[\underline{L},\underline{S}]}{[S]}\begin{Bmatrix} l & K & l \\ L & \underline{L} & L' \end{Bmatrix}(l^n\alpha LS|\}l^{n+1}\underline{\alpha}\,\underline{L}\,\underline{S})(l^{n+1}\underline{\alpha}\,\underline{L}\,\underline{S}\{|l^n\alpha' L'S').$$

Here U^K is the Racah symmetric unit tensor operator for the l^n shell.
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