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Sum rules for polarization-dependent x-ray absorption

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A complete set of sum rules is obtained for polarization-dependent x-ray-absorption fine structure and x-ray circular magnetic dichroism (CMD), analogous to those for CMD derived by Thole *et al.* These sum rules relate x-ray-absorption coefficients to the ground-state expectation values of various operators. Problems with applying these sum rules are discussed.

I. INTRODUCTION

A connection between the integrated x-ray circular magnetic dichroism (CMD) signal and the ground-state value of the projection of orbital angular momentum on the magnetization axis was suggested by Thole, Carra, and van der Laan.[1] Later the same authors derived a second sum rule using graphical angular-momentum techniques.[2] There are many approximations in the derivation of these sum rules. There is even some arbitrariness in the choice of integration range and in the number of holes. These troublesome features were analyzed by Wu, Wang, and Freeman.[3] Using a limited integration range, they found that the sum rules are valid to within 10%, and even within 5% if one deducts contributions from hybridization. Another comparison between sum-rule predictions and band-structure results is given by Guo *et al.*[4]

Here we want to show that the same sum rules can be derived without graphical techniques, simply using analytical expressions for $3j$ symbols, in a manner similar to that used by Altarelli[5] for the first sum rule. Four additional sum rules are found, which yield additional information about magnetic properties, provided independent measurements of μ_0 as well as μ_+ and μ_- are made. Here μ_0 is the x-ray-absorption coefficient for x rays with polarization along the z axis and μ_+ and μ_- are, respectively, the coefficients for the absorption of right and left circularly polarized x rays.

II. DERIVATION OF SUM RULES

We start from Fermi's golden rule for the x-ray-absorption coefficient within the independent electron approximation. In the dipole approximation the absorption at the j edge with polarization $\hat{\epsilon}$ is

$$\mu^j(\omega) = \frac{2\pi}{\hbar} \sum_{m_j} \sum_{f}^{\text{unocc}} \langle j, m_j | \mathbf{p} \cdot \hat{\epsilon}^* | f \rangle \langle f | \mathbf{p} \cdot \hat{\epsilon} | j, m_j \rangle \times \delta(\omega - E_f + E_j) \,. \quad (1)$$

Integration over *all* ω is trivial, and, using the completeness relation $\Sigma_f |f\rangle\langle f| = \hat{\mathbf{1}}$ to change from consideration of unoccupied to occupied states, we obtain for the integrated intensities

$$\overline{\mu}^j = \frac{2\pi}{\hbar} \sum_{m_j, m_l, m_s} \langle j, m_j | l, m_l, s, m_s \rangle \langle l, m_l, s, m_s | \mathbf{p} \cdot \hat{\epsilon}^* \left(\hat{\mathbf{1}} - \sum_{f}^{\text{occ}} |f\rangle\langle f| \right) \mathbf{p} \cdot \hat{\epsilon} \sum_{m_l', m_s'} |l, m_l', s, m_s'\rangle \langle l, m_l', s, m_s' | j, m_j \rangle. \quad (2)$$

From the dipole selection rules we can only have transitions $l \to l' = l \pm 1$. We can rewrite Eq. (2) in terms of the one-particle density matrix for the ground state as

$$\rho(\alpha;\beta) = \sum_{f}^{\text{occ}} \langle \alpha | f \rangle \langle f | \beta \rangle = \langle \Psi_0 | c_\alpha^\dagger c_\beta | \Psi_0 \rangle. \quad (3)$$

Without loss of generality we can restrict consideration to $\hat{\epsilon}_+$, $\hat{\epsilon}_-$, and $\hat{\epsilon}_0$ for right-circular, left-circular, and z-axis polarizations, defined as usual[6] [$\hat{\epsilon}_+ = -(\hat{x} + i\hat{y})/\sqrt{2}$, $\hat{\epsilon}_0 = \hat{z}$, $\hat{\epsilon}_- = (\hat{x} - i\hat{y})/\sqrt{2}$]. From the Wigner-Eckart theorem we obtain

$$\overline{\mu}_\epsilon^j = \frac{2}{3}\pi\hbar(2j+1)\left[\int dr R_j(r) r\left(\frac{-\partial^2}{\partial r^2}+\frac{l(l+1)}{r^2}\right) r R_j(r) - \sum_{nl',n'l'',\text{all } m} \sqrt{l'_> l''_>} R_{j,n'l''} R_{j,nl'}\, \rho(n'l'', m_l, m_s; nl', m'_l, m'_s)\right.$$
$$\left.\times 3(-)^p \begin{pmatrix} l & 1/2 & j \\ m_l-\epsilon & m_s & -m_j \end{pmatrix}\begin{pmatrix} l & 1 & l'' \\ -m_l+\epsilon & -\epsilon & m_l \end{pmatrix}\begin{pmatrix} l' & 1 & l \\ -m'_l & \epsilon & m'_l-\epsilon \end{pmatrix}\begin{pmatrix} l & 1/2 & j \\ m'_l-\epsilon & m'_s & -m_j \end{pmatrix}\right], \quad (4)$$

where $p = m_l - m'_l + (l''-l')/2$; $\epsilon = +1, -1$, and 0 for the absorption of right-circular, left-circular, and z-axis polarized x rays; $l'_>$ is the larger of l or l'; n is the principal quantum number; $R_j(r)$ are radial wave functions; and dipole matrix elements, evaluated in the ∇ form, are $R_{j,nl'} = \int dr\, r R_j(r)\{\partial/\partial r - [l(l+1)-l'(l'+1)]/2r\} r R_{nl'}(r)$.

Equation (4) is the principal result because, given the density matrix for the ground state of any theoretical model, we can calculate experimentally measurable integrated intensities and thereby check the validity of that model. Furthermore, we can make some approximations to obtain sum rules, which show more explicitly the connection between integrated intensities and ground-state properties.

Here we neglect possible cross terms due to hybridization (e.g., between $3d$ and $4s$) because they are suppressed by the ratio of the dipole matrix elements $R_{j,l-1}/R_{j,l+1}$, and we suppose that only one nl shell is partly filled for each l. If we have several $l+1$ shells with non-negligible partial filling, then our sum rules can still be valid if the dipole matrix element for one transition nl' is much larger than the others.

The sum over all m for the completely filled shells can be done analytically. If we can make the assumption for the partly occupied shells that the transition amplitude to the one of them (nl') is much larger than to the others or that the density matrix elements for other shells are negligible, then we obtain

$$\overline{\mu}_\epsilon^j = \overline{\mu}_c^j + 2\pi\hbar(2j+1) l_> R^2_{j,nl'} \sum_{\text{all } m}[1-\rho(nl', m_l, m_s; nl', m'_l, m'_s)](-)^{m_l-m'_l}$$
$$\times \begin{pmatrix} l & 1/2 & j \\ m_l-\epsilon & m_s & -m_j \end{pmatrix}\begin{pmatrix} l & 1 & l' \\ -m_l+\epsilon & -\epsilon & m_l \end{pmatrix}\begin{pmatrix} l' & 1 & l \\ -m'_l & \epsilon & m'_l-\epsilon \end{pmatrix}\begin{pmatrix} l & 1/2 & j \\ m'_l-\epsilon & m'_s & -m_j \end{pmatrix}, \quad (5)$$

where $\overline{\mu}_c^j$ is a contribution that is independent of polarization. These matrix elements can be obtained from atomic calculations,

$$\overline{\mu}_c^j = \frac{2}{3}\pi\hbar(2j+1)\left[\int dr R_j^*(r) r\left(\frac{-\partial^2}{\partial r^2}+\frac{l(l+1)}{r^2}\right) r R_j(r) - \sum_{nl'j'}^{\text{occ}'} R^2_{j,nl'j'}\, l_>(2j'+1)\begin{Bmatrix} 1 & j' & j \\ 1/2 & l & l' \end{Bmatrix}^2\right], \quad (6)$$

where occ′ means the sum over fully occupied shells and the important partly occupied (nl') shell. The contribution from the $l \to l-1$ transitions is usually an order of magnitude less important and can often be neglected. However, we have enumerated the sum rules for both $l' = l \pm 1$. Usually we have only one partly filled nl shell, for which we can neglect the difference of the $nlj_\pm$ wave functions, where $j_\pm = l \pm 1/2$. These results imply that we can connect the j and ϵ dependence of the integrated absorption with ground-state values of various operators. From the six possible integrated intensities (three polarizations times two for $j_\pm$) we can extract six linearly independent operators $\hat{O}(j, l', \epsilon)$. These operators can be found upon substitution of the analytic expressions for the $3j$ symbols.[6] After tedious but straightforward algebra, we find that

$$\overline{\mu}_\epsilon^j = \overline{\mu}_c^j + \pi\hbar \frac{\langle \hat{O}(j, l', \epsilon)\rangle R^2_{j,nl'}}{(2l+1)^2(2l'+1)}, \quad (7)$$

where the expectation value $\langle \hat{O}(j, l', \epsilon)\rangle$ means

$$\langle \hat{O}(j, l', \epsilon)\rangle = \sum_{\text{all } m} \langle nl', m'_l, s, m'_s | \hat{O}(j, l', \epsilon) | nl', m_l, s, m_s\rangle \rho(nl', m_l, s, m_s; nl', m'_l, s, m'_s), \quad (8)$$

and $\hat{O}(j, l', \epsilon)$ are given in Table I as an operator expansion,

$$\hat{O}(j, l', \epsilon) = \sum_i c_i(j, l', \epsilon)\hat{O}_i, \quad (9)$$

where

$$\hat{O}_1 = \hat{\mathbf{l}} \cdot 2N_h l_>(2l+1)/(3N_e),$$
$$\hat{O}_2 = (-)^k l_z(2l+1),$$
$$\hat{O}_3 = l_z^2 - \hat{\mathbf{l}} \cdot l'(l'+1)/3,$$
$$\hat{O}_4 = 2l(l+1)[s_z + (-)^{k+1}(l_z \boldsymbol{l}\cdot\mathbf{s} + \boldsymbol{l}\cdot\mathbf{s}\, l_z)/l_>],$$
$$\hat{O}_5 = 2\boldsymbol{l}\cdot\mathbf{s}\, l(l+1)/l_>^2,$$
$$\hat{O}_6 = 2l_z \boldsymbol{l}\cdot\mathbf{s}\, l_z + (-)^{k+1} 2l_z s_z (l+1), \quad (10)$$

where all angular-momentum operators are in the units of $\hbar$, $k = (l+1-l')/2$, and N_e and N_h are the number of electrons and holes in the nl' shell. We note that normalized integrated cross sections can be defined by dividing out the radial matrix element, i.e.,

$$\chi_\epsilon^j = \frac{\overline{\mu}_\epsilon^j - \overline{\mu}_c^j}{2\pi\hbar R^2_{j,nl'}}. \quad (11)$$

Thus, making appropriate linear combinations, we can construct the following sum rules:

TABLE I. Coefficients $c_i(j,l',\epsilon)$ in the operator expansion $\hat{O}(j,l',\epsilon) = \Sigma_i c_i(j,l',\epsilon)\hat{O}_i$. The operators $\hat{O}_i$ are defined in the text [Eq. (10)], and $l_> = \max[l,l']$.

$i=$	1	2	3	4	5	6
$c_i(j_+,l',+1)$	$l+1$	$-(l+1)$	$-(l+1)$	$+1$	$-l(l+1)$	-1
$c_i(j_-,l',+1)$	l	$-l$	$-l$	-1	$+l(l+1)$	$+1$
$c_i(j_+,l',0)$	$l+1$	0	$2(l+1)$	0	$-2l_>^2$	$+2$
$c_i(j_-,l',0)$	l	0	$+2l$	0	$+2l_>^2$	-2
$c_i(j_+,l',-1)$	$l+1$	$l+1$	$-(l+1)$	-1	$-l(l+1)$	-1
$c_i(j_-,l',-1)$	l	l	$-l$	$+1$	$+l(l+1)$	$+1$

$$\rho = \frac{(\chi_+^{j_+} - \chi_-^{j_+}) + (\chi_+^{j_-} - \chi_-^{j_-})}{N} = \frac{(-)^{k+1}\langle l_z\rangle}{N_h\, l_>}, \tag{12}$$

$$\delta = \frac{(\chi_+^{j_+} - \chi_-^{j_+}) - (1+1/l)(\chi_+^{j_-} - \chi_-^{j_-})}{N} = \frac{\langle 2(l+1)[s_z + (-)^{k+1}(l_z\boldsymbol{l}\cdot\mathbf{s} + \boldsymbol{l}\cdot\mathbf{s}\, l_z)/l_>]\rangle}{N_h(2l+1)l_>}, \tag{13}$$

$$\gamma = \frac{(\chi_+^{j_+} + \chi_-^{j_+} - 2\chi_0^{j_+}) + (\chi_+^{j_-} + \chi_-^{j_-} - 2\chi_0^{j_-})}{N} = \frac{-3\langle l_z^2\rangle + l'(l'+1)N_e}{N_h(2l+1)l_>}, \tag{14}$$

$$\beta = \frac{(\chi_+^{j_+} + \chi_-^{j_+} - 2\chi_0^{j_+}) - (1+1/l)(\chi_+^{j_-} + \chi_-^{j_-} - 2\chi_0^{j_-})}{N} = \frac{-\langle 2(l_>^2-1)\boldsymbol{l}\cdot\mathbf{s} - 6l_z\boldsymbol{l}\cdot\mathbf{s}\, l_z + (-)^k 6(l+1)l_z s_z\rangle}{N_h(2l+1)l_> l}, \tag{15}$$

$$\alpha = \frac{(\chi_+^{j_+} + \chi_-^{j_+} + \chi_0^{j_+}) - (1+1/l)(\chi_+^{j_-} + \chi_-^{j_-} + \chi_0^{j_-})}{N} = \frac{-2(l+1)\langle\boldsymbol{l}\cdot\mathbf{s}\rangle}{N_h\, l\, l_>}, \tag{16}$$

$$N = (\chi_+^{j_+} + \chi_-^{j_+} + \chi_0^{j_+}) + (\chi_+^{j_-} + \chi_-^{j_-} + \chi_0^{j_-}) = N_h l_>/(2l'+1). \tag{17}$$

Following the classification of the six fundamental x-ray photoemission spectra,[7] we can assign names for the sum rules as follows: orbit (ρ), spin (δ), anisotropic orbit (γ), anisotropic spin magnetic (β), spin orbit (α), and isotropic (N). Note that for $l = 0$ we do not have j_- terms, and we need only use the three sum rules for ρ, γ, and N.

Thus the problem of the normalization in using the sum rules[3] can be overcome by using atomic calculations and absolute measurements of $\mu_{\pm,0}$. Note that in the first four sum rules we do not even have to know number of holes, nor do we need to calculate $\overline{\mu}_c^j$, because these factors cancel out in the final expressions. We just need the dipole matrix elements $R_{j,nl'}$ for filled states, which can be computed to high accuracy. The use of the last two sum rules does depend on the calculation of $\overline{\mu}_c^j$ and also on how well absorption from two edges can be separated. When two edges are very close in energy, the sum rule for α is probably useless because of the ambiguity in the separation of $\overline{\mu}_\epsilon^{j\pm}$.

The first two sum rules for ρ and δ are the same as in the original papers,[1,2] but they are corrected for the case when one cannot neglect the difference between the $j_\pm$ wave functions. An overall "$-$" sign in our formulas is due to our opposite definition of right- and left-circular polarization directions. We assume that light going in the positive z direction with right-circular polarization is the polarization causing the transition $\Delta m = +1$. This sign is important because otherwise values of $\langle L_z\rangle$ and $\langle S_z\rangle$ extracted from experimental values could have the wrong sign. In order to compare with Ref. 2, we have to express the operator $T_z = \Sigma_i t_{z,i}$ in terms of our operators. This can be done within one l shell as

$$(2l+3)(2l-1)\langle l,m_l,s,m_s|t_z|l,m_l',s,m_s'\rangle = \langle l,m_l,s,m_s| - 2l(l+1)s_z + 3[l_z(l\cdot s) + (l\cdot s)l_z]|l,m_l',s,m_s'\rangle. \tag{18}$$

Substituting this equation into the expression for δ in Ref. 2 for the $l \to l'$ transition ($c = l$, $l = l'$), we recover the same result.

The last four sum rules are new. These additional sum rules are useful when a measurement of μ_0 is also made, as is generally done in practice. The third and forth sum rules (γ and β) show that the assumption $\overline{\mu}_+ + \overline{\mu}_- = 2\overline{\mu}_0$ is generally invalid, even for integrated intensities. This equality can hold in special cases, however, e.g., for the model when the density matrix for an open shell is

$$\rho(m_l,m_s;m_l',m_s') = \delta_{m_l,m_l'}\delta_{m_s,m_s'}\delta_{m_s,1/2}N_e/(2l+1) \qquad [N_e < (2l+1)].$$

This model predicts all sums to be zero except the second and the last one. For Gd, which has a half-filled f shell with all spins up, this model should work and gives $\delta = -1/3$, in agreement with experiment and the prediction by Carra *et al.*,[2] who had to assume all spins down to get the same $-$ sign.

III. SUMMARY

We have derived a complete set of independent sum rules for polarization-dependent x-ray absorption based on the independent electron approximation and the dipole approximation for transition rates. Our results are

stated in terms of the ground-state density matrix. Thus they can also apply to extended systems, and accordingly the number of holes need not be an integer. The two previously derived sum rules for CMD are improved by the inclusion of dipole matrix elements. Four additional sum rules are derived, which illustrate the importance of the measurement of μ_0 to extract additional information about magnetic systems. We have also shown that the problem of the arbitrary range of integration in the previously derived sum rules can be overcome with the help of atomic calculations and absolute measurements. We do not make the additional assumption that radial matrix elements are constant for all transitions, as in Refs. 1 and 2. Instead, we assume that one partly filled shell is important, either because the transition amplitude to the other shells is much smaller or the occupation number of the other shells is small. This assumption is generally satisfied.

The main uncertainty in these sum rules comes from the $l \rightarrow l-1$ dipole transitions and the neglect of the quadrupole transitions for the heavier elements. Hybridization tends to increase this uncertainty, due to the even smaller power of the transition amplitudes ratio involved. The applicability of the sum rules can be checked with atomic or band-structure calculations.[3,4] Even if the conditions for approximate use of sum rules are not met, the integrated intensities can still be used to extract information about the density matrix and ground-state properties from Eq. (4), but the connection will not be as clear as that stated by the sum rules.

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