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Sum rules for X-ray magnetic circular dichroism spectra in strongly correlated ferromagnets

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Abstract. It is proven that the sum rules for X-ray magnetic dichroism (XMCD) spectra that are used to separate spin and orbital contributions to the magnetic moment are formally correct for an arbitrary strength of electron-electron interactions. However, their practical application for strongly correlated systems can become complicated due to the spectral density weight spreading over a broad energy interval. Relevance of incoherent spectral density for the XMCD sum rules is illustrated by a simple model of a ferromagnet with orbital degrees of freedom.

PACS. 78.70.Dm X-ray absorption spectra – 78.70.En X-ray emission spectra and fluorescence – 75.30.Mb Valence fluctuation, Kondo lattice, and heavy-fermion phenomena – 71.28.+d Narrow-band systems; intermediate-valence solids

X-ray magnetic circular dichroism (XMCD) [1,2] is a powerful technique to investigate both bulk and surface magnetic properties of materials. In particular, it allows to measure separately spin and orbital contributions to the magnetic moment of ferromagnets. Examples of numerous applications of this method are recent studies of magnetism in thin metallic films [3], cobalt nanoparticles and clusters [4], in magnetite Fe_3O_4 [5], and in dilute magnetic alloys [6]. A concrete way to separate the orbital and spin magnetic moments is using the XMCD sum rules [7, 8,2]

$$\begin{aligned} 3N_h \frac{\int d\omega (\Delta\mu_{L_3} - 2\Delta\mu_{L_2})}{\int d\omega (\mu_{L_3}^{tot} + \mu_{L_2}^{tot})} &= \langle S_z \rangle + 7 \langle T_z \rangle \\ 2N_h \frac{\int d\omega (\Delta\mu_{L_3} - 2\Delta\mu_{L_2})}{\int d\omega (\mu_{L_3}^{tot} + \mu_{L_2}^{tot})} &= \langle L_z \rangle \end{aligned} \quad (1)$$

where N_h is the number of holes in d -band, $\mu_{L_{2,3}}(\omega)$ are spectral intensities for $L_{2,3}$ spectra, $\Delta\mu$ is the difference between the spectra for left and right circularly polarized radiation and μ^{tot} is the total absorption intensity for unpolarized one, S_z , L_z and T_z are projections of the total spin, orbital moment and the spin dipole operator on the magnetization direction: $\mathbf{S} = \sum_i \mathbf{s}_i$, $\mathbf{L} = \sum_i \mathbf{l}_i$, $\mathbf{T} = \sum_i (\mathbf{s}_i - 3\mathbf{r}_i (\mathbf{r}_i \mathbf{s}_i) / r_i^2)$ with \mathbf{s}_i and \mathbf{l}_i being the spin and orbital moments for i -th electron, \mathbf{r}_i the coordinate operators.

A simple derivation of the XMCD sum rules in the independent electron approximation was presented in Ref. [9]. This derivation is based on a purely band picture of elec-

tron states in solids. The opposite case of strongly localized electrons which are characterized by atomic states with well-defined term and multiplet structure has been considered in Refs. [7,10] (a somewhat more simple derivation with the use of second quantization formalism for the atomic states was presented in the paper [8]). At the same time, many interesting systems such as magnetite [5] should be considered as strongly correlated systems demonstrating simultaneously both itinerant and localized features of “magnetic” electrons [11,12]. Actually, the sum rules are widely exploited by experimentalists for such systems as well. In this work we present a formal justification of this simple way to proceed. At the same time, we discuss separately contributions to the sum rules from coherent and incoherent parts of the electron spectral density. We demonstrate that a proper account of the incoherent (nonquasiparticle) contributions is necessary for consistent treatment of the XMCD spectra of strongly correlated systems.

The spectral intensity $\mu(\omega)$ of the X-ray absorption and emission spectra (XAS and XES, respectively) is determined in the dipole approximation by the imaginary part of the Green’s function [13,14]

$$\langle\langle \mathbf{p} \cdot \mathbf{e}^* | \mathbf{p} \cdot \mathbf{e} \rangle\rangle_\omega = e_\alpha^* e_\beta G_{\alpha\beta}(\omega) \quad (2)$$

$$G_{\alpha\beta}(\omega) = \langle\langle p_\alpha | p_\beta \rangle\rangle_\omega = -i \int_0^\infty dt e^{i\omega t} \langle [p_\alpha(t), p_\beta] \rangle \quad (3)$$

where \mathbf{e} is the photon polarization vector and \mathbf{p} is the momentum operator, α, β are the Cartesian indices and the brackets stand for the Gibbs average in the initial

state. For the case of XAS only the part of this operator works which corresponds to the transitions from core states $|a\rangle$ (with the annihilation operators b_a) to the conduction electron states $|\lambda\rangle$ created by operator c_λ^\dagger

$$p_\alpha^{(+)} = \sum_{a\lambda} \langle \lambda | p_\alpha | a \rangle c_\lambda^\dagger b_a, \quad (4)$$

and only the Hermitian conjugated part $p_\alpha^{(-)}$ works for the XES. For the case of L_2 (L_3) spectra a labels total moment projection for $2p_{1/2}$ ($2p_{3/2}$) states, correspondingly, and λ labels spin projection and orbital indices for $3d$ -electrons. Transitions to s -states, which are also allowed in the dipole approximation, are irrelevant for magnetism (in particular, they practically do not contribute to XMCD) and therefore will be neglected further.

It is important that Eqs.(3), (4) are formally exact irrespective to the degree of localization or delocalization of d -electrons. The use of the atomic representation for the states $|\lambda\rangle$ allows to obtain explicit expressions for the matrix elements $\langle \lambda | p_\alpha | a \rangle$ in terms of $3nj$ -symbols, fractional parentage coefficients and irreducible matrix elements [7, 8, 10]. However, for the derivation of the sum rules such a concretization is not necessary and using the λ -representation yields a simpler way to proceed. Actually, total intensities of the XAS for different photon polarizations which are needed to obtain the XMCD sum rules are determined by the integrals of the spectral density in the infinite limits. Due to the Kramers-Kronig relations, the latter are equal to

$$-\int_{-\infty}^{\infty} \frac{d\omega}{\pi} \text{Im} G_{\alpha\beta}(\omega) = \lim_{\omega \rightarrow \infty} [\omega \text{Re} G_{\alpha\beta}(\omega)] = \langle [p_\alpha, p_\beta] \rangle \quad (5)$$

Here we have used the equations of motion for the Green's functions [14]. On substituting Eq.(4) into the right-hand side of Eq.(5) one can see that the commutator contains just the one-particle density matrices which are expressed in terms of the corresponding anticommutator Green's functions:

$$\rho_{\lambda\lambda} = \langle c_\lambda^\dagger c_\lambda \rangle = - \int_{-\infty}^{\infty} \frac{dE}{\pi} f(E) \text{Im} \langle \langle c_\lambda | c_\lambda^\dagger \rangle \rangle_E \quad (6)$$

where $f(E)$ is the Fermi function; similarly we introduce the core density matrix

$$\rho_{a'a}^{\text{core}} = \langle b_a^\dagger b_a \rangle \quad (7)$$

Assuming that in the initial state the core electron states are completely occupied, i.e., $\rho_{a'a}^{\text{core}} = \delta_{a'a'}$, one can receive the expression for the total spectral weight (integrated intensity) of $L_{2,3}$ spectra:

$$\begin{aligned} \bar{\mu}_j &= 2\pi \sum_{m_j m \sigma m' \sigma'} \langle j m_j | l m \frac{1}{2} \sigma \rangle \langle l m \frac{1}{2} \sigma | \mathbf{p} \cdot \mathbf{e}^* \\ &\times (\hat{\mathbf{1}} - \hat{\rho}) \mathbf{p} \cdot \mathbf{e} | l m' \frac{1}{2} \sigma' \rangle \langle l m' \frac{1}{2} \sigma' | j m_j \rangle \end{aligned} \quad (8)$$

which differs from Eq.(2) of Ref. [9] only by the replacement of one-electron expression for the density matrix $\rho_{mm'}$ by the exact one. Here $l = 2, j = 1/2$ ($3/2$) for L_2 (L_3) spectra, m, m' and σ, σ' are the orbital and spin projections of d -electrons, respectively, m_j is the total moment projection for the core states. It is worthwhile to stress that using the orbital indices for itinerant electrons does not mean any approximation: for any particular method of band structure calculations it is always possible to re-expand the Wannier functions at a given site into the spherical harmonics. Thus the density matrix $\rho_{mm'}$ is in general a linear combination of the band structure occupation numbers with a proper symmetry. Since the total spin and orbital moment as well as the spin dipole operator are one-particle operators, their averages are completely determined by the density matrix. Further use of the Wigner-Eckart theorem to extract angular dependences of the matrix elements and transformations of the arising $3j$ -symbol products repeat the derivation in Ref. [9]. Therefore the XMCD sum rules (1) are formally valid without any restrictions.

On the other hand, the values of $\langle S_z \rangle$ and $\langle L_z \rangle$ obtained in band calculations can violate the sum rules. The calculation of the one-particle density matrix for strongly correlated systems remains a quite nontrivial problem. Generally, this quantity contains both coherent (quasiparticle) contributions which are formally connected with the poles of the Green's function and incoherent (nonquasiparticle) ones which are formally connected with the branch cuts [15]. In a number of cases (for example, for strongly correlated metals in the vicinity of the Mott transition or for doped Mott insulators [16]) the quasiparticle spectral density is much narrower than the incoherent one. One should be therefore careful to avoid a confusion of the incoherent part with a spectrum background.

In practice, the use of the XMCD sum rules for strongly correlated systems is not a completely well-defined procedure since it is impossible to integrate the spectral density in infinite limits. Atomic multiplet structure leads sometimes to much broader distribution of the spectral density in comparison with a standard band picture. This fact has been recently demonstrated [17] for the case of $(\text{La}, \text{Sr})\text{MnO}_3$ where the configuration-interaction calculations for Mn^{3+} ion gave the spectral density with the width of order of $6 \div 7$ eV, in comparison with the value $2 \div 3$ eV within the local density approximation (LDA) or LDA+U. At the same time, the energy separation between L_2 and L_3 spectra varies from $6 \div 8$ eV for the light $3d$ metals (Ti, V) to $15 \div 20$ eV for heavy ones (Co, Ni, and Cu). This means that for strongly correlated systems L_2 and L_3 spectra can overlap appreciably. The energy distribution of the atomic multiplet structure can be comparable with the spin-orbit splitting of the relevant core levels also for rare earth systems which leads to some problems with the practical applications of the XMCD sum rules in the latter case [18].

It is a common practice to interpret the core-level spectra for isolated atoms in terms of many-electron multiplet picture rather than one-electron quantum numbers

$|\lambda\rangle$ used above. These two approaches can be related via the representation of one-electron operators in terms of the Hubbard X-operators [19] $X^{\Gamma, \Gamma'} = |\Gamma\rangle\langle\Gamma'|$ where $\Gamma = \{nLSM\Sigma\}$ labels atomic configuration n , term LS and moment projections M, Σ :

$$c_{lm\sigma}^\dagger = \sum_{n\Gamma_n\Gamma_{n-1}} \sqrt{n} G_{\Gamma_{n-1}}^{\Gamma_n} \langle L_n M_n | L_{n-1} M_{n-1} l m \rangle \times \langle S_n \Sigma_n | S_{n-1} \Sigma_{n-1} \frac{1}{2} \sigma \rangle X^{\Gamma_n, \Gamma_{n-1}} \quad (9)$$

where $G_{\Gamma_{n-1}}^{\Gamma_n}$ are the fractional parentage coefficients (see Refs. [20, 21]). Eq.(9) enables one to reproduce the sum rules in the form yielding a detailed information concerning term and multiplet structure [7, 8, 10].

At the same time, for a solid the atomic description can be inappropriate. In particular, ferromagnetism itself is an essentially band phenomenon. Moreover, it cannot be properly described in the simplest Hubbard-I approximation [22] which assumes a formation of individual Hubbard subbands from separate transitions between the atomic levels. In particular, for a narrow-band ferromagnet we cannot satisfy the sum rules (kinematic relations) for the X-operators in this approximation.

To demonstrate this we consider a simple model of a narrow-band itinerant electron ferromagnet with orbital degrees of freedom which generalizes the standard infinite- U Hubbard model:

$$\mathcal{H} = \sum_{\mathbf{k}m\sigma} t_{\mathbf{k}m} X_{-\mathbf{k}}^{0,\sigma m} X_{\mathbf{k}}^{\sigma m,0} \quad (10)$$

where $t_{\mathbf{k}m}$ is the orbital-dependent band energy, $X_{\mathbf{k}}^{\alpha,\beta}$ is the Fourier transform of the Hubbard operators and 0 labels the hole state at a site.

For this model the exact sum rules should be satisfied for arbitrary m, σ :

$$\begin{aligned} \delta \equiv n_0 &= \langle X^{0,0} \rangle = \langle X_i^{0,\sigma m} X_i^{\sigma m,0} \rangle = \sum_{\mathbf{k}} \langle X_{-\mathbf{k}}^{0,\sigma m} X_{\mathbf{k}}^{\sigma m,0} \rangle \\ &= - \sum_{\mathbf{k}} \int_{-\infty}^{+\infty} \frac{dE}{\pi} f(E) \text{Im} \langle \langle X_{\mathbf{k}}^{\sigma m,0} | X_{-\mathbf{k}}^{0,\sigma m} \rangle \rangle_E. \quad (11) \end{aligned}$$

where δ is the concentration of current carriers (holes). The Hubbard-I approximation for this model reads

$$\langle \langle X_{\mathbf{k}}^{\sigma m,0} | X_{-\mathbf{k}}^{0,\sigma m} \rangle \rangle_E = [E - t_{\mathbf{k}m}(N_0 + N_{\sigma m})]^{-1}. \quad (12)$$

According to this expression, the quasiparticle pole for $\sigma = \downarrow$ corresponds to a narrowed band and lies (for the saturated ferromagnet case) above the Fermi level of the holes which obviously violates the sum rule (11). In fact, these sum rules are satisfied only due to incoherent (non-quasiparticle) states which are present below the Fermi level for the Hubbard model [23]. Similar to these papers one obtains for the minority-spin Green's functions in the leading order in small parameter δ

$$- \frac{1}{\pi} \text{Im} \langle \langle X_{\mathbf{k}}^{\downarrow m,0} | X_{-\mathbf{k}}^{0,\downarrow m} \rangle \rangle_E$$

$$= \sum_{\mathbf{q}m'} f(E_{\mathbf{k}-\mathbf{q}\uparrow m'}) \delta(E - E_{\mathbf{k}-\mathbf{q}\uparrow m'} + \omega_{\mathbf{q}mm'}). \quad (13)$$

where $E_{\mathbf{k}\uparrow m} = t_{\mathbf{k}m}(N_0 + N_{\uparrow m})$, $\omega_{\mathbf{q}mm'}$ are the frequencies of the corresponding spin-flip transitions. Thus we have 100% incoherent contribution to the spectral density below the Fermi level. As the hole concentration increases, the ferromagnetic state becomes non-saturated and a narrow quasiparticle minority-spin band occurs [24]. However, the main spectral density for this spin projection is still due to the nonquasiparticle contribution. This example demonstrates that, despite the XMCD sum rules for strongly correlated ferromagnets have formally a standard ‘‘one-electron’’ form, the energy distribution of the spectral weight can be drastically different from usual band picture.

The theoretical consideration [25] shows that the non-quasiparticle contributions to XES and XAS should be clearly observed. Moreover, such contributions should be considerably enhanced by the interaction with the core hole [25]. As well as for XES and XAS in general, the main nonquasiparticle effects in the XMCD are connected with the occurrence of the incoherent spectral density in the energy gap for the half-metallic ferromagnets [26]. These states arise either only below the Fermi energy (for the majority-gap half-metallic ferromagnets such as magnetite) or only above it (for the minority-gap half-metallic ferromagnets such as Heusler alloys or CrO_2); therefore they can be studied by XES and XAS methods, correspondingly. Whereas a standard band theory predicts 100% polarization for the conduction electron (or hole) states, the depolarization due to the nonquasiparticle states can be very strong (for example, in the infinite- U Hubbard model limit there is no polarization at all [23]). At the same time, *ab initio* calculations of the correlation effects for the half-metallic Heusler alloy NiMnSb give a rather small spectral weight of the nonquasiparticle states (about 4%) [27] and therefore it would be preferable to investigate them for the half-metallic ferromagnets with more strong correlations such as Fe_3O_4 (by XES) and CrO_2 (by XAS).

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