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Theoretical justification of ground-state moment analysis of magnetic dichroic x-ray absorption spectra for 3*d* transition metals

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A theoretical justification is given for the phenomenologically introduced method of ground-state moment analysis of magnetic dichroic x-ray absorption spectra of 3*d*-transition metals. This method allows us to determine in an element-specific manner ground-state moments such as, e.g., spin and orbital moments of atoms in solids, from the line shape of the dichroic spectra rather than from the use of sum rules. It may be used for early transition metals for which the spin-orbit coupling for the core states is so small that the L_2- and L_3-absorption spectra overlap and the sum rule analysis thus cannot be used.

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I. INTRODUCTION

The application of sum rules[1,2] for the analysis of experimental spectra of x-ray magnetic dichroism[3,4] (XMCD) has become a very powerful tool to extract in an element-specific manner the spin and orbital moments for systems with late 3*d*-transition metals such as Fe, Co, and Ni. In these systems there is a large spin-orbit splitting of the $2p_{1/2}$- and the $2p_{3/2}$-core states, and the L_2 and L_3 edges are well separated. This separation is a precondition for the determination of the spin momentum via the spin sum rule,[2] as the latter involves a weighted subtraction of the two energy-integrated spectra. For early 3*d*-transition metal atoms such as Cr or V the spin-orbit splitting is smaller, and this constitutes two problems.

(i) The $2p_{1/2}$- and $2p_{3/2}$-wave functions do no longer appear as pure core states, but there is a quantum mechanical mixing. As a result, the so-called branching ratio which qualifies the relative contributions of the $2p_{1/2}$ and $2p_{3/2}$ absorption, deviates from the "ideal" value. It is generally accepted that this mixing is due to a many-body effect, i.e., the Coulomb interaction between the core hole (created by the x-ray absorption) and the valence electrons, but there is also a single-electron contribution arising from the effect of the aspherical effective potential on the core states.[5] A simple phenomenological approach to obtain quantitative information from XMCD spectra on the core-state mixing in light transition metals has been suggested recently by Goering.[6]

(ii) The L_2 and L_3 edges overlap, and this renders the determination of the spin moment via the spin sum rule difficult or even impossible.

In the present paper we want to develop a method to obtain ground-state moments of the system, e.g., the spin and orbital moment, from the spectral shape of the absorption signal at the L_2 and L_3 edges rather than from the energy-integrated spectra (as in the sum rule analysis).

The idea to extract ground-state moments from the spectral shape has been introduced by van der Laan.[7] He considered single ions in a solid and neglected the effect of a crystal field exerted by the rest of the system on the electronic states of the ion as well as the hybridization of the electronic orbitals localized at various atomic sites, i.e., the band broadening. However, he took into account the splitting of the core levels with total angular momentum j into $2j+1$ sublevels by an effective exchange field, i.e., the contributions of the jm sublevels, convoluted with a Lorentzian, respectively, determine the shape of the absorption spectrum at the L_2 and L_3 edge. Van der Laan managed to represent the resulting spectrum in terms of ground-state moments, among which are the spin and the orbital moment. In metallic magnetic solids, however, the shape of the XMCD signal is much stronger influenced by the band broadening than by the exchange splitting of the core levels. Goering *et al.*[8] therefore have developed an intuitive approach called moment analysis in order to incorporate in a phenomenological manner the effect of the band broadening into van der Laan's model.

In the present paper, we represent the shape of the absorption signal in terms of single-electron expectation values of ground-state operators. The information on the type of the considered electronic system is completely given by the energy- and angular-momentum-resolved density matrix for the single-electron eigenstates. Specifying this density matrix further, we thus can treat on equal footing both, the case of an ionic model in a crystal field or the case of a metallic band magnet. The exchange splitting of the core levels, which gives only a minor contribution to the shape of the absorption signal for the late 3*d*-transition metals and which is hard to incorporate mathematically, will be neglected. It then will be shown that under certain preconditions the ground-state moments can be obtained from a fit to the experimental spectra. The calculations represent a theoretical justification of the general strategy of the moment analysis suggested intuitively by Goering *et al.*[8] although the details of the two fitting procedures are slightly different (e.g., because we neglected the exchange splitting of the core levels).

II. CALCULATIONAL PROCEDURE

Ankudinov and Rehr[9] have calculated the energy-integrated absorption coefficient for x rays within a single-electron description, thereby solving the involved angular-momentum recoupling problem by use of analytical expressions for $3jm_j$ symbols. They managed to represent the absorption coefficient in terms of single-electron expectation values of six ground state operators $\hat{\mathcal{O}}_i$.

In contrast, Carra *et al.*[2] started from a multiplet description to calculate the absorption coefficient for an ion, and they used graphical methods to solve the involved angular-momentum recoupling problems. They managed to represent the absorption coefficient by multiplet expectation values of eight ground-state operators $\hat{W}_0^{(xy)a}$ (see below), and the operators $\hat{\mathcal{O}}_i$ can be represented as linear combinations of the operators $\hat{W}_0^{(xy)a}$. These operators appear also in van der Laan's calculation[7] of the absorption spectrum for an ion in an effective exchange field, and in the intuitive phenomenological extension of van der Laan's theory by Goering *et al.*[8] to the case of band magnets, and in the resulting moment analysis of the XMCD spectra. Because we want to give a theoretical basis for the justification of such a moment analysis, we combine the single-particle approach of Ankudinov and Rehr[9] with the graphical techniques of Carra *et al.*[2] which leads to the involvement of the desired operators $\hat{W}_0^{(xy)a}$. Because the various steps of our calculation are analogous to the corresponding steps in Refs. 2, 7, and 9 we give only a short summary of our procedure.

We start with the general single-particle expression for the coefficient $\mu_q(\omega)$ as a function of frequency ω for the absorption of electromagnetic waves with polarization[10] q by electric dipole transitions from initial states $|i\rangle$ to final states $|f\rangle$,

$$\mu_q(\omega) = \frac{4\pi^2 m_e e^2}{c\,\hbar\,V}\,\omega \sum_i^{\text{occ}} \sum_f^{\text{unocc}} \langle i|r\hat{C}_q^{1^\dagger}|f\rangle\langle f|r\hat{C}_{-q}^{1}|i\rangle\,\delta(\omega-\omega_{fi}). \tag{1}$$

Here m_e and e denote the mass and the charge of the electron, c is the speed of the light, V is the volume of the sample, and $\hbar\omega_{fi}=E_f-E_i$ is the energy difference of the initial and final states $|i\rangle$ and $|f\rangle$, respectively. The operator $\hat{C}_q^1(\vartheta,\varphi)$ represents the normalized spherical harmonics with angular-momentum quantum number 1 and magnetic quantum number q

$$\hat{C}_q^1(\vartheta,\varphi) = \sqrt{\frac{4\pi}{3}}\,Y_q^1(\vartheta,\varphi). \tag{2}$$

In the following we represent the initial core states $|i\rangle$ by the eigenfunctions $|nhjm_j\rangle=|R_{nhj}\rangle|hjm_j\rangle$ of a spherically symmetric Hamiltonian including spin-orbit coupling, where n,h,j,m_j denote the principal quantum number, the orbital-momentum quantum number, the total angular-momentum quantum number, and the magnetic quantum number of the total angular momentum, respectively. Accordingly, we represent the final unoccupied valence states by the eigenfunctions $|n'lm_lm_s\rangle=|R_{n'l}\rangle|lm_lm_s\rangle$ of the spherically symmetric Hamiltonian without spin-orbit coupling, where n',l,m_l,m_s denote the principal quantum number, the angular-momentum quantum number, and the magnetic quantum number for the orbital and spin momentum, respectively.

For a simplification of Eq. (1) we perform the following approximations: Because we want to describe the L_2 and L_3 absorption, we have $n=2$ and $h=1$. For electric dipole transitions the angular momentum quantum number of the final state is $l=h\pm 1$. Thereby the contributions from the transitions $h\rightarrow l=h-1$ are usually an order of magnitude less important.

The first approximation is to neglect these contributions, and thus we have $l=2$. As a second approximation we consider only transitions to $n'=3$, $l=2$ but neglect transitions to d states with $n'>3$. In a third approximation we assume that j and m_j are good quantum numbers for the initial states, i.e., we neglect the mixing of the $2p_{1/2}$ and $2p_{3/2}$ states and the mixing of different m_j components by the aspherical part of the effective potential.

The initial and final states then may be written as

$$|i\rangle = \hat{c}_{jm_j}^\dagger|0\rangle, \tag{3a}$$

$$|f\rangle = \sum_{m_lm_s}\langle m_lm_s|f\rangle\hat{l}_{m_lm_s}^\dagger|0\rangle, \tag{3b}$$

where $\hat{c}_{jm_j}^\dagger$ and $\hat{l}_{m_lm_s}^\dagger$ are the creation operators for the states $|21jm_j\rangle$ and $|32m_lm_s\rangle$, and $|0\rangle$ is the vacuum state. Finally, we neglect the exchange-splitting of the initial core level with quantum number j into $2j+1$ sublevels, and therefore we can replace within Eq. (1) the quantity ω_{fi} in the argument of the δ function by ω_{fj}.

Representing $r\hat{C}_q^{1^\dagger}$ in second quantization, i.e.,

$$r\hat{C}_q^{1^\dagger} = \sum_{jm_j}\sum_{lm_lm_s}\langle 21jm_j|r\hat{C}_q^{1^\dagger}|32m_lm_s\rangle\hat{c}_{jm_j}^\dagger\hat{l}_{m_lm_s}, \tag{4}$$

decomposing the $|21jm_j\rangle$ state by means of Clebsch-Gordan coefficients into $|21m_hm_s'\rangle$ components where m_h and m_s' denote the angular-momentum quantum number and the corresponding magnetic quantum number, and using the Wigner-Eckardt theorem, (1) can be rewritten to

$$\mu_q(\omega) = \sum_j \mu_{j,q}(\omega), \tag{5a}$$

where[11]

$$\begin{aligned}\mu_{j,q}(\omega) \sim \omega \sum_{\substack{m_jm_h\\ m_j'm_h'}}\sum_{\substack{m_lm_s\\ m_l'm_s'}}\sum_i^{\text{occ}}\sum_f^{\text{unocc}}(-)^{1-q}(2j\\ +1)P_{1j2}^2\langle i|\hat{c}_{jm_j}^\dagger\hat{l}_{m_lm_s}|f\rangle\langle f|\hat{l}_{m_l'm_s'}^\dagger\hat{c}_{jm_j'}|i\rangle\\ \times\begin{pmatrix}1/2 & 1 & j\\ m_s & m_h & m_j\end{pmatrix}\begin{pmatrix}1 & 1 & 2\\ m_h & q & m_l\end{pmatrix}\begin{pmatrix}1/2 & 1 & j\\ m_s' & m_h' & m_j'\end{pmatrix}\\ \times\begin{pmatrix}1 & 1 & 2\\ m_h' & -q & m_l'\end{pmatrix}\delta(\omega-\omega_{fj})\end{aligned} \tag{5b}$$

represents the single j edges of the absorption spectrum. This may be compared to the expression (2) within Ref. 2.

In Eq. (5b) the expression in parenthesis is a $3jm_j$ symbol. Furthermore one has

$$P_{1j2} = \langle 1\|C^{1^\dagger}\|2\rangle R_{j2}^{23} \tag{6}$$

with the reduced matrix element and the radial matrix elements

TABLE I. The coupled tensor operators $\hat{W}^{(xy)a}$. The index η refers to the single electrons of the 3d shell.

$-\hat{W}_0^{(00)0}\sim$	$\sum_{\lambda\sigma}\hat{l}^{\dagger}_{\lambda\sigma}\hat{l}_{\lambda\sigma}=\hat{N}$	number operator
$-\hat{W}_0^{(11)0}\sim$	$\sum_{\eta}[\hat{\mathbf{l}}\cdot\hat{\mathbf{s}}]_{\eta}=\hat{\Gamma}_{ls}$	spin-orbit coupling
$-\hat{W}_0^{(01)1}\sim$	$\sum_{\eta}\hat{s}_{z,\eta}=\hat{S}_z$	total spin momentum
$-\hat{W}_0^{(10)1}\sim$	$\sum_{\eta}\hat{l}_{z,\eta}=\hat{L}_z$	total orbital momentum
$-\hat{W}_0^{(21)1}\sim$	$\sum_{\eta}\frac{1}{2}[\hat{\boldsymbol{\sigma}}-3\mathbf{r}(\mathbf{r}\cdot\hat{\boldsymbol{\sigma}})r^{-2}]_{z,\eta}=\sum_{\eta}[Q_{\mu\nu}\hat{\sigma}_{\nu}]_{z,\eta}=\hat{T}_z$	anisotropy of the spin distribution
$-\hat{W}_0^{(20)2}\sim$	$\sum_{\eta}\frac{1}{2}[3\hat{l}_z^2-\hat{\mathbf{l}}^2]_{\eta}=\hat{Q}_{zz}$	charge anisotropy
$-\hat{W}_0^{(11)2}\sim$	$\sum_{\eta}\frac{1}{2}[3\hat{l}_z\hat{s}_z-\hat{\mathbf{l}}\cdot\hat{\mathbf{s}}]_{\eta}=\hat{P}_{zz}$	$\hat{\mathbf{l}}\hat{\mathbf{s}}$ orientation
$-\hat{W}_0^{(31)2}\sim$	$\sum_{\eta}\frac{1}{4}[5\hat{l}_z(\hat{\mathbf{l}}\cdot\hat{\mathbf{s}})\hat{l}_z-(\hat{\mathbf{l}}^2-2)\hat{\mathbf{l}}\cdot\hat{\mathbf{s}}-(2\hat{\mathbf{l}}^2+1)\hat{l}_z\hat{s}_z]_{\eta}=R_{zz}$	$\hat{\mathbf{l}}\hat{\mathbf{s}}$ alignment

$$\langle 1\|C^{1^{\dagger}}\|2\rangle = 5\begin{pmatrix} 1 & 1 & 2 \\ 0 & 0 & 0 \end{pmatrix} \quad \text{and} \quad R^{23}_{j2}=\langle R_{21j}|r|R_{32}\rangle, \quad (7)$$

respectively.

The angular factor in Eq. (5b) given by summations over a product of four $3jm_j$ symbols has exactly the same structure as the corresponding angular factor in Eq. (2) of Ref. 2. From Eq. (5b) the j edges of the so-called dichroic spectra $\mu_j^{(a)}(\omega)$ can be obtained via linear combinations over the polarization index q including a $3jm_j$ symbol, i.e.,

$$\mu_j^{(a)}(\omega) := n_{1a}^{-1}\sum_{q}(-)^{1-q}\begin{pmatrix} 1 & a & 1 \\ -q & 0 & q \end{pmatrix}\mu_{j,q}(\omega),$$

where $n_{1a}:=\begin{pmatrix} 1 & a & 1 \\ -1 & 0 & 1 \end{pmatrix}$ is a normalization factor.

The quantity a now classifies the different types of dichroic spectra: $\mu_j^{(a=0)}=\mu_{j,1}+\mu_{j,0}+\mu_{j,-1}$ denotes the isotropic spectrum, $\mu_j^{(a=1)}=\mu_{j,1}-\mu_{j,-1}$ denotes the XMCD spectrum, $\mu_j^{(a=2)}=\mu_{j,1}+\mu_{j,-1}-2\mu_{j,0}$ denotes the spectrum of the x-ray magnetic linear dichroism (XMLD). Using the same graphical methods as in Ref. 2, the basic result for the j edges of the dichroic spectra is

$$\mu_j^{(a)}(\omega)\sim -n_{1a}^{-1}P_{1j2}^2\,\omega\sum_{xy}\zeta_j^{(xy)a}\sum_{f}^{\text{unocc}}\langle f|\hat{W}_0^{(xy)a}|f\rangle\delta(\omega-\omega_{fj}). \quad (8)$$

Within the coefficients

$$\zeta_j^{(xy)a}=(2j+1)(2x+1)(2y+1)(-)^{j+3/2}\begin{Bmatrix} 1 & 1/2 & j \\ 1/2 & 1 & y \end{Bmatrix} \times\begin{Bmatrix} 2 & 1 & 1 \\ 2 & 1 & 1 \\ x & y & a \end{Bmatrix}, \quad (9)$$

the expressions in the curly brackets denote the 6j and the 9j symbols, respectively. The quantities $\hat{W}_0^{(xy)a}$ are coupled tensor operators which are evaluated in Table I. The different sets $(xy)a$ of Table I are obtained via the conditions for nonvanishing coefficients $\zeta_j^{(xy)a}$.

Inserting Eq. (3b), Eq. (8) can be rewritten in terms of a density matrix which yields our final result for the dichroic spectra

$$\mu_j^{(a)}(\omega) \sim - n_{1a}^{-1} P_{1j2}^2 \omega \sum_{xy} \zeta_j^{(xy)a} \times \sum_{\substack{m_l m_s \\ m_l' m_s'}} \langle m_l m_s | \hat{W}_0^{(xy)a} | m_l' m_s' \rangle \varrho^{(j)}_{m_l m_l', m_s m_s'}(\omega), \tag{10}$$

where the quantity

$$\varrho^{(j)}_{m_l m_l', m_s m_s'}(\omega) := \sum_{f}^{\text{unocc}} \langle f | m_l m_s \rangle \langle m_l' m_s' | f \rangle \delta(\omega - \omega_{fj}) \tag{11}$$

is the energy- and angular-momentum resolved density matrix for the final valence states.

The physical character of the system (localized electrons, band electrons, etc.) is described by this density matrix. In the following section we will consider first the density matrix for a single ion with open $3d$ shell in a cubic crystal field. This will give us the general idea for a moment-analysis of the absorption spectra by a suitable approximation for the density matrix of a solid.

III. REPRESENTATION OF ABSORPTION SPECTRA VIA GROUND-STATE MOMENTS

To motivate the method of moment analysis of dichroic spectra, which we will suggest within this section, we first consider an isolated ion in a cubic crystal field. According to group theory, an unperturbed fivefold degenerate nd level with energy E_{nd} splits into a twofold degenerate level with energy E_{e_g} and a threefold degenerate level with energy $E_{t_{2g}}$ if the spherical symmetry is reduced to cubic symmetry. Within perturbation theory, the corresponding orbital parts of the eigenfunctions may be represented in terms of the eigenfunctions $|ndm_d\rangle$ of the unperturbed nd-shell (spin-orbit coupling is neglected for the moment)

$$|\varphi_1^{(e_g)}\rangle = |nd\ 0\rangle, \quad |\varphi_3^{(t_{2g})}\rangle = |nd+1\rangle,$$

$$|\varphi_2^{(e_g)}\rangle = \frac{1}{\sqrt{2}}(|nd+2\rangle + |nd-2\rangle), \quad |\varphi_4^{(t_{2g})}\rangle = |nd-1\rangle,$$

$$|\varphi_5^{(t_{2g})}\rangle = \frac{1}{\sqrt{2}}(|nd+2\rangle - |nd-2\rangle).$$

For the final states, including the spin functions, then one has $|f\rangle \in \{|\varphi_{1,2}^{(e_g)}\rangle |\bar{m}_s\rangle, |\varphi_{3,4,5}^{(t_{2g})}\rangle |\bar{m}_s\rangle\}$ and the corresponding density matrix reads[12]

$$\begin{aligned}\varrho^{(j)}_{m_l m_l', m_s m_s'}(\omega) = &\sum_{m_{e_g} \bar{m}_s}^{\text{unocc}} N_{m_{e_g}}^{-2} \delta_{m_{e_g} m_l} \delta_{m_l m_l'} \delta_{\bar{m}_s m_s} \delta_{m_s m_s'} \\ &- \delta(E_{e_g} - \omega - E_j) \\ &+ \sum_{m_{t_{2g}} \bar{m}_s}^{\text{unocc}} N_{m_{t_{2g}}}^{-2} \delta_{m_{t_{2g}} m_l} \delta_{m_l m_l'} \delta_{\bar{m}_s m_s} \delta_{m_s m_s'} \\ &- \delta(E_{t_{2g}} - \omega - E_j),\end{aligned} \tag{12}$$

with

$$m_{e_g} = 0, \pm 2, \quad \text{where } N_{m_{e_g}}^{-2} = \begin{cases} 1 & \text{for } m_{e_g} = 0, \\ \frac{1}{2} & \text{for } m_{e_g} = \pm 2, \end{cases}$$

$$m_{t_{2g}} = \pm 1, \pm 2, \quad \text{where } N_{m_{t_{2g}}}^{-2} = \begin{cases} 1 & \text{for } m_{t_{2g}} = \pm 1, \\ \pm\frac{1}{2} & \text{for } m_{t_{2g}} = \pm 2. \end{cases} \tag{13}$$

Inserting Eq. (12) into Eq. (10) yields

$$\mu_j^{(a)}(\omega) \sim - n_{1a}^{-1} P_{1j2}^2 \omega \sum_{xy} \zeta_j^{(xy)a} \left\{ \underbrace{\sum_{m_{e_g} \bar{m}_s}^{\text{unocc}} \sum_{m_l m_s} \langle m_l m_s | \hat{W}_0^{(xy)a} | m_l m_s \rangle N_{m_{e_g}}^{-2} \delta_{m_{e_g} m_l} \delta_{\bar{m}_s m_s}}_{=:\langle \hat{W}_0^{(xy)a} \rangle_{\text{unocc}}^{(e_g)}} \delta(E_{e_g} - \omega - E_j) + \underbrace{\sum_{m_{t_{2g}} \bar{m}_s}^{\text{unocc}} \sum_{m_l m_s} \langle m_l m_s | \hat{W}_0^{(xy)a} | m_l m_s \rangle N_{m_{t_{2g}}}^{-2} \delta_{m_{t_{2g}} m_l} \delta_{\bar{m}_s m_s}}_{=:\langle \hat{W}_0^{(xy)a} \rangle_{\text{unocc}}^{(t_{2g})}} \delta(E_{t_{2g}} - \omega - E_j) \right\}. \tag{14}$$

Obviously, for an ion in a cubic crystal field the situation is rather simple. The density matrix exhibits two peaks at the e_g and t_{2g} level and is diagonal with respect to the orbital angular momentum and spin quantum numbers. Accordingly, the absorption coefficient consists also of two peaks at these two energies, and their height is determined by the expectation values of the operators $\hat{W}_0^{(xy)a}$ evaluated with the unoccupied e_g and t_{2g} eigenfunctions, respectively.

The situation becomes more complicated when going from the isolated ion in a cubic crystal field to a cubic solid with finite bandwidth of the electronic states. Then, the density matrix is a continous function of the energy and is in general nondiagonal in the orbital angular momentum and spin quantum numbers. However, especially for the systems with small bandwidth, it is likely that the density matrix is distinctly peaked at some energies and that the angular momentum character of the density matrix is about the same $\xi^{(i)}_{m_l m_l',m_s m_s'}$, close to these peak energies.

We then can approximate the density matrix by

$$\varrho^{(j)}_{m_l m_l',m_s m_s'}(\omega) \approx \sum_f^{\text{unocc}} \langle f|m_l m_s\rangle\langle m_l' m_s'|f\rangle \delta(\omega-\omega_{fj})$$
$$= \sum_i \xi^{(i)}_{m_l m_l',m_s m_s'} \mathcal{D}^{(i)}(\omega+E_j-E_i). \qquad (15)$$

From now on all energies E_f, E_j, E_i are measured from the lower edge of the valence band. We thereby decomposed the total energy-resolved density of unoccupied states $\mathcal{D}(\omega+E_j)$ into contributions $\mathcal{D}^{(i)}(\omega+E_j-E_i)$ centered around the peak energies E_i, i.e.,

$$\mathcal{D}(\omega+E_j) = \sum_i \mathcal{D}^{(i)}(\omega+E_j-E_i) \qquad (16)$$

with

$$\int_{\text{unocc}} d\omega \mathcal{D}(\omega+E_j) = \sum_i \int_{\text{unocc}} d\omega \mathcal{D}^{(i)}(\omega+E_j-E_i) = \sum_i N_h^{(i)}$$
$$= N_h, \qquad (17)$$

where $N_h^{(i)}$ is the number of holes associated with $\mathcal{D}^{(i)}$ and N_h is the number of holes contained in the complete valence band. The function $\mathcal{D}^{(i)}$ then may be normalized according to

$$\mathcal{D}^{(i)}(\omega+E_j-E_i) =: N_h^{(i)} \mathcal{D}_N^{(i)}(\omega+E_j-E_i). \qquad (18)$$

In the following we neglect the difference of the quantities P_{1j2} for different j, which, according to Eqs. (6) and (7), means that we neglect the difference of the radial core wave functions $|R_{21j}\rangle$ for different j (as in Ref. 9).

Inserting Eqs. (15) and (18) into Eq. (10) then yields

$$\mu_j^{(a)}(\omega) \sim \omega \sum_{xy,i} \langle \hat{W}_0^{(xy)a}\rangle^{(i)}_{\text{unocc}} \Lambda^{(xy)a}_{i(j)}(\omega+E_j-E_i) \qquad (19)$$

with the profile functions

$$\Lambda^{(xy)a}_{i(j)}(\omega+E_j-E_i) =: n_{1a}^{-1} \zeta_j^{(xy)a} D_N^{(i)}(\omega+E_j-E_i). \qquad (20)$$

The quantities

$$\langle \hat{W}_0^{(xy)a}\rangle^{(i)}_{\text{unocc}} = \sum_{\substack{m_l m_s \\ m_l' m_s'}} \langle m_l' m_s'|\hat{W}_0^{(xy)a}|m_l m_s\rangle \xi^{(i)}_{m_l m_l',m_s m_s'} N_h^{(i)} \qquad (21)$$

are expectation values of the operators $\hat{W}_0^{(xy)a}$ evaluated with the unoccupied valence states corresponding to section i on the ω scale as follows from Eq. (8). The expectation value over the whole unoccupied part of the valence band thus is

$$\langle \hat{W}_0^{(xy)a}\rangle_{\text{unocc}} = \sum_i \langle \hat{W}_0^{(xy)a}\rangle^{(i)}_{\text{unocc}}. \qquad (22)$$

The desired ground state moments $\langle \hat{W}_0^{(xy)a}\rangle$, i.e., the expectation values of the operators $\hat{W}_0^{(xy)a}$ over the occupied part of the valence band are

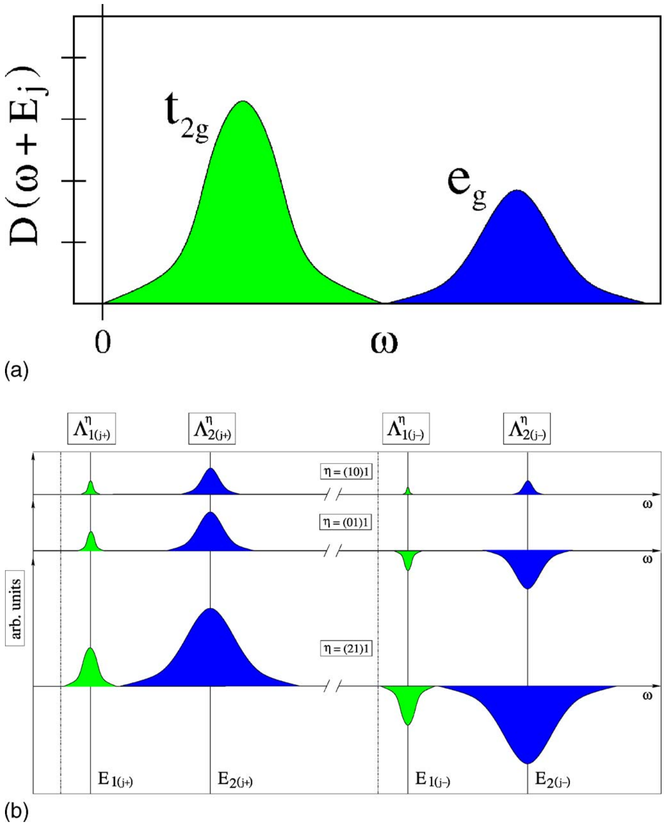

FIG. 1. (Color online) Schematic depiction of the profiles $\Lambda^{(xy)1}_{i(j)}$ for various (xy) for a model density of states curve with two distinct peaks. As an example on the left hand side a schematic density of states curve is shown for a cubic solid with small bandwidth. On the right hand side the onset of the L_3 and L_2 absorption, respectively, is marked by a dash-dotted horizontal line.

$$\langle \hat{W}_0^{(xy)a}\rangle = -\langle \hat{W}_0^{(xy)a}\rangle_{\text{unocc}} \qquad (23)$$

with the exception of $-\langle \hat{W}_0^{(00)0}\rangle$ which gives the number of electrons in the valence d-band and which is ten minus the number of holes.

IV. GROUND-STATE MOMENT ANALYSIS OF DICHROIC SPECTRA

Based on Eq. (19) we suggest the following fitting procedure to extract the ground-state moments from experimental dichroic spectra.

(i) Determine the energies E_i from the main peaks in the energy-resolved density of unoccupied d states $\mathcal{D}(\omega-E_j)$. This is simple if the density is available, either from *ab initio* calculations or from inverse photoemission experiments. If not, the positions of the main peaks of the experimental absorption spectrum $\mu_j^{(0)}(\omega)$ can be used, hoping that these coincide with the peak positions of the density of states.

(ii) Choose a spectral form for the normalized functions $D_N^{(i)}(\omega+E_j-E_i)$, e.g., a Gaussian or a Lorentzian function, with widths τ_i, respectively. Determine the quantities $N_h^{(i)}$ and τ_i by fitting the expression

$$\mathcal{D}(\omega+E_j-E_i)=\sum_i N_h^{(i)}\mathcal{D}_N^{(i)}(\omega+E_j-E_i,\tau_i) \tag{24}$$

to the energy-resolved density of states $\mathcal{D}(\omega)$. If the latter is not available we can fit the expression

$$\mu_j^{(0)}(\omega)\overset{!}{=}\omega\sum_i A^{(i)}\langle N_h^{(i)}\rangle\mathcal{D}_N^{(i)}(\omega+E_j-E_i,\tau_i) \tag{25}$$

to the experimental absorption spectrum, hoping that we can describe the absorption spectrum with the same functions $\mathcal{D}_N^{(i)}(\omega+E_j-E_i,\tau_i)$ as the density of states. Of course, the latter fit does not determine the quantities $N_h^{(i)}$ of Eq. (18), which, however, are not required anyway because later on we will fit the $\langle\hat{W}_0^{(xy)a}\rangle_{\text{unocc}}$ as given by Eq. (21) as whole entities which include the quantities $N_h^{(i)}$.

(iii) Calculate the profiles $\Lambda_{i(j)}^{(xy)a}(\omega+E_j-E_i)$ according to Eq. (20) and place them at the positions $E_{i(j)}=E_i-E_j$ on the ω scale, see Fig. 1. Logically, this corresponds to Fig. 1(b) of Ref. 7. As explained in Sec. I, in this reference the band broadening of the valence states has been neglected but the splitting of the core levels by an exchange field has been taken into account, whereas we neglect the exchange splitting but focus on the band broadening. Accordingly, our positions $E_{i(j)}$ correspond to the positions E_{jm} in Ref. 7. Finally, our step (iii) corresponds to the third step in the fitting procedure of Ref. 8 where the authors have positioned the whole set of exchange-split profiles of Ref. 7 at the peak energies E_i of the density of states. If they had neglected the exchange splitting, their third step would be equivalent to our step (iii).

(iv) The quantities $\langle\hat{W}_0^{(xy)a}\rangle_{\text{unocc}}^{(i)}$ are fitted to the experimental spectrum $\mu^{(a)}(\omega)=\Sigma_j\mu_j^{(a)}(\omega)$ according to Eq. (19), i.e.,

$$\mu^{(a)}(\omega)\sim\omega\sum_{xy,i}\langle\hat{W}_0^{(xy)a}\rangle_{\text{unocc}}^{(i)}[\Lambda_{i(j_+)}^{(xy)a}(\omega+E_{j_+}-E_i)+\Lambda_{i(j_-)}^{(xy)a}(\omega+E_{j_-}-E_i)]. \tag{26}$$

It is clear that such a fit is able to determine separate values for the various $\langle\hat{W}_0^{(xy)a}\rangle_{\text{unocc}}^{(i)}$ only if the profile functions in the square brackets are linearly independent for different $(xy)a$. As becomes obvious from Eqs. (19) and (20), this is not the case if $\zeta_{j_+}^{(xy)a}/\zeta_{j_+}^{(x'y')a}=\zeta_{j_-}^{(xy)a}/\zeta_{j_-}^{(x'y')a}$. This holds in case of XMCD for (01)1 and (21)1 as well as for (11)2 and (31)2 in case of XMLD. Then, the fits can yield just the sum $\langle\hat{W}_0^{(xy)a}\rangle_{\text{unocc}}^{(i)}+\langle\hat{W}_0^{(x'y')a}\rangle_{\text{unocc}}^{(i)}$.

(v) Determination of the ground-state moments according to Eqs. (22) and (23). The keypoint of the fitting procedure is that it requires neither the knowledge of $N^{(i)}$ nor the knowledge of $\xi_{m_l m_l', m_s m_s'}^{(i)}$ because the $\langle\hat{W}_0^{(xy)a}\rangle^{(i)}$ which contain these quantities are fitted as whole entities.

V. CONCLUSIONS

We have developed a procedure to determine the ground-state moments of a magnetic solid (e.g., spin and orbital moment) from the shape of dichroic x-ray absorption spectra $\mu_j^{(a)}(\omega)$ rather than by the use of sum rules. The method may be used for early transition metals with small spin-orbit coupling for which the spectra $\mu_j^{(a)}(\omega)$ for $j=j_-=1/2$ and $j=j_+=3/2$ overlap so that a sum rule analysis is not possible. Of course, it can also be used for a consistency check of the sum rules for late transition metals. A precondition for such a ground-state moment analysis is that there are sections on the ω axis for which the orbital character of the density matrix of the valence states varies only slowly with ω. For systems with rather well localized electronic states and hence rather small bandwidth and distinctly structured density of states this is well justified. Our paper yields the theoretical basis for a justification for the intuitive phenomenological method of ground-state-moment-analysis of E. Goering *et al.*[8] In Ref. 8 an explicite example for the practical use of the ground-state-moment-analysis of experimental data for an early transition metal, i.e., Cr in CrO_2, is given.

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[10] $q=\pm 1$ denotes waves with right and left circular polarization and $q=0$ denotes linear polarization along the z axis.

[11] The prefactor $-\frac{4\pi^2 m_e e^2}{c\hbar V}$ will be skipped from now on.

[12] The factor $\hbar$ will be skipped within the argument of the δ function from now on.