Limitation of the Magnetic-Circular-Dichroism Spin Sum Rule for Transition Metals and Importance of the Magnetic Dipole Term

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Magnetic-circular-dichroism (MCD) spectra and the spin magnetic dipole term ($\langle T_z \rangle$) for bulk 3d transition metals and their surfaces were calculated from full potential linearized augmented plane wave electronic band structure results. The recently proposed MCD spin sum rule is found to result in a much larger error [of up to 50% for the Ni(001) surface] than does its orbital counterpart. In support of recent experiments for bulk, we find that by combining the MCD orbital and spin sum rules the ratio of spin and orbital moments can be determined from the MCD spectra even for low dimension systems with an error of 10% when the $\langle T_z \rangle$ contribution is included.

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The possibility to determine both the orbital and spin moments (denoted as $\langle L_z \rangle$ and $\langle S_z \rangle$, respectively) directly from x-ray magnetic-circular-dichroism (MCD) [1–3] spectra by applying recently proposed simple but powerful MCD sum rules [4,5] has attracted considerable excitement and attention [6,7]. Since these sum rules have been derived from a single ion model, their validity for complex materials (e.g., transition metals) with strong multishell hybridization (excluded in the original derivation [4,5]) needs to be verified. We have previously confirmed the validity of the MCD orbital sum rule to within 10% for Fe systems in both ground and core-excited states within the local density energy band approach in which all the complexities of real materials are included [8]. In this Letter, we determine the MCD spectra for bulk Fe, Co, and Ni and their surfaces using state of the art local density energy band results and demonstrate that the effects from s, p states become much more important for the more recently derived MCD spin sum rule, which results in a large error to as much as about 50% for the Ni(001) surface. Instead, the ratio of spin and orbital moments can be determined even for reduced dimensional systems from the MCD spectra with an error of 10% by combining the MCD spin and orbital sum rules—as found in a recent experiment for bulk transition metals [9]. Significantly, we show for the first time that the directly calculated spin magnetic dipole term, which is an intrinsic part of the spin sum rule, is indeed important for atoms in a noncubic environment, such as at surfaces and interfaces.

As is well known, MCD measures the difference in absorption cross sections between left (σ_+) and right (σ_-) circularly polarized incident light at inner shell absorption edges in magnetic materials during the process of electric transitions from core states (i.e., 2p for L_3 and L_2 transitions in 3d transition metals) to the unoccupied valence states. As stated in the MCD sum rules [4,5], integrations of the MCD and total absorption spectra relate directly to $\langle L_z \rangle$, $\langle S_z \rangle$, and $\langle T_z \rangle$ for the unoccupied states

$$\frac{I_m = \int_{L_3+L_2} \sigma_m dE}{I_t = \int_{L_3+L_2} \sigma_t dE} = \frac{\langle L_z \rangle /2}{N_h = \int \rho(E) dE} \tag{1}$$

and

$$\frac{I_s = \int [\sigma_s = \int (\sigma_{m,L_3} - 2\sigma_{m,L_2})] dE}{I_t = \int_{L_3+L_2} \sigma_t dE} = \frac{\langle S_e \rangle = (\langle S_z \rangle + 7\langle T_z \rangle)/3}{N_h}, \tag{2}$$

where $\sigma_m = \sigma_+ - \sigma_-$ and $\sigma_t = \sigma_+ + \sigma_- + \sigma_z$. **T** is the spin magnetic dipole operator, i.e., $\vec{T} = \frac{1}{2}[\vec{S} - 3\hat{r}(\hat{r} \cdot \vec{S})]$, [$T_z = S_z(1 - 3\cos^2\theta)/2$ for $\vec{S}$ aligned along the z direction]. The number of valence holes, N_h, can be obtained from an integration over the unoccupied density of states [$\rho(E)$].

Before describing the first principles results, helpful physical insights can be obtained from a simple spin-orbit coupling perturbation model ($\mathrm{H_{SOC}} = \xi \mathbf{L} \cdot \mathbf{S}$). Listed in Table I are the values of σ_t, σ_s, σ_m, L_z, T_z, and S_e calculated analytically up to first order in ξ for the Slater-Koster d and s basis with minority spin ($S_z = -1$). Here, R_d and R_s denote the radial parts of the momentum matrix elements for d and s states, respectively; and $\alpha = \frac{\xi}{2(E_{d_{x^2-y^2}} - E_{d_{xy}})}$ and $\beta = \frac{\xi}{2(E_{d_{xz}} - E_{d_{yz}})}$. For d states, and independent of their angular momentum wave function character, we found the relations: (i) $\sigma_t = \frac{4R_d}{5}$; (ii) $\sigma_{mt} = \sum_{L_2,L_3} \sigma_m = \frac{4R_d}{5}\frac{L_z}{2}$; and

TABLE I. Values of σ_t, σ_s, σ_{mt}, L_z, T_z, S_z, and S_e for each Slater-Koster basis.

State	σ_t	σ_s	σ_{mt}	$L_z/2$	$7T_z$	S_z	S_e
$\mathbf{e_g}$							
$d_{x^2-y^2}$	$4R_d/5$	$-4R_d/5$	$-16\alpha R_d/5$	-4α	-2	-1	-1
d_{z^2}	$4R_d/5$	$4R_d/15$	0	0	2	-1	1/3
$\mathbf{t_{2g}}$							
d_{xy}	$4R_d/5$	$-4R_d/5$	$16\alpha R_d/5$	4α	-2	-1	-1
d_{xx}	$4R_d/5$	0	$-4\beta R_d/5$	$-\beta$	1	-1	0
d_{yz}	$4R_d/5$	0	$4\beta R_d/5$	β	1	-1	0
s	$5R_s/3$	$4R_s/3$	0	0	0	-1	$-2/3$

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(iii) $\sigma_s = \sigma_{m,L_3} - 2\sigma_{m,L_2} = \frac{4R_d}{5}S_e$. From (i) and (ii), we obtain the MCD orbital sum rule Eq. (1) [4] if only the d states are involved. Obviously, (i) and (iii) demonstrate the proportionality between the numerators and denominators on both sides of Eq. (2) for each d state and thus the MCD spin sum rule [5] is also a natural result of this simple single atom in a crystal field model.

Obviously, the validity of the sum rules is based on two assumptions: (i) the values of ξ, R_d, and R_s are energy independent, and (ii) there is no intershell hybridization, i.e., l is a good quantum number. It is known that both of these assumptions fail in real solids due to interatomic interactions. First, the wave function of a bonding state (lower in energy, with strong amplitude in the intermediate region between neighbors) has a larger spatial extension than that of an antibonding state (higher in energy, with a node in the intermediate region between neighbors). It turns out that the calculated R_d and ξ for Ni shown in Fig. 1 increase almost linearly by as much as about 30% from the bottom to the top of the d band and track each other perfectly in the whole energy range. This proportionality ensures the almost perfect tracking between σ_m and L_z shown in Fig. 2(a) for the Ni(001) surface layer since (i) L_z is proportional to ξ and σ_m is proportional to R_d, and (ii) the s,p states contribute to neither σ_m nor L_z.

By contrast, for the spin sum rule, while the contributions from d states to I_s and I_t ($\propto R_d$) are enhanced monotonically from the bottom to the top of the d band, each state (even s,p states) contributes equally to $\langle S_e \rangle$ and N_h independent of its energy. In addition, s,p contributions to I_s and I_t are almost negligible because, as shown in Fig. 1, R_s is much smaller in magnitude (by 50–60 times) than R_d. As a result, while the calculated σ_s and S_e for the Ni(001) surface layer in Fig. 2(b) track each other somewhat less well than do σ_m and L_z, although their proportionality still appears to hold. Much larger deviations can be found in Fig. 2(c) between $\rho(E)$ and σ_t due to either the effects of s,p states (above 0.5 eV) and the energy dependence of R_d (below -1.3 eV).

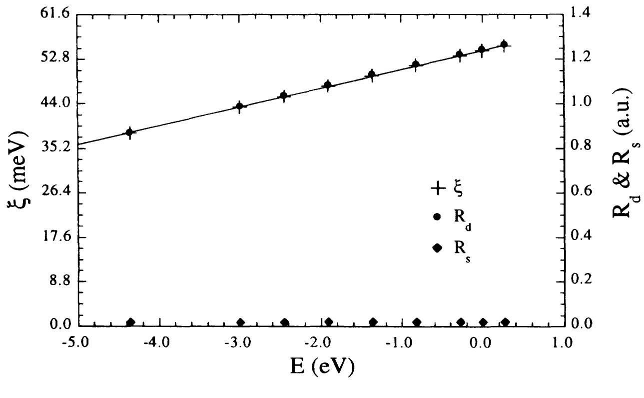

FIG. 1. The calculated energy dependence of ξ, R_d, and R_s for the Ni(001) surface layer.

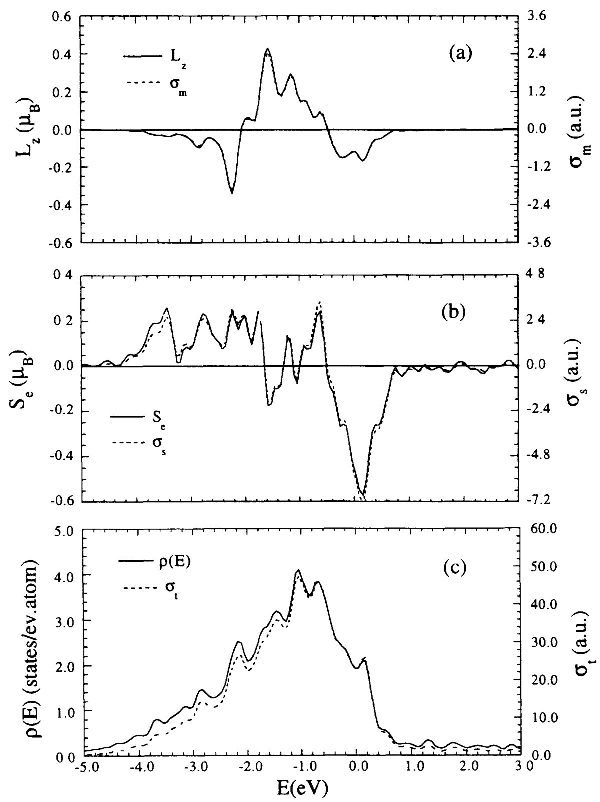

FIG. 2. The calculated energy dependencies of (a) L_z and σ_m, (b) σ_s and S_e, and (c) σ_t and $\rho(E)$ for the Ni(001) surface layer. Zero energy denotes the position of E_F.

To examine in detail the possible validity of the spin sum rule, we carried out the energy integrations for the numerators and denominators of Eq. (2). As before [8], an upper integration limit of 6 eV above E_F is adopted for the integrals. The lower-limit of the integrations, i.e., E_F, is employed as a parameter with zero denoting the position of the real Fermi level. The calculated results for I_t, N_h, I_s, and $\langle S_e \rangle$ are plotted in Fig. 3(a) for the Ni surface layer. The scaling factor (γ) for I_s and I_t, which is obtained by fitting a linear function of $\sigma_m = \gamma L_z/2$, is 12.0 for Ni. This factor decreases for Co ($\gamma = 11.1$) and Fe ($\gamma = 10.0$), however, it is insensitive to changes in environment for a given transition metal as found in our recent calculations for interfaces such as Co/Pd(001). For the denominators, the N_h and I_t curves exhibit a clear separation even from 3 eV above E_F due to the accumulation of the deviation between $\rho(E)$ and σ_t in the higher energy region [cf. Fig. 2(c)]. This result indicates the importance of the high-lying s,p states. Quantitatively, as denoted in Table II by $R_1 = \frac{I_s}{I_t} / \frac{\langle S_e \rangle}{N_h} - 1$, the application of the spin sum rule results in much larger errors, up to 52% for the Ni surface.

Obviously, the hybridization between different l shells is the main mechanism causing the failure of the MCD spin sum rule for the transition metals. This can be seen from Fig. 3(b), where all the quantities presented in Fig. 3(a) were recalculated without s,p contributions. In

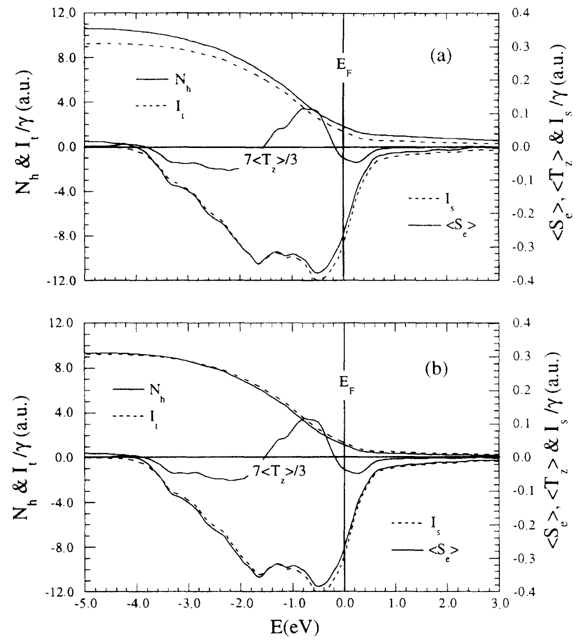

FIG. 3. The calculated energy dependencies of N_h and I_t (left scale) and I_s, $\langle T_z\rangle$, and $\langle S_e\rangle$ (right scale) for the Ni(001) surface layer from (a) all states and (b) *d* states only. Zero energy denotes the position of E_F.

such a *model* situation, the agreement between I_t and N_h and I_s and $\langle S_e\rangle$ becomes much better, especially in the energy range above E_F. As a result, the error of the MCD spin sum rule can be reduced to within 10% even for the Ni surface. Note that the *s*, *p* effects are a serious problem not only for Ni, but also for Co and even Fe. We found that the ratio between the numbers of *s*, *p* and *d* holes can be 40%–50% for Ni systems, and remains as much as 20% and 15% for Co and Fe, respectively. For Co and Fe, as also listed in Table II, the errors of the MCD spin sum rule are still sizable—up to 25% and 15%, respectively. Furthermore, the energy dependence of R_d also brings in some additional errors for Fe.

TABLE II. Calculated values of $\langle L_z\rangle$, $\langle S_z\rangle$, $\langle T_z\rangle$, $\langle S_e\rangle$, N_h, and sum rule errors $R_1 = \frac{I_s}{I_t}/\frac{\langle S_e\rangle}{N_h} - 1$ and $R_2 = \frac{I_m}{I_s}/\frac{\langle L_z\rangle}{2S_e} - 1$ for Ni(001), Co(0001), and Fe(001) surface (*S*) and bulklike center (*C*) layers.

Atom	$\langle L_z\rangle$[a]	$\langle S_z\rangle$	$7\langle T_z\rangle$	$\langle S_e\rangle$	N_h	R_1	R_2
Ni(*S*)	−0.069	−0.67	−0.082	−0.250	1.81	0.52	−0.10
Ni(*C*)	−0.051	−0.62	−0.027	−0.215	1.66	0.36	−0.11
Co(*S*)	−0.090	−1.61	0.240	−0.457	2.60	0.24	−0.09
Co(*C*)	−0.078	−1.52	0.014	−0.502	2.55	0.22	−0.10
Fe(*S*)	−0.111	−2.71	0.230	−0.828	3.70	0.16	−0.04
Fe(*C*)	−0.063	−2.10	0.028	−0.691	3.34	0.15	−0.09

[a] See Ref. [11].

We have previously [8] emphasized the need for proper energy cutoff for the integrations in order to eliminate the error introduced by the high lying energy states. Further, since I_m and $\langle L_z\rangle$ were found to be strictly proportional, we suggested the use of absolute absorption cross-section measurements as a means to eliminate errors introduced by the denominators in the orbital sum rule. Now as shown above, it is again the errors in the denominators that cause most of the error in the spin sum rule. Thus, another way to eliminate the errors due to the denominators is to combine the $\langle L_z\rangle$ and $\langle S_z\rangle$ sum rules, as was done recently in some experiments on bulk transition metals [9]. We indeed find that the applicability of the MCD sum rules can be improved by combining Eqs. (1) and (2) as

$$\frac{I_m}{I_s} = \frac{\langle L_z\rangle}{2\langle S_e\rangle}. \tag{3}$$

From our first principles calculations, we found that the error for Eq. (3), denoted in Table II by $R_2 = \frac{I_m}{I_s}/\frac{\langle L_z\rangle}{\langle S_e\rangle} - 1$, is now 10% or so for all systems studied. Unfortunately, Eq. (3) cannot provide $\langle L_z\rangle$ and $\langle S_e\rangle$ separately, but only their ratio. One may argue that $\langle S_e\rangle$ can be considered to be known or can be obtained easily using other techniques by assuming that (i) the $\langle S_z\rangle$ for the *unoccupied* states is equal in magnitude to the usual spin magnetic moment $\langle S_z'\rangle$ for the *occupied* states and (ii) the T_z term is negligible. In fact, $\langle S_z\rangle$ is not necessarily equal to $\langle S_z'\rangle$ due to the induced *s*, *p* magnetization; the calculated $\langle S_z\rangle$ is usually about 5% smaller than $\langle S_z'\rangle$, especially for Fe.

For the $\langle T_z\rangle$ term, we found from Table I that, although the sum of T_z over the whole *d* band or over the t_{2g} and e_g subsets (each separately degenerate in O_h symmetry) is zero, the T_z term is very large for each *d* state. Therefore, the $\langle T_z\rangle$ term is negligible only for atoms with cubic symmetry (cf. Table II for "bulk" atoms labeled *C*). For atoms in noncubic environments such as surfaces and interfaces, T_z should be a strong oscillatory function over the *d* band. Indeed, as shown in Fig. 4, from the first

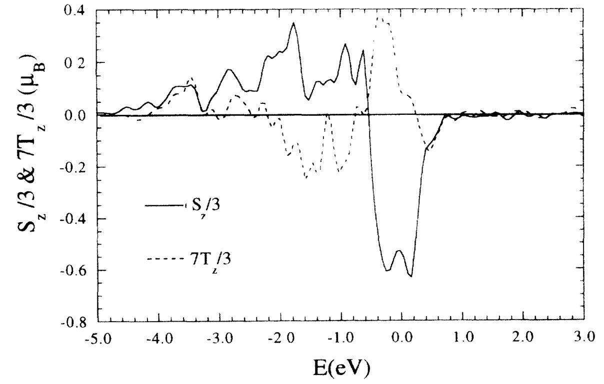

FIG. 4. The calculated energy dependencies of S_z and T_z for the Ni(001) surface layer. Zero energy denotes the position of E_F.

principles FLAPW results for S_z and T_z obtained for the Ni surface, the amplitude of $7T_z/3$ is almost as large as $S_z/3$. Obviously, the proportionality established between σ_s and S_e in Fig. 2(b) will fail completely without T_z. Even the integrated value of $7\langle T_z \rangle/3$, shown in Fig. 3, is clearly not negligible at the Ni surface. Quantitatively, as seen from Table II, while the $\langle T_z \rangle$ term remains small for bulk atoms, its importance is obvious at surfaces since its magnitude becomes 8.5%, 12%, and 15% of $\langle S_z \rangle$ at E_F for Fe(001), Ni(001), and Co(0001), respectively. Thus, first principles determinations of both the MCD spectra and ground state properties (e.g., S_z and T_z, etc.) are necessary for interpreting experimental results on surfaces and interfaces using Eq. (3).

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