First Principles Investigation of the Validity and Range of Applicability of the X-Ray Magnetic Circular Dichroism Sum Rule

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X-ray magnetic circular dichroism (MCD) spectra and orbital angular momentum, $\langle L_z \rangle$, for transition metal bulk and surfaces were studied for both ground state and core hole excitations using a highly precise local density approach. For Fe(001), we predict a double peak structure in both the MCD and total absorption spectra and a strong enhancement of $\langle L_z \rangle$. Surprisingly, the MCD orbital sum rule is found to be valid to within (5–10)%. Finally, the results suggest possible solutions to several problems faced in applying the MCD sum rule to measure $\langle L_z \rangle$.

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The observation of soft x-ray magnetic circular dichroism (MCD) by Schütz *et al.* [1] in 1987, followed by important experimental and theoretical work [2–7], has led to the establishment of MCD as an exciting, and in some respects unique, new powerful tool for investigating the magnetism of transition and rare-earth metal systems. Compared to other techniques, the high element selectivity of MCD is especially useful for identifying the magnetism from different specific atoms (e.g., in alloys, as impurities, at surfaces or interfaces, etc.) [8]. It also offers potential applications for element-specific magnetic microscopy [9]. Recently, as a result of a new magneto-optical sum rule derived for x-ray MCD [10], considerable interest has centered on these measurements as the only practical way to determine the orbital angular momentum, $\langle L_z \rangle$, in bulk and reduced dimensional systems. Thus, for example, it has been used to detect the enhancement of the orbital magnetic moment at Co/Pd interfaces [11]. This powerful sum rule, however, was derived from a simple model system, namely, a single ion in a crystal field with the valence shell only partially filled. Thus, as emphasized by several authors [3, 8], there is still some question as to the validity and range of applicability of this sum rule to real condensed matter systems such as transition metals with their strongly hybridized multiband structure.

In this Letter, we report results of a detailed local density energy band study of the x-ray MCD spectra in several transition metal bulk and surface systems in which both ground state and core excitations (treated as a supercell impurity) are investigated. The sum rule is found to be valid to within (5–10)%, the error being due to *s*-*d* hybridization. Thus any further deviations from the sum rule may be attributed to additional many-body effects. We also address several problems faced by experimentalists in applying the MCD sum rule and offer suggestions and possible solutions. Some MCD results are presented for the Fe(100) surface which provide a test of our electronic structure approach.

As is well known, MCD measures the difference in absorption between right- and left-circularly polarized incident light during the process of electric transitions from core states to unoccupied valence states. Because of the spin-orbit coupling (SOC) between valence states, the MCD signals of σ_m $(=\sigma_+ - \sigma_-)$ for the L_2 and L_3 absorption edge for $3d$ transition metals no longer cancel each other as they do in the absence of SOC where the integrated L_2 and L_3 signals are equal and opposite. Here, σ_+ and σ_- represent the absorption cross sections for left- and right-circularly polarized light, respectively. Stated as a sum rule, MCD and total absorption spectra were found to be directly related to the small average orbital magnetic moment $\langle L_z \rangle$ for each atom [10]. Specialized for transitions from $2p$ core states, it is

$$\frac{I_m = \int_{E_F}^{E} (\sigma_+ - \sigma_-) dE|_{L_3+L_2}}{I_t = \int_{E_F}^{E} (\sigma_+ + \sigma_- + \sigma_0) dE|_{L_3+L_2}} = \frac{\langle L_z \rangle}{2N_h}. \tag{1}$$

Here N_h is the number of holes, σ_0 is the absorption cross section for light linearly polarized along the magnetization direction, and E is some energy cutoff. Some problems associated with applying the sum rule include: (i) the choice of N_h, which is not a well defined quantity in solid state since the concept of a shell no longer exists; (ii) the range of integration for the absorption, for which there is no clear meaningful cutoff.

As a check of the validity of the sum rule for real systems with many bands and strong hybridization, we have carried out separate calculations of the numerators and denominators on both sides of Eq. (1)—all of which are well established conceptually in the local density energy band approach. We employ a second-variational procedure to treat the SOC, in which the wave functions of the unperturbed states, namely $|\psi^i\rangle = \sum_j c_j^i |\phi^j\rangle$ (where $|\phi^j\rangle$ is the augmented plane wave basis in semirelativistic calculations), are used as basis functions to expand the SOC Hamiltonian. In this approach, the matrices of the non-SOC Hamiltonian, H^0, are already in a diagonalized

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form. Since the off-diagonal matrix elements from the SOC are very small (usually a few meV), a much smaller energy cutoff (e.g., 0.5 Ry above E_F) can be adopted in the diagonalization of eigenvalue equation

$$(H_{ij}^0 + \xi \mathbf{s}\cdot\mathbf{L})|C_j\rangle = \lambda|C_j\rangle \tag{2}$$

with a perturbed wave function, $\psi_i' = \sum_j C_j^i \psi^j$. [From the perturbed wave functions, $\langle L_z\rangle$ can be evaluated as $\langle L_z\rangle = \int_k \sum_{imn} C_m^{i*} C_n^i (L_z)_{mn}$.] This procedure has proved to be very efficient in calculating magnetocrystalline anisotropy [12]. More importantly, it allows us to treat the effects of SOC for many interesting real materials by drastically reducing the computing time compared to the fully relativistic approaches [13].

To calculate the MCD spectra from first principles, we first determine the energy dependence of the difference between σ_+ and σ_-. For electric dipole transitions from core to valence bands,

$$\sigma_{\pm(0)}(E) = \frac{8\pi^2}{3}\int_k |\langle\psi_c|p_{\pm(z)}|\psi_v'\rangle|^2 \delta(E_v - E_c - E)\,dk, \tag{3}$$

and in the second variational procedure described above we have

$$\langle\psi_c|p_n|\psi_v'\rangle = \sum_{j,k} C_j^v c_k^j \langle\psi_c|p_n|\phi_k\rangle, \quad n = \pm, z. \tag{4}$$

A summation over 36 k points in the 1/8 irreducible 2D Brillouin zone is employed for the k space integration. The angular and spin momentum parts in Eq. (4) result in the well-known selection rules: $\Delta l = \pm 1$, $\Delta m = \pm 1$, $\Delta s = 0$.

We have investigated x-ray MCD in bulk and surface Fe, Co, and Ni using the full-potential linearized augmented plane wave (FLAPW) method for thin films with the SOC treated in the second variational way outlined above. For clarity and because of space limitations, we concentrate here on the results obtained for Fe. Figure 1(a) shows the energy dependence of the σ_n calculated separately for the L_2 and L_3 edges at the center ("bulk") layer of a seven layer Fe(001) slab. The main peaks show that overall the relation $\sigma_0 = \frac{1}{2}(\sigma_+ + \sigma_-)$ holds for bulk Fe and even more so when an energy integrated value is used.

We see structure above the main peaks and a tail that extends to high energy—also shown for the total absorption cross section in Fig. 1(b). (Since the local density approach may not be valid at these high energies, these results must be viewed cautiously.) By contrast, the MCD spectrum in Fig. 1(b) converges quickly in energy and shows two well separated peaks for L_3 and L_2. The small positive peak at the onset of the L_3 peak arises from the small number of majority spin holes in Fe; it does not appear in the spectra for Co and Ni. We shall see later that, as expected, it also does not appear in the MCD spectra for the surface layer (cf. Fig. 2).

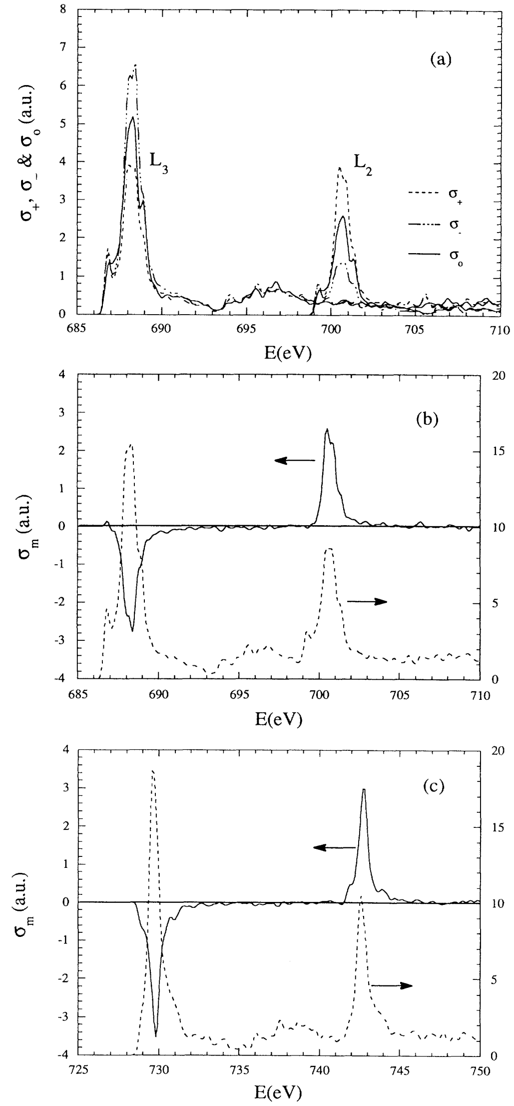

FIG. 1. The calculated energy dependencies of (a) cross sections σ_+ (dashed line), σ_- (dash-dotted line), and σ_0 (solid line); (b) MCD signal σ_+-σ_- (solid line) and total absorption (dashed line) for the center layer of Fe(001); and (c) core hole supercell calculations for σ_+-σ_- (solid line) and total absorption (dashed line) for the center layer. Spectra were Gaussian broadened by 0.2 eV (here and in Fig. 3).

The main L_2 and L_3 MCD peaks are almost structureless even with a small Gaussian broadening width (0.2 eV)—unlike the relativistic tight binding results for Fe presented earlier and attributed to a breakdown of the local density approach [7].

In order to determine the effects on the spectra of a photoinduced core hole, we have carried out separate self-consistent $c(2\times 2)$ supercell calculations for a $2p$ hole localized in the center layer of the seven layer bcc Fe(001) slab. The effects of the core-hole impurity are found to

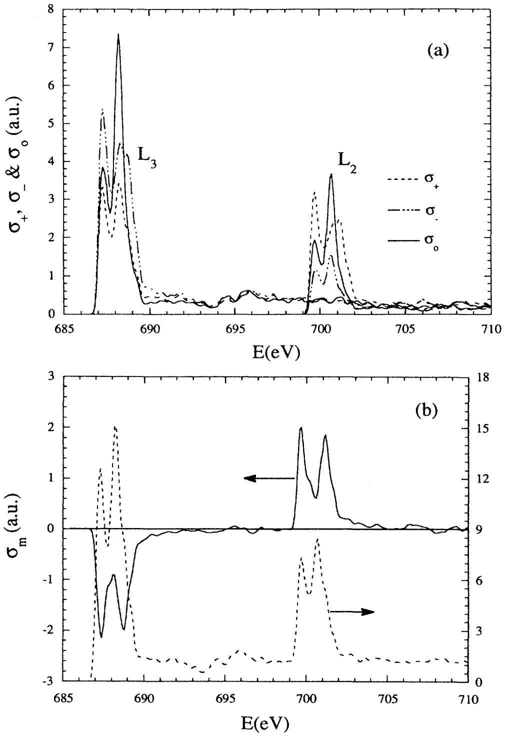

FIG. 2. The calculated energy dependencies of (a) cross sections σ_+ (dashed line), σ_- (dash-dotted line), and σ_0 (solid line); (b) MCD signal σ_+-σ_- (solid line) and total absorption (dashed line) for the surface layer of Fe(001).

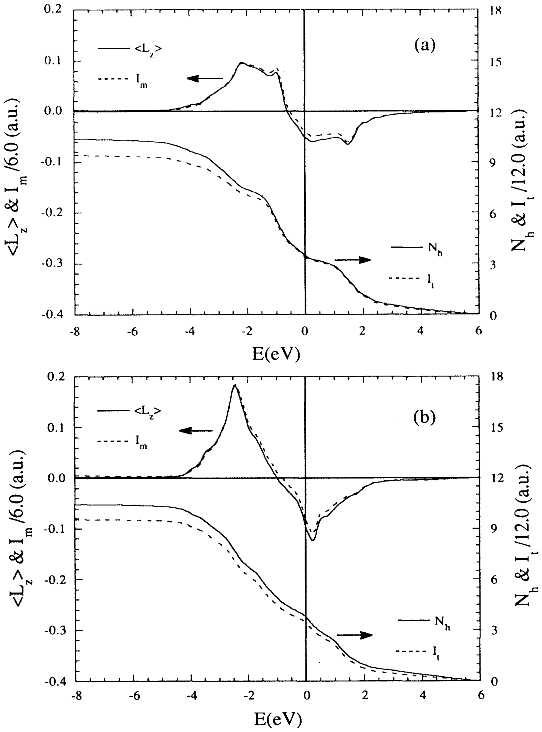

FIG. 3. The dependence of the integrated quantities $\langle L_z \rangle$ (solid line, left scale), I_m (dashed line, left scale), N_h (solid line, right scale), and I_t (dashed line, right scale) on the band filling in (a) for the center layer and (b) for the surface layer of Fe(001). $E = 0$ corresponds to the position of the physical E_F.

decay very quickly to almost zero at its second-neighbor site—indicating that the cell size used here is sufficient. Surprisingly, while the density of states, magnetic moment (to $1.84\mu_B$), and local valence charge density are strongly affected, the core hole does not significantly affect the profile of the MCD spectra as shown in Fig. 1(c), except for the removal of the small positive peak at the onset of the L_3 peak. By contrast, the shoulder peak in the total absorption curve is removed because, unlike the case for MCD spectra, the contributions from the two spin parts have the same sign. Note that the core-hole overshifts the $2p$ binding energy due to the weakened screening of the nuclear attraction; it also increases the $2p_{\frac{3}{2}}$ and $2p_{\frac{1}{2}}$ SOC energy difference (by 0.6 eV to 12.9 eV—which is now very close to the experimental value, 13.0 eV). Because of the core-hole relaxation, one should not simply compare the LDA eigenvalues with the excitation energy through use of Koopman's theorem, as shown in Fig. 1, but use the difference of the total energy determined self-consistently for the initial and the final states. In this way, the calculated excitation energies are 702.9 eV and 715.8 eV for the L_3 and L_2 adsorption edges, respectively—agree very well with the measured values of 707 eV and 720 eV for bulk Fe [5, 7].

The effects at the surface layer in bcc Fe(001) are shown in Fig. 2(a). Unlike the case of the center layer (or "bulk"), the generally assumed relation [11] $\sigma_0 = \frac{1}{2}(\sigma_+ + \sigma_-)$ does not hold for the surface layer since the z direction is no longer equal to the x, y directions. The high peak of σ_0 over the σ_+ and σ_- indicates the separation of the $d_{xz,yz}$ states (with a large contribution to σ_0 but a very small contribution to MCD) from the d_{xy} state (no contribution to σ_o, large contribution to MCD). Further, there is some splitting of the L_3 and L_2 peaks not seen in the center layer case. This structure becomes dramatically clear as two distinct peaks in both L_3 and L_2, as shown in Fig. 2(b) for MCD and total absorption, and so represents a striking prediction for either experimental confirmation or rejection.

To investigate the validity of the MCD sum rule and to obtain a deeper meaning of the physics involved, the four quantities that appear as numerators and denominators in Eq. (1) are considered as a function of band filling (in the rigid band sense). Thus, we extend the starting point of the integration to have E_F range from the bottom of the valence band and fix the upper-limit of E to be 6 eV. For I_m and I_t we sum the contributions from L_3 and L_2. Figure 3 compares $\langle L_z \rangle$ with a scaled I_m (the MCD signal) and N_h with a scaled I_t (the total absorption) as a function of band filling. We see from Fig. 3 that in the physically interesting region, i.e., for E_F around zero, the proportionality between both numerators and both denominators—hence the sum rule—holds to within 10%.

There are two assumptions in the derivation of the sum rule [10]: (i) the radial matrix elements are constant for all transitions, and (ii) no hybridization exists between different l shells (i.e., l is a good quantum number). As is well known, both assumptions fail in real materials and thus weak $s, p-d$ hybridization (which affects both assumptions) is important for the validity of the sum rule. (In fact, by eliminating in model calculations the effects of $s, p-d$ hybridization on the calculated L_z and adsorption spectra, the error in the sum rule can be reduced further to $< 5\%$.) Since the effects of s, p states are inherent in the real materials and thus in the experimental spectra, an *arbitrary* cutoff is needed for the integrations in order to stay within the d band region.

Indeed, it is this cutoff that insures the validity of the sum rule as seen from Fig. 3(a): While $\langle L_z \rangle$ and I_m quickly approach zero with an almost zero slope above 4 eV, this is not the case for N_h and I_t whose slope is obviously not zero at the arbitrary energy cutoff of 6 eV [cf. the high energy tail in Figs. 1(b) and 2(b)]. However, with this cutoff, N_h and I_t remain almost parallel to each other, and hence the sum rule holds. For energy cutoffs above 6 eV, the deviation between these two curves becomes larger and the sum rule gradually fails as more and more s, p states become involved.

Obviously, s, p effects for the I_m is weak due to either the selection rule (p states) or the cancellation between the two spin parts (s states). Thus, we can thus use the MCD curves to derive a criterion to determine the range of the d bands for the integration of the total absorption: terminate the integration for the I_t where the MCD counterparts become acceptably close to zero for both L_3 and L_2. In fact, this criterion has already been used in experiments [8, 11] by determining the energy cutoff for the I_t according to the MCD spectrum using a spline-fit and a step function subtraction. Now we know that this procedure serves to eliminate the contributions from high lying s and p states (or continuum states) and thus ensures the validity of the sum rule.

For the Fe(001) surface layer, as plotted in Fig. 3(b), the proportionality between both the numerators and the denominators holds with the same scaling factor as the center layer—indicating the insensitivity of the radial part of the integration in Eq. (4) to the change of environment. Indeed, it is quite striking how the I_m values track the $\langle L_z \rangle$ curve even for this large change in shape and value of $\langle L_z \rangle$. Now, if we assume that this scaling factor between I_m and $\langle L_z \rangle$ is the same in other Fe systems, then it may be possible to determine $\langle L_z \rangle$ merely from the measured MCD signal, I_m, without the uncertainties involved in obtaining the normalization factors, I_t and N_h. Such a proportionality is also found for Co and Ni, but each with its own scaling factor. This may well indicate the possible universal nature of the scaling. While very difficult to perform, absolute absorption cross section measurements are now being undertaken.

Compared to the center layer, the surface band is narrowed which results in an enhanced SOC between the valence states. As a result, the shape of the $\langle L_z \rangle$ curve is significantly narrowed and its peak value is significantly enhanced over that for the center layer. For Fe(001), the $\langle L_z \rangle$ at E_F is $0.095\mu_B$ for the surface layer—and is enhanced by 80% from the bulk value ($0.055\mu_B$). These values agree with a previous linearized muffin-tin orbital calculation [14] in the atomic sphere approximation, i.e., $0.12\mu_B$ and $0.05\mu_B$ for the surface and the center layer of Fe(001). The 20% difference for the surface layer arises from our full potential treatment at the surface.

In conclusion, this first precise local density energy band study has focused on the validity and range of applicability of the MCD sum rule to measure $\langle L_z \rangle$ in transition metal systems. It has identified some problems associated with applications of the sum rule and has offered some suggestions and potential solutions. The local spin density band structure approach appears to offer a valuable means (i) to address some important problems in the developing field of MCD, (ii) to provide clear physical insight and guidance for the analysis and interpretation of MCD spectra, and (iii) to predict magneto-optical properties of bulk and low dimensional systems which may be important for both the basic science and application of the MCD technique to the development of high density magneto-optical storage.

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