Real-space multiple-scattering theory of XMCD including spin-orbit interaction in scattering process

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Abstract. The effects of the spin-orbit interaction on surrounding atoms for XMCD spectra are studied by a real-space multiple-scattering theory. The present numerical calculation for Fe $K$-edge XMCD spectra from BCC iron demonstrates the importance of the spin-orbit interaction on scattering atoms, which has been disregarded in previous works. These effects will be inevitable for $K$-edge XMCD analyses of light elements surrounded by heavy magnetic atoms.

1. Introduction
XMCD spectra of light elements have been measured to study spintronic materials and nanostructures such as graphene/Ni(111) [1]. For a bulk system, O $K$-edge XMCD intensity was also obtained in CrO$_2$ [2]. To observe XMCD signals, both the spin-orbit interaction (SOI) and spin polarization are inevitable. In case of the X-ray absorption by light elements like carbon, XMCD are still observed, which implies the importance of electron scattering by heavy magnetic element like Fe. Fujikawa et al. [3, 4] developed a real-space multiple-scattering (MS) XMCD theory with relativistic corrections: they neglected the SOI except that on the X-ray absorbing atom. This approximation does not work well for the XMCD spectrum of light elements. Although MS codes already include relativistic effects on all sites [5, 6, 7], influence of the SOI on scattering sites was not studied intensively for XMCD spectra. Before the investigation of complicated systems including light elements, we carefully study the SOI on surrounding atoms, and numerically calculate Fe $K$-edge XMCD spectra for BCC iron.

2. Theory
The absorption intensity $I(\omega, m_p)$ for the incident photon energy $\omega$ with the helicity $(m_p = \pm 1)$ of circularly polarized X-rays is written as [4]

$$ I(\omega, m_p) = -2\text{Im} \langle c | H^1_{ep}(m_p) g_D(\varepsilon) H_{ep}(m_p) | c \rangle $$

$$ = T_{11}(\omega, m_p) + T_{12}(\omega, m_p) + T_{21}(\omega, m_p) + U_{11}(\omega, m_p) + \cdots $$

$$ U_{11}(\omega, m_p) \sim -2\text{Im} \langle \varphi_c | \Delta^* (m_p) g(\varepsilon) \delta V g(\varepsilon) \Delta (m_p) | \varphi_c \rangle $$

where $g_D(\varepsilon)$ is the one-electron Dirac Green’s function with the photoelectron energy $\varepsilon$, $H_{ep}(m_p)$ is the electron-photon interaction operator with the photon helicity $m_p$, and $| c \rangle$ is the 4-spinor...
core orbital. As demonstrated by Gestztesy et al. [8], \( g_D(\varepsilon) \) is expanded by the correlated non-relativistic Green’s function \( g(\varepsilon) \), which yields \( T_{11}, T_{12}, T_{21} \) and \( U_{11} \). The intensity \( T_{11} \) corresponds to the term in the non-relativistic limit. It does not contribute to the \( K \)-edge XMCD intensity because the 1s\(_{1/2} \) core state, and the final state (pholectron) in \( T_{11} \) have no SOI. The intensities \( T_{12} \) and \( T_{21} \) reflect some relativistic effects only on the absorbing atom. The intensity \( U_{11} \) includes SOI \( \delta V \) for the photoelectron state as shown \((3)\). The large component \( [\varphi_c] \) of the 4-spinor \( |c\rangle \) is influenced by \( \Delta_{mp} \), the electron-photon interaction operator in the 2-spinor form. The total SOI \( \delta V \) can be separated into each atomic site contribution as \( \delta V \sim \sum_\alpha \delta v_\alpha \), where \( \delta v_\alpha \) is the SOI on the site \( \alpha \). Then, we derive MS expansion for \( U_{11} \). If we go beyond this perturbation prescription, the SOI should be renormalized and embedded in full MS paths.

The non-relativistic Green’s function \( g(\varepsilon) \) is expanded in terms of the site-\( t \) matrix \( t_\alpha(=v_\alpha+v_\alpha g_0 t_\alpha) \):

\[
g = (1 - \delta_{ab}) g_b v_\alpha g_a + g_a + g_b \sum_{\alpha(\neq a,b)} t_\alpha g_a + g_\beta \sum_{\beta(\neq a,b)} t_\beta g_0 + \sum_{\alpha(\neq a)} t_\alpha g_a + \cdots
\]  

(4)

The site-\( t \) matrix \( t_\alpha \) describes the full inner atomic scattering at the \( \alpha \) site without the SOI. The first term vanishes when the \( a \) and \( b \) sites represent the same site, for instance, the absorbing atom in the case of the X-ray absorption intensity calculation. The intensity \( U_{11} \) is separated into the non-scattering and scattering terms as \( U_{11} = U_{11,A} + U_{11,sc} \), where \( A \) is the absorbing site. The intensity \( U_{11,A} \) includes the SOI on \( A \) in non-scattering processes: the photoelectron is affected by the SOI when it initially goes out from or finally comes back to \( A \). This term has already been derived in references [3, 4]. On the other hand, \( U_{11,sc} \) involves the SOI on scattering sites which include \( A \). The scattering term \( U_{11,sc} \) is written as

\[
U_{11,sc}(m_p) = -\frac{2}{\pi} \text{Im} \sum_{\sigma} \rho_\sigma^2 \left( u_{m_p,\sigma}^{GG} + u_{m_p,\sigma}^{ZG} + u_{m_p,\sigma}^{Z\prime} \right)
\]

(5)

\[
u^{GG}_{m_p,\sigma} = \sum_{B(\neq A)} \sum_{L} G_{1m_p,\sigma}^{AB,L} \left( m\sigma \left\{ [\xi_B^{\sigma}]_{L}^{jj} - 4ik[\langle \xi_B^{\sigma}\rangle_{B_l}^{jj} - 4k^2[\langle \xi_B^{\sigma}\rangle_{B_l}^{jj}] \right\} \right) G_{B,1m_p}^{BA,\sigma}
\]

(6)

\[
u^{ZG}_{m_p,\sigma} = \sum_{B(\neq A)} \sum_{L} Z_{1m_p,\sigma}^{AB,L} \left( m\sigma \left\{ 2[\xi_B^{\sigma}]_{B_l}^{Rj} - 4ik[\langle \xi_B^{\sigma}\rangle_{B_l}^{Rj}] \right\} \right) G_{B,1m_p}^{BA,\sigma}
\]

(7)

\[
u^{Z\prime}_{m_p,\sigma} = \sum_{\alpha} \sum_{L} Z_{1m_p,\sigma}^{AA,\alpha,L} \left( m\sigma \left\{ \xi_{\alpha}^{\sigma}\right\}_{RR} \right) Z_{L,1m_p}^{\alpha A,\sigma}
\]

(8)

The spin index \( \sigma \) is \(+(-)\) for the up (down) spin of the photoelectron, \( \rho \) is the dipole radial integral and \( k \) is the momentum of the photoelectron. The propagator \( G_{B,1m_p}^{BA} \) corresponds to the photoelectron migration from \( A \) with angular momentum \((1, m_p)\) to \( B \) with \( L \), while \( Z_{1m_p,L}^{AA} \) describes the migration from \( A \) to \( \alpha \) with MS from double scattering up. We note that \( G \) is arisen from the first and second terms of the expansion described by eq. (4), which are the zeroth order of \( t \). In addition, the atomic potential \( v \) in eqs. (6) and (7) is not replacement of site-\( t \) matrix, but comes from \( g_B v_B g_A \) in eq. (4). The sandwiched terms \((\cdots)\) by \( G \) or \( Z' \) describe overlaps between the photoelectron wavefunction and the SOI on a scattering site. The radial integrals \([\cdots]\) are written as

\[
[\xi_{\alpha}^{\sigma}]_{l}^{\varphi_1 \varphi_2} = \int dr r^2 \varphi_{1,l}(kr)\xi(r)\varphi_{2,l}(kr)_{\alpha,\sigma}
\]

(9)

\[
[(\xi_v)^{\sigma}]_{l}^{\varphi_1 \varphi_2} = \int dr dr' r^2 r'^2 \varphi_{1,l}(kr)\xi(r)R_l(kr_\alpha)_{\alpha,\sigma}f_l(kr_\alpha)v(r')\varphi_{2,l}(kr')
\]

(10)
$$
[(vξv)_α]^{σ_2} = \left[ \int dr' dr'' r'^2 r''^2 \right. \\
\times \left. \varphi_1 j(kr)v(r)R_l(kr_<)f_l(kr_>)(kr_<)R_l(kr'_<)f_l(kr'_>)v(r'')\varphi_2 j(kr'') \right]_{α,σ} \quad (11)
$$

where $ξ$ is the radial part of the SOI. The wavefunctions $φ_1$ and $φ_2$ are the spherical Bessel function $j$ or the numerical regular solution $R$. The $R$ and numerical irregular solutions $f$ in $[(ξv)]$ and $[(νξν)]$ describe the intra atomic propagation between $ξ$ and the atomic potential $ν$. The integral variables $r_{<}(>)$ and $r'_{<}(>)$ represent the $max(min)(r, r')$ and $max(min)(r', r'')$, respectively. We numerically check the effect of the scattering site SOI in the next section.

3. Results & Discussion

We calculate Fe $K$-edge XMCD for BCC iron to investigate the contribution of the SOI on scattering sites. We adopt the muffin-tin potential for phaseshift calculations. The cluster to calculate MS matrices includes 113 atoms within a 7 Å distance from the absorbing atom. XMCD spectra are obtained by $ΔI = I(+) - I(-)$ under the antiparallel magnetization to the incident X-rays. XMCD intensity is obtained in percentage of a main peak one of a corresponding XAS spectrum (not shown).

![Figure 1](image1.png)

**Figure 1.** Calculated Fe $K$-edge XMCD spectra for BCC iron. Three different approximations are used: the SOI in all processes (red solid), in only non-scattering processes (green dashed) and in only scattering processes (blue dotted) are considered. The experimental result (gray dot) is shown for comparison [9].

![Figure 2](image2.png)

**Figure 2.** Calculated XMCD spectra for the components of $U_{sc}$: $U_{GG}$ (red dashed), $U_{Z'G}$ (green dots) and $U_{Z'Z'}$ (blue chain). The scattering term $U_{sc}$ (gray solid) is also shown for comparison.

Figure 1 shows the calculated Fe $K$-edge XMCD spectra for three different approximations: the SOI in all processes, in only non-scattering processes and in only scattering processes are considered for the XMCD calculations. The scattering term corresponds $ΔU_{sc} = U_{sc}(+) - U_{sc}(-)$. The non-scattering term is obtained by $ΔU_A + 2ΔT_{12}$, which includes the usual non-SOI MS [4]. In Fig. 1, the scattering term is comparable in intensity to the non-scattering term. Although the calculated spectra need to a scale factor to be compared with the experimental one [9], the all processes spectrum is improved by the scattering one. These indicate that the SOI on scattering sites is still important for $K$-edge XMCD spectra of transition metals. Figure 2 shows XMCD spectra for the components of $ΔU_{sc}$. The component $U_{GG}$ is obtained by $U_{GG} = -\frac{1}{\pi} im \sum_\sigma \rho_\sigma U_{GG}^{\frac{1}{2}}$. The components $U_{Z'G}$ and $U_{Z'Z'}$ are also obtained similarly.
All components of $\Delta U_{sc}$ have comparable in intensity to $U_{sc}$. The previous calculation of the single SOI scattering showed negligibly weak XMCD, and suggested that the weak XMCD is attributed to the absence of exchange (site-$t$ matrix) scattering [3]. However, the single SOI scattering $U^{GG}$ is not negligible, and comparable in intensity to $U^{ZG}$ and $U^{Z'G}$ which include the exchange scattering in $Z'$ as shown in (7) and (8). To understand this discrepancy, we investigate the components of $U^{GG}$ in (6).

Figure 3 shows radial integrals which compose $U^{GG}$. In Fig. 3, $I_3 \left(\left[\left(\xi v\right)_{jj}\right]\right)$ is considerably large compared with the other terms. Because $\xi$ is the gradient of the atomic site potential $v$, $\xi$ is strong only near the nucleus. The free photoelectron described by the $j$ function has small amplitude near the nucleus. Then, $\left[\xi\right]_{jj}$ and $\left[\xi v\right]_{jj}$, which include the direct overlap between $\xi$ and $j$, are negligible. The result for $\left[\xi\right]_{jj}$ is the same as the previous result [3]. On the other hand, the potential $v$ can intermediate and enhance the overlap between the $j$ function and $\xi$ in $\left[\left(\xi v\right)_{jj}\right]$. Thus, $U^{GG}$ gives the comparable XMCD intensity. Similarly, $U^{ZG}$ \left(\left[\left(\xi v\right)_{Rl}\right]\right)$ and $U^{Z'G}$ \left(\left[\left(\xi\right)_{Rl}\right]\right)$ are also enhanced by $v$: the $R$ function already includes the effect of $v$, and has relatively larger amplitude near the nucleus than the $j$ function. This indicates that the photoelectron should be affected by the attractive potential $v$ and the SOI $\xi$ simultaneously.

The present numerical calculations for Fe $K$-edge XMCD clearly show the importance of the SOI on scattering sites, which was not specifically studied before. This result should be important for the XMCD analyses in case that a light absorber is surrounded by rather heavy atoms.

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