Relativistic many-body XMCD theory including core degenerate effects

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Abstract. A many-body relativistic theory to analyze X-ray Magnetic Circular Dichroism (XMCD) spectra has been developed on the basis of relativistic quantum electrodynamic (QED) Keldysh Green’s function approach. This theoretical framework enables us to handle relativistic many-body effects in terms of correlated nonrelativistic Green’s function and relativistic correction operator Q, which naturally incorporates radiation field screening and other optical field effects in addition to electron-electron interactions. The former can describe the intensity ratio of $L_2/L_3$ which deviates from the statistical weight (branching ratio) 1/2.

In addition to these effects, we consider the degenerate or nearly degenerate effects of core levels from which photoelectrons are excited. In XPS spectra, for example in Rh 3d sub level excitations, their peak shapes are quite different: This interesting behavior is explained by core-hole moving after the core excitation. We discuss similar problems in X-ray absorption spectra in particular excitation from deep 2p sub levels which are degenerate in each sub levels and nearly degenerate to each other in light elements: The hole left behind is not frozen there. We derive practical multiple scattering formulas which incorporate all those effects.

1. Introduction

Many-body X-ray Absorption Fine Structure (XAFS) theory has been developed on the basis of many-body scattering theory [1, 2] and Keldysh Green’s function theory [3, 4, 5] in the framework of non-relativistic theory. In contrast to XAFS analyses, the relativistic effects are crucial in the analyses of XMCD spectra even for light transition elements. An excellent review article is available now [6]. Brouder et al. have developed a one-electron XMCD theory based on Gesztesy expansion, which represents the Dirac Green’s function in terms of full non-relativistic Green’s function [7]. A similar one-electron relativistic XMCD theory is applied to K-edge XMCD analyses [8]. Alternative interesting one-electron relativistic approaches are also used in XMCD analyses where electron-electron interaction is included within mean-field approximation [9, 10].

Some recent works discuss the large deviation of the intensity ratio $L_2/L_3$ from the branching ratio 1/2. This observation was ascribed to be primarily due to the electron core-hole interaction. A simple approach to include core hole effects was applied by calculating the final state wave functions for a core-hole potential [7]. A more sophisticated approach has been developed in the framework of the time-dependent density functional theory and linear response formalism [11]. Application to the $L_{2,3}$ absorption spectra of 3d transition metals demonstrates that electron core-hole interaction intermixes the $L_2$ and $L_3$ spectra strongly affecting the branching ratio.
Further applications to more complicated systems are found in literature [12]. Similar approach is also proposed by use of time dependent density functional theory [13]. These approaches are practically useful, but it is hard for us to relate them to the local field (radiation field screening) effects.

In addition to these effects, we consider the degenerate or nearly degenerate effects of core levels from which photoelectrons are excited. In XPS spectra, for example in Rh 3d sub level excitations, their peak shapes are quite different: This interesting behavior is explained by core-hole moving [14]. Onodera discussed asymmetry line shape of X-ray absorption spectra at Na L2 and L3 edges influenced by the nearly degenerate core-hole effects [15]. We discuss similar problems in X-ray absorption spectra in particular excitation from deep 2p sub levels which are degenerate in each sub levels and nearly degenerate to each other: The hole left behind is not frozen there.

In this work we develop a new many-body XMCD theory based on quantum electrodynamics (QED) where relativistic Keldysh Green’s functions are extensively used because of their wide applicability. So far the present author has developed a relativistic QED XAFS theory in the framework of Keldysh Green’s function theory [16, 17]. There main interests are to develop a sound many-body XAFS theory which also includes some important relativistic effects. Here we show that the above theoretical framework can naturally take the two important many-body effects (screening effects and core-hole degenerate effects) into account in the QED and Keldysh Green’s function theoretical framework, and we derive a practical XMCD formula which incorporates those two effects in relativistic multiple-scattering theory.

2. Relativistic QED Theory for X-ray Absorption Processes

We define the nonequilibrium photon Green’s function $D^{\mu\nu}(1,2)$ by use of the functional derivative of $<A^\mu(1)>$ with respect to external current $j^\mu_{\text{ext}}(1=(t_1, r_1))$

$$\frac{4\pi}{c} D^{\mu\nu}(1,2) = \frac{\delta <A^\mu(1)>}{\delta j^\nu_{\text{ext}}(2)} , \quad (\mu, \nu = 0, 1, 2, 3)$$

which is also written as correlation function for space components ($T_c$ is the path ordering operator on the Keldysh closed contour, $i,j =1,2,3$),

$$D^{ij}(1,2) = \frac{ip_2}{4\pi} <T_c[\delta A^i(1)\delta A^j(2)]>, \quad \delta A^i(1) = A^i(1) - <A^i(1)>.$$  \hspace{1cm} (2)

When $t_2$ is on + leg ($+\infty \rightarrow -\infty$), $p_2 = 1$, and $-1$ on $-$ leg ($-\infty \rightarrow +\infty$). Only the time component $D_{00} = D^{00}$ has singular part $v$ (bare Coulomb potential)

$$W(1,2) = 4\pi D^{00}(1,2) = v(1-2) + ip_2 \int_c d3d4\nu_c(1-3)\nu_c(2-4) <T_c[\delta n(3)\delta n(4)]>, \quad (3)$$

where $\delta_c(t_1-t_2)$ is the delta function on the closed path. Electron Green’s function for the Dirac field is defined by

$$iG(1,2) = <T_c[\psi(1)\bar{\psi}(2)]>, \quad \bar{\psi}(2) = \psi^\dagger(2)\gamma^0$$

which satisfies the Dyson equation written in a.u. ($c = 137$)

$$\left[ic\gamma_\mu(\partial^\mu - \frac{i}{c} <A^\mu(1)> - c^2)\right] G(1,2) - \int_c d3\Sigma(1,3)G(3,2) = \delta_c(1-2).$$
The time integration is taken over the closed path \( c, -\infty \rightarrow +\infty \rightarrow -\infty \). The electron selfenergy \( \Sigma \) describes both electron-electron and electron-photon interaction in the QED theory in the Coulomb gauge [18]

\[
\Sigma(1, 3) = -4\pi p^1\gamma_\mu \int_c d4d5G(1, 4)\Gamma_\nu(43; 5)D^{\mu\nu}(5, 1^+),
\]

\[
\Gamma_\nu(43; 5) = \delta G^{-1}(4, 3)/\delta < A^\nu(5) >.
\]

(6)

Of course all of these are meaningless, unless they are renormalized.

The X-ray absorption rate of the photons in the state \( k = (k, s) \) is obtained by use of the time derivative of the averaged photon number

\[
w(k) = -\frac{d}{dt} < n_k(t) > \bigg|_{t=0}.
\]

(7)

We should note that the rate \( w(k) \) has different contributions from X-ray emission and also scattering in addition to the absorption. We now define \( d_i(k; r) \) \((i = x, y, z)\) by use of the photon polarization vector \( e(k) \) \((e(k) \perp k, s = 1, 2; V \) is the volume for the normalization box),

\[
d_i(k; r) = \exp(ik \cdot r)e_i(k)/\sqrt{V}.
\]

The integral

\[
i \int d\mathbf{r}_1 d\mathbf{r}_2 d_i(k; \mathbf{r}_1)d^{>lm}(1, 2)d^*_m(k; \mathbf{r}_2)\bigg|_{t_2 \rightarrow t_1}
\]

really includes the averaged photon number \(< n_k(t) >\) which contributes to the X-ray absorption intensity \([16, 17]\).

Our main task is thus to systematically calculate the photon Green’s function \( d^{>lm} \), which satisfies the Dyson equation slightly changed from the conventional one

\[
d^{>lm} = d_0^{>lm} + (\bar{D}_0P\bar{D}_0 + \bar{D}_0P\bar{D}_0)^{>lm},
\]

(8)

where matrix product \( AB \) is defined as \( \int_c A(1, 3)B(3, 2)d3, d_0^{\lambda} \) is the free photon Green’s function shown later, and we have defined

\[
\bar{D}^{\mu\nu}(1, 2) = -p_2D^{\mu\nu}(1, 2), \quad P^{\mu\nu}(1, 2) = \frac{4\pi}{c} \frac{\delta < j^\mu(1) >}{\delta < A_\nu(2) >}.
\]

The photon Green’s function used in eq. (8) is now given by

\[
d^{>lm}(1, 2) \equiv \bar{d}^{>lm}(1, 2) = < \delta A^l(1)\delta A^m(2) >.
\]

(9)

The first term of eq. (8) cannot describe the electron-photon interaction. To obtain the X-ray absorption rate, we calculate the time derivative of the second term, which yields the following formula by use of infinitesimal small positive \( \eta \) to take causality into account

\[
2\eta \int \frac{d\varepsilon}{2\pi} [\bar{D}_0(\varepsilon)P(\varepsilon)\bar{D}_0(\varepsilon) + \bar{D}_0(\varepsilon)P(\varepsilon)\bar{D}(\varepsilon)P(\varepsilon)\bar{D}_0(\varepsilon)]^{>lm}.
\]

From eq. (8) to the above equation, we change the time integral from \( \int_c dt \) to \( \int_0^\infty dt \) and take Fourier transform of it. Explicit formulas of the free photon Green’s functions show that only \( d_0^{\lambda} \) and \( d_0^* \) have terms linear in the averaged photon number \(< n_k >\), which contribute to the X-ray absorption processes, for example, \((\bar{k} = (-k, s))\)

\[
d_0^{>lm}(\mathbf{r}_1, \mathbf{r}_2; \omega) = -i\pi c^2 \sum_k d_i^*(k; \mathbf{r}_1)d_m(k; \mathbf{r}_2)/\omega_k [< n_k + 1 > \delta (\omega - \omega_k) + < n_k > \delta (\omega + \omega_k)].
\]

(10)
The linear term in \( n_k + 1 \) contributes to the X-ray emission processes. We pick up all terms contributing to the X-ray absorption, which yields a fundamental formula to describe relativistic X-ray absorption rate \cite{16, 17}:

\[
w(k) \propto -\text{Im} \left[ < d_l(k) | (P + P \Delta P)^{>lm}(\omega_k) | d_m(k) > \right] < n_k > .
\]  

We first calculate the lowest order term in eq. (11)

\[
< d_l(k) | P^{>lm}(\omega_k) | d_m(k) > \approx < d_l(k) | P_0^{>lm}(\omega_k) | d_m(k) >
\]

\[
= -4\pi i \int d\mathbf{r}_1 d\mathbf{r}_2 d^4 \mathbf{k} \int \frac{d\varepsilon}{2\pi} \text{Tr} \left[ \gamma^l g^>(\mathbf{r}_1, \mathbf{r}_2; \varepsilon) \gamma^m g^< (\mathbf{r}_2, \mathbf{r}_1; \varepsilon - \omega_k) \right] d^m(\mathbf{k}; \mathbf{r}_2). \quad (12)
\]

By using the Gordon relation \cite{19} and a spectral representation of \( g^< \) which neglects unphysical negative energy states,

\[
g^<(\mathbf{r}_1, \mathbf{r}_2; \varepsilon) = 2\pi i \sum_n g'_n(\mathbf{r}_1) g^n(\mathbf{r}_2) \delta(\varepsilon - \varepsilon_n),
\]

\[
g'_n(\mathbf{r}) = < n, N - 1 | \psi(\mathbf{r}) | 0, N > \approx S_n \phi_c(\mathbf{r}), \quad S_n = < n, N - 1 | b | 0, N >,
\]

we have a compact formula for the absorption rate \( w(k) \) \cite{16}

\[
w(k) \propto -2\text{Im} \sum_n |S_n|^2 < \phi_c | \Delta^r \Delta^< (\omega_k + \varepsilon_n) \Delta_k | \phi_c > .
\]  

The relativistic 4 \times 4 retarded Green’s function \( g^r \) with Hartree potential and selfenergy \( \Sigma^r \)

\[
g^r(\omega) = \left( \omega + c^2 - c\alpha \cdot \mathbf{p} - V_{\text{H}} - \beta c^2 - \beta \Sigma + i\eta \right)^{-1} \beta
\]

can be expanded up to the relativistic order in terms of correlated nonrelativistic 2 \times 2 Green’s functions by use of nonrelativistic kinetic energy operator \( T_c = p^2/2 \) \cite{20},

\[
g^r(\omega) = \left( \begin{array}{cc}
g'^r_{11} + \delta g'^r_{11} & \frac{g'^r_{11} Q}{Q g'^r_{11} + 1/(2c^2)} \\
Q g'^r_{11} & Q g'^r_{11} + 1/(2c^2) \end{array} \right), \quad \delta g'^r_{11} = g'^r_{11} \Sigma_{21} g'^r_{11} + g'^r_{11} \Sigma_{22} g'^r_{11} + g'^r_{11} Q (\Sigma^r_{22} + V_{\text{H}} - \omega) Q g'^r_{11}, \quad Q = \sigma \cdot \mathbf{p} / (2c).
\]

The quasi nonrelativistic one-electron Green’s function \( g'^r_{11} \) satisfies the closed Dyson equation for the quasi nonrelativistic electron selfenergy \( \Sigma^r_{11} \). The relativistic electron-self energies \( \Sigma_{12} \) and \( \Sigma_{21} \) are in the order of \( Q \), and \( \Sigma_{22} \) is in the order of \( c^{-2} \). We write the core function \( \phi_c \) in terms of large component \( \varphi_c \) and small component \( \chi_c \),

\[
\phi_c(\mathbf{r}) = \left( \begin{array}{c}
\varphi_c(\mathbf{r}) \\
\chi_c(\mathbf{r}) \end{array} \right), \quad \varphi_c(\mathbf{r}) = g_c(\mathbf{r}) y^l_{j,\gamma_c}(\mathbf{r}), \quad \chi_c(\mathbf{r}) = i f_c(\mathbf{r}) \sigma \cdot \mathbf{r} y^l_{j,\gamma_c}(\mathbf{r}).
\]
Both \( \varphi_c \) and \( \chi_c \) are eigenstates of \( J_z^2 \), \( L_z^2 \) and \( J_z \), and are given in terms of Pauli spinor \( y_{j\mu} \) and radial functions \( g_c \) and \( f_c \). We thus obtain a useful many-body relativistic X-ray absorption formula

\[
\begin{align*}
  w(k) &\sim -\text{Im} \sum_n |S_n|^2 \left< \varphi_c | \Delta_k g_{11}^r (\varepsilon_n + \omega_k) \Delta_k | \varphi_c > 
\right.
\nonumber \\
  &+ \left< \varphi_c | \Delta_k g_{11}^r (\varepsilon_n + \omega_k) Q (V_H - \varepsilon_n - \omega_k) Q g_{11}^r (\varepsilon_n + \omega_k) \Delta_k | \varphi_c > 
\right.
\nonumber \\
  &- \left< \varphi_c | \Delta_k g_{11}^r (\varepsilon_n + \omega_k) Q \Delta_k | \chi_c > + \chi_c | \Delta_k Q g_{11}^r (\varepsilon_n + \omega_k) \Delta_k | \varphi_c > + \ldots \right).
\end{align*}
\]

(17)

The first term has finite contribution even in the nonrelativistic limit \( c \rightarrow \infty \), whereas the others vanish in that limit.

We next take the second term in eq. (11) \( P \bar{D} P \) into account. The space element \( (P \bar{D} P)^{lm} \) is written down as

\[
(P \bar{D} P)^{lm} = P^{l0} \bar{D}^{00} P^{0m} + P^{li} \bar{D}^{ij} P^{jm} + P^{l0} \bar{D}^{0i} P^{im} + P^{li} \bar{D}^{00} P^{0m}.
\]

As electron-electron interaction is much stronger than electron-photon interaction in conventional XAFS measurements, only the first term plays an important role. By noticing the relation (3) and \( P + PWP = P + PeP + P(vP)^2 + \ldots \), we obtain an important relation by applying the Langreth rule

\[
(P + PWP)^{>} = (1 - P^r v)^{-1} P^{>} (1 - vP^a)^{-1}.
\]

A symmetric relation for the irreducible polarization \( P^r \) and \( P^a \)

\[
P^r (r_1, r_2; \omega) = P^{a*} (r_2, r_1; \omega)
\]

leads to the following relativistic formula for the X-ray absorption intensity including the radiation field screening,

\[
w(k) \sim -2 \text{Im} \sum_n |S_n|^2 \left< \varphi_c | \Delta_k^{\text{sc}} g_{11}^r (\omega_k + \varepsilon_n) \Delta_k^{\text{sc}} | \varphi_c > .
\end{align*}
\]

(18)

We thus obtain a practical formula to calculate the X-ray absorption intensity including the screened radiation field by replacing \( \Delta_k \) by \( \Delta_k^{\text{sc}} \). We define the dynamically screened electron-photon interaction operator \( \Delta_k^{\text{sc}} \) as

\[
\Delta_k^{\text{sc}} = [1 - vP^a (\omega_k)]^{-1} \Delta_k = \left( \varepsilon^{-1} \right)^a (\omega_k) \Delta_k.
\]

(19)

It is better to note that the linear response theory cannot derive eq. (18) \[11\] because it includes only linear term of \( P^{>} \), whereas infinite order terms are renormalized in eqs. (18) and (19). To incorporate the radiation field screening in XAFS formula (18), we only use the Langreth rule for the calculation of \( (P + PWP)^{>} \). In contrast we have to use the mixed photon Green’s functions like \( D^{00} \) and \( D^{0i} \) to incorporate it in the photoemission formula \[21\]. The inverse dielectric function \((\varepsilon^{-1})^a (\omega_k)\) plays an important role near edge region in X-ray absorption processes. This suggests that we should also include the radiation field screening in the analyses of XMCD spectra. A very similar XAFS formula has been obtained in terms of inverse dielectric function for the radiation field screening in nonrelativistic theory \[28\]. We, however, note that relativistic effects are partly included in \( P^a \) in eq. (19), but they are small enough. We can
thus use nonrelativistic approximation for \((\varepsilon^{-1})^a(\omega_k)\), which is explicitly written by use of
\[ n_\mu(r) = \langle p|\psi^\dagger(r)\psi(r)|0 \rangle \]
thus
\[ (\varepsilon^{-1})^a(r, r'; \omega) = \delta(r - r') + \int \nu(r - r_1)\pi^a(r_1, r'; \omega)dr_1, \]
\[ \pi^a(r_1, r'; \omega) = \sum_p \left( \frac{n_p^*(r_1)n_p(r') - n_p(r_1)n_p^*(r')}{\omega - \omega_p - i\eta \omega + \omega_p - i\eta} \right), \]
As \(\omega\) is close to the core threshold \(\omega \approx \varepsilon_0\), the second term can be neglected because of large energy denominator. The reducible polarization \(\pi^a\) is thus simplified, after we restrict the excited states \(p\) to the core hole states on \(c\)
\[ \pi^a(r_1, r'; \omega) = \frac{\varphi_c^*(r_1)\varphi_c(r')}{\omega - \varepsilon_0 - i\Gamma/2} \left[ \delta(r_1 - r') - \rho_c(r_1, r') \right], \]
where \(\varphi_c\) is the large component of \(\phi_c\), \(\rho_c\) is the density matrix which describes the electronic structure of ionized systems: one core electron is ejected from the core level \(\phi_c\) but outer valence electrons are not relaxed. Near threshold \(\eta\) is replaced by finite positive value \(\Gamma/2\) taking the lifetime effects of the core hole \[23\]. By use of these approximations, the screened electron-photon interaction operator \(\Delta_c^\pi\) explicitly gives rise to resonant features near threshold, whose explicit expressions will be separately shown later for different core excitations.
So far we have used an approximation for the four-spinor Dyson amplitude \(g'_n \approx S_n\phi_c\) in eq. (13), which works quite well for deep core X-ray absorption. For \(L_{2,3}\) core excitation, some examples show the breakdown of the above simple approximation. The spinor function \(g'_n\) satisfies the equation with bound state boundary condition
\[ \left( c\alpha \cdot p + V_H + \beta c^2 + \beta \Sigma'(\varepsilon_n) \right)g'_n = (c^2 + \varepsilon_n)g'_n. \]
To solve the above equation we can safely apply degenerate perturbation theory, since we can expand \(g'_n\)
\[ g'_n(r) = \sum_\mu <n^*|b_\mu|0 > \phi_\mu(r) \]
where \(b_\mu\) is the electron annihilation operator for the core level \(\phi_\mu\) and we notice that
\[ H^0\phi_\mu(r) = \left( c\alpha \cdot p + V_H + \beta c^2 \right)\phi_\mu(r) = (c^2 + \varepsilon_\mu)\phi_\mu(r). \]
All energies \(\varepsilon_\mu\) are quite close to \(\varepsilon_0\). We thus expect that the electron selfenergy \(\Sigma\) can mix the degenerate hole states each other.

3. \(L_{23}\)-edge XMCD
Relativistic effects split \(2p\) core levels into two different sub-levels with \(j_c = 1/2\) and \(3/2\). XMCD formulas are considerably different for the excitation from heavy and light elements; for the latter \(L_2\) and \(L_3\) edges are close enough and their hole states are nearly degenerate.

3.1. XMCD for heavy absorbers
In this case the energy separation between the \(L_2\)- and \(L_3\)-edges is sufficiently large. The \(L_2\)-edge XMCD is thus not influenced by the \(L_3\)-edge excitation because the core degenerate effects can be neglected. In each atomic region the density matrix \(\rho_c\) can be approximated by
\[ \rho_c(r_1, r_2) = \sum_L \left( \begin{array}{ccc} \rho^L_1(r_1, r_2) & 0 \\ 0 & \rho^L_1(r_1, r_2) \end{array} \right) Y_L(\hat{r}_1)Y_L^*(\hat{r}_2), \]
where electron distribution in each atomic core region is assumed to be spherically symmetric. This simple approximation works so well for spherical atoms like Gd. Substitution of this density matrix into eq. (22) yields an explicit formula for the screened electron-photon interaction,

\[
\Delta_{k}^{\pm}(r; \omega)_{\pm} = \left( r + \frac{G(r) - F^{\pm}(r)}{\omega - \varepsilon_0 - i\Gamma/2} \right) Y_{1,\pm 1}(\tilde{r}) \equiv \tilde{A}^{\pm}(\omega; r)Y_{1,\pm 1}(\tilde{r}).
\]

(25)

We should note that the radial part \( \tilde{A}^{\pm}(\omega; r) \) depends on the photon energy \( \omega \) and the circular polarization. For the L\(_{2}\)-edge excitation \( (j_c = 1/2) \), we have

\[
G(r) = \frac{2}{3} G_{c}(r), \quad F^{+}(r) = [G_{21}^{1}(r) + 3G_{21}^{2}(r) + 2G_{01}^{1}(r)]/9,
\]

\[
F^{-}(r) = [3G_{21}^{1}(r) + G_{21}^{2}(r) + 2G_{01}^{1}(r)]/9.
\]

The radial function \( G_{c} \) and \( F^{\pm} \) originate from the first and the second term in \( [ \] \) of eq. (22): \( F^{\pm}(r) \) depends on the X-ray circular polarization through spin polarization in the X-ray absorbing atom. In the case where it is nonmagnetic, they do not depend on the circular polarization, \( F^{+} = F^{-} \). By use of the core radial part, they are defined

\[
G_{c}(r) = \int g_{c}^{2}(r') \frac{r_{<}^{2} dr'}{r_{>}}, \quad \left( r_{>} = \text{max}(r, r'), r_{<} = \text{min}(r, r') \right)
\]

(26)

\[
G_{\mu_{s}}^{m}(r) = \int r_{1}^{2} dr_{1} r_{2}^{2} dr_{2} \rho_{\lambda_{1}}^{m_{s}}(r_{1}, r_{2}) \delta(r_{1} + g_{c}(r_{1}) g_{c}(r_{2})), \quad \left( r_{>} = \text{max}(r_{1}, r_{2}), r_{<} = \text{min}(r_{1}, r_{2}) \right).
\]

For the L\(_{3}\)-edge excitation \( (j_{c} = 3/2) \), we have

\[
G(r) = \frac{4}{3} G_{c}(r), \quad F^{+}(r) = [5G_{21}^{1}(r) + G_{21}^{2}(r) + G_{01}^{1}(r) + 2G_{01}^{1}(r)]/9,
\]

\[
F^{-}(r) = [3G_{21}^{1}(r) + 3G_{21}^{2}(r) + 2G_{01}^{1}(r) + G_{01}^{1}(r)]/9.
\]

We again obtain the relation \( F^{+} = F^{-} \) for the X-ray absorption at nonmagnetic atom, as observed before.

We can obtain \( g_{\mu}^{2} \) by diagonalizing the matrix \( \langle \phi_{\mu} | \beta \Sigma' | \phi_{\mu'} \rangle \), which is approximated by \( \langle \phi_{\mu} | \Sigma_{11} | \phi_{\mu'} \rangle \) (see eq. (23), \( \varphi_{\mu} = g_{d}(r) y^{(1/2)}_{\mu}(\tilde{r}) \)), where only the large components are taken into account. The quasi nonrelativistic electron selfenergy \( \Sigma_{11} \) has exchange \( V_{ex} \) and polarized \( GW \) term \( GW_{p} \) \( (W = v + W_{p}) \) in lowest order. For the exchange potential we only need the density matrix near the nucleus which is approximated spherically symmetric distribution but spin dependent

\[
V_{ex}(r, r') = -v(r - r') \rho(r, r'),
\]

\[
\rho(r, r') = \sum_{L} \left( \begin{array}{cc} \rho_{L}^{0}(r, r') & 0 \\ 0 & \rho_{L}^{0'}(r, r') \end{array} \right) Y_{L}(\tilde{r})Y_{L}^{*}(\tilde{r}').
\]

(27)

The matrix \( \langle \phi_{\mu} | V_{ex} | \phi_{\mu'} \rangle \) is already diagonal,

\[
\langle \phi_{\mu} | V_{ex} | \phi_{\mu'} \rangle = \frac{\delta_{\mu \mu'}}{36\pi} \sum_{LL'}(2l + 1)(2l' + 1) < ll'0|10 \rangle \langle 10|l'0 \rangle \left( \frac{3}{2} (\rho_{ll'}^{0} + \rho_{l'l}^{0}) + \mu \left( \rho_{l'l'}^{0} - \rho_{ll'}^{0} \right) \right),
\]

where

\[
\rho_{ll'}^{m_{s}} = \frac{4\pi}{2l + 1} \int_{r_{<}^{l+1}}^{r_{>}^{l+1}} g_{d}(r) g_{d}(r') \rho_{l'l'}^{m_{s}}(r, r') r^{2} r'^{2} dr dr'.
\]
The diagonal elements depend on \( \mu \) if there exits spin polarization at the X-ray absorption site; in that case the core hole threshold is splitted into two. Equation (27) is only applicable to the XMCD from spherical ions like Gd\(^{3+}\) \((4f^7; 8S_7/2)\) and Mn\(^{2+}\) \((3d^5; 6S_3/2)\). For the XMCD from nonspherical ions like Ce\(^{3+}\) \((4f^1; 2F_5/2)\,\), we should slightly generalize eq. (27)

\[
\rho(r, r') = \sum_L \begin{pmatrix}
\rho_{\uparrow \uparrow}^L(r, r') Y_L(\hat{r}) Y_L^*(\hat{r}') & \rho_{\uparrow \downarrow}^L(r, r') Y_L(\hat{r}) Y_{L+1}^*(\hat{r}') \\
\rho_{\downarrow \uparrow}^L(r, r') Y_L(\hat{r}) Y_{L-1}^*(\hat{r}') & \rho_{\downarrow \downarrow}^L(r, r') Y_L(\hat{r}) Y_{L}^*(\hat{r}')
\end{pmatrix}.
\] (28)

By using this density matrix, we can obtain a diagonal matrix in terms of Gaunt integral

\[
G(LL'|L'') = \int d\hat{r} Y_L(\hat{r}) Y_{L'}(\hat{r}) Y_{L''}^*(\hat{r}).
\]

\[
< \varphi_{\mu} | V_{ex} | \varphi_{\mu'} > = \frac{\delta_{\mu\mu'}}{3} \left[ (1.5 - \mu) \sum_{LL'} G(LL'|1\mu - 1/2)^2 \rho_{\mu,LL'}^\uparrow + (1.5 + \mu) \sum_{LL'} G(LL'|1\mu + 1/2)^2 \rho_{\mu,LL'}^\downarrow - 2\sqrt{9/4 - \mu^2} \sum_{LL'} G(LL'|1\mu - 1/2) G(LL'|1\mu + 1/2) \rho_{\mu,LL'}^\uparrow \right],
\] (29)

where \( \rho_{\mu,LL'}^\uparrow, \rho_{\mu,LL'}^\downarrow \) and \( \rho_{\mu,LL'}^\uparrow \) are defined

\[
\rho_{\mu,LL'}^\uparrow = 4\pi \int \frac{r'}{r^2} g(d(r)) g(d(r')) \rho_{LL'}^\uparrow(r, r') r^2 r' d^4d', \quad (q = \uparrow, \downarrow, >).
\]

The electron selfenergy whose lowest order term \( V_{ex} \) thus splits the core hole threshold depending on \( \mu \). The photoelectron wave \( k_\mu^\uparrow \) and \( k_\mu^\downarrow \) depend on \( \mu \) and the spin polarization through the spin dependent \( E_0 \)

\[
k_\mu^\uparrow = \sqrt{2(\omega - \varepsilon_\mu - E_0^\uparrow)}.
\]

Including these many-body effects and applying spin-dependent multiple scattering theory, we have a practical XMCD formula

\[
\Delta I_{1/2}(\omega) \propto -\text{Im} \sum_{\mu} \left[ \left( \frac{3}{2} - \mu \right) < g_d Y_{1,\mu-1/2} | \Delta + g_0^\uparrow(k_\mu^\uparrow) \Delta | g_d Y_{1,\mu-1/2} > 
+ \left( \frac{3}{2} + \mu \right) < g_d Y_{1,\mu+1/2} | \Delta + g_0^\downarrow(k_\mu^\downarrow) \Delta | g_d Y_{1,\mu+1/2} > \right] - \left( + \text{pol.} \rightarrow - \text{pol.} \right)
= -\sum_{\mu} \left[ \left( \frac{3}{2} - \mu \right) \Gamma_{1/2}^\uparrow(k_\mu^\uparrow) + \left( \frac{3}{2} + \mu \right) \Gamma_{1/2}^\downarrow(k_\mu^\downarrow) \right] - \left( + \text{pol.} \rightarrow - \text{pol.} \right)
\] (30)

where \( + \text{pol.} \rightarrow - \text{pol.} \) means the matrix elements calculated for the \( - \) circular polarization of the first parenthesis, and we have defined \( \Gamma \) in terms of \( \hat{G}_{LL'}\) \(= \left[ G(1 - tG)^{-1} \right]_{LL'} \); \( G \) and \( t \) are widely used free propagator and \( T \) matrix in angular momentum representation which are familiar to us in XPD and XAFS calculations \( [8] \)

\[
\Gamma_{1/2}^\uparrow(k_\mu^\uparrow) = \sum_{l' \nu} R_{1/2}^\uparrow(k_\mu^\uparrow) R_{1/2}^\uparrow(k_\mu^\uparrow) G(1 - 2/1, 1, \pm 1/2) G(1 - 2/1, 1, \pm 1/2) 
\times \exp[i(\delta_{\nu}^A + \delta_{\nu}^A)] G_{l\mu-1/2, l', \mu-1/2, \pm 1}^\uparrow(k_\mu^\uparrow),
\]

\[
\Gamma_{1/2}^\downarrow(k_\mu^\downarrow) = \sum_{l' \nu} R_{1/2}^\downarrow(k_\mu^\downarrow) R_{1/2}^\downarrow(k_\mu^\downarrow) G(1 + 2/1, 1, \pm 1/2) G(1 + 2/1, 1, \pm 1/2) 
\times \exp[i(\delta_{\nu}^A + \delta_{\nu}^A)] G_{l\mu+1/2, l', \mu+1/2, \pm 1}^\downarrow(k_\mu^\downarrow).
\]
The radial matrix element \( R_{jk}^l (k; \omega) \) is given by use of the radial part \( g_{jk} \) of large component of the core function, \( R_l(k, r) \) of photoelectron wave with orbital angular momentum \( l \), and the radial part \( A^{mr} \) of \( \Delta_k^{sc} \) (see eq. (25)); \( A^{mr} \) depends on \( g_{jk} \),

\[
R_{jk}^l (k; \omega)_{m_p} = \int dr R_l(k^l_1 r) g_{jk}(r) A^{m_p} (\omega; r) r^2, \quad (m_p = \pm 1)
\]

(31)

The spin-dependence of the core hole wavefunction was stressed by Ebert [24].

For the L\(_3\)-edge, the XMCD spectra is given in terms of \( \Gamma_{3/2}^{\alpha} \)

\[
\Delta I_{3/2}(\omega) = -\text{Im} \sum_{\nu = -3/2}^{3/2} \left[ \left( (3/2 + \nu) \Gamma_{3/2}^1 (k^1_\nu) + (3/2 - \nu) \Gamma_{3/2}^1 (k^1_{\nu}) \right) - \left( \text{pol.} \rightarrow -\text{pol.} \right) \right].
\]

(32)

The polarization dependent \( \Gamma \) are slightly different from those given above for the L\(_2\)-edge XMCD, for example,

\[
\Gamma_{3/2}^1 (k^1_\nu) = \sum_{\mu} R_{3/2}^l (k^1_\nu) \pm R_{3/2}^l (k^1_{\nu}) G(1\nu - 1/2, 1, \pm 1|\mu)(1\nu - 1/2, 1, \pm 1|\mu')
\]

\[
\times \exp[i(\delta^{A^1} + \delta^{A^1})] G_{1\nu - 1/2,1',\nu - 1/2\pm 1}(k^1_\nu).
\]

In case the X-ray absorbing atom is nonmagnetic, the radial matrix element \( R_{jk}^l (k; \omega) \) does not depend on the circular polarization. In eq. (31) the core function \( g_{jk} \) is different for the different cores at L\(_2\) and L\(_3\) thresholds. For light elements the difference is small. We thus obtain a simple relation which works so well for XMCD from light 3d elements with small orbital moments

\[
\Delta I_{3/2} = -\Delta I_{1/2}.
\]

(33)

In other cases we observe the breakdown of the relation (33).

3.2. XMCD for light absorbers

In this case the nearly degenerate effects between L\(_2\) and L\(_3\) edges have to be taken into account. We thus have to calculate inter sub shell matrix elements like \(< g_{1/2} y_\mu | V_{ex} | g_{3/2} y_\nu > \) where we use abbreviation for Pauli spinors \( y_\nu = y_{3/2,\nu}, y_\mu = y_{1/2,\mu} \). In the spherical approximation (27), we obtain by use of the radial matrix elements \( \rho_{LL'}^{\mu \nu} \) similar to \( \rho_{LL'}^{\mu \nu} \) but with mixing of \( g_{1/2} \) and \( g_{3/2} \)

\[
< g_{1/2} y_\mu | V_{ex} | g_{3/2} y_\nu > = -\delta_{\mu \nu} \frac{1}{4} - \frac{\mu^2}{9} \sum_{LL'} G(LL'|1)^2 (\rho_{LL'}^{\mu} - \rho_{LL'}^{\nu}) = -\delta_{\mu \nu} a.
\]

(34)

This mixing is negligible when the X-ray absorbing atom is nonmagnetic because \( \rho_{LL'}^{1} = \rho_{LL'}^{1} \). The mixing factor \( a \) is the same for \( \mu = \pm 1/2 \), so that we drop the subscript \( \mu \). The diagonalization of the 2×2 matrix

\[
\begin{pmatrix}
\varepsilon_{so} & -a \\
-a & 0
\end{pmatrix}
\]

(35)

gives larger energy splitting than \( \varepsilon_{so} \) (the energy splitting of L\(_2\) and L\(_3\) edges in the Hartree approximation; it is about 6.5eV for Tl), and also gives mixing between \( g_{1/2} y_{1/2,\mu} \) and \( g_{3/2} y_{3/2,\nu} \).

More general density matrix (28) also provides very similar diagonal matrix to that shown by eq. (35). The mixing thus has influence on radial part for the one-electron states with \( \mu = \pm 1/2 \):
The radial parts with $\nu = \pm 3/2$ are not affected by the mixing. For the levels with $\mu = \pm 1/2$, the mixed radial functions $g'_{1/2}$ and $g'_{3/2}$ are written in linear combination

$$g'_{1/2} = d_2 g_{1/2} + d_3 g_{3/2}, \quad g'_{3/2} = c_2 g_{1/2} + c_3 g_{3/2}$$

where the mixing coefficients are determined by diagonalizing the matrix (35). Even for Ti $\varepsilon_{so}$ ($\approx 6$ eV) is much larger than the lifetime broadening of L\textsubscript{23} levels ($\approx 0.2$ eV). One pole approximation (25) should be quite good, but we can easily generalize $A^\pm$ in eq. (25) to multipoles approximation. These considerations yield XMCD formula similar to the previous formulas: For $\Delta I_{1/2}(\omega)$, the radial function $g_{1/2}$ is replaced by $g'_{1/2}$ in eq. (31), and for $\Delta I_{3/2}(\omega)$ the radial function $g_{3/2}$ is only replaced by $g'_{3/2}$ when the sum over $\nu$ runs over $\nu = \pm 1/2$ in eq. (32).

So far we have considered the degenerate effects on the 4 spinor $g'_\mu$, which split the degenerate energy $\varepsilon_d$ (L\textsubscript{2} level energy) and $\varepsilon_c$ (L\textsubscript{3} level energy) into 2 and 4 different levels which explicitly depends on $\mu$ and $\nu$. These effects can also mix the inter sub levels with the same $\mu$ and $\nu$. Furthermore we should investigate these effects on photoelectrons. To describe the photoelectron propagation in solids after the core excitation, the quasi nonrelativistic retarded Green’s function $g_{11}(\varepsilon)$ in eq. (18) plays a crucial role

$$g_{11}(\varepsilon) = \frac{1}{\varepsilon - h_{sc} - \Sigma'(\varepsilon)}$$

where $h_{sc}$ and $\Sigma' = \Sigma_{11}$ describe elastic scatterings of photoelectrons: The latter describes the photoelectron damping responsible for photoelectron mean free path [26] and also core degenerate effects on photoelectron propagation. In the present case it is sufficient to consider the projected Green’s function. For the description, we now introduce the projection operators $P_\mu$ and $P_\nu$, which project photoelectron scattering states into the states under the influence of core hole states on $\mu$ and $\nu$. To obtain an X-ray absorption formula including the degenerate effects on photoelectrons, we should calculate the diagonal parts $P_\mu g^\mu P_\mu$ (hereafter we use abbreviation $g^\mu$ for $g_{11}$). Direct calculation yields with aid of projection operator algebra [23, 25]

$$P_\mu g^\mu P_\mu = g^\mu P_\mu + g^\mu \sum_{\mu'(\neq \mu)} P_\mu \Sigma P_{\mu'} g_{0} \Sigma' g^\mu + g^\mu \sum_\nu P_\mu \Sigma' P_{\nu} g_{0} \Sigma' g^\mu + \ldots,$$  \hspace{1cm} (37)

$$g^\mu = g_{0} P_\mu + g_{0} P_\mu \Sigma' P_\mu g^\mu, \quad g_{0}(\varepsilon) = \frac{1}{\varepsilon - h_{sc} + i\eta}.$$  

The first term of eq. (37) $g^\mu P_\mu$ describes the X-ray absorption processes where hole left behind is fixed even after the core excitation, the second the hole is moving inside the same sub level, while the third the hole is moving to another sub level. We can also include all these effects in the multiple scattering XMCD formulas (30) and (31).

We should add a caution concerning the Dyson orbital $g'_n$ which is defined by eq. (13) and satisfies eq. (23). In the Hartree-Fock frozen approximation it is simply reduced to the initial level wavefunction, however, it is affected both from initial and final states as defined by eq. (13) beyond the simple approximation: The energy $\varepsilon_n$ corresponds to the exact core hole threshold energy for the $n$th core hole state in the nonrelativistic approximation.

4. K-edge XMCD

In this case the degenerate core effects can be neglected. The screened electron-photon interaction operator is again written as eq. (25), and $G$ and $F^\pm$ are now now given by

$$G(r) = G_c(r)/3, \quad F^\pm(r) = (G_{11}^1(r) + G_{11}^1(r))/3$$
The factor $F^\pm$ does not depend on the circular polarization, and that is also the case for $A^\pm$ defined in eq. (25).

So far our main concern has been focused on the first term of eq. (17), because the splitted shells caused by the relativistic effects mainly contribute to the XMCD. On the other hand the relativistic effects for photoelectrons play a crucial role in K-edge XMCD [7, 8]. The second term of eq. (17) includes the operator $Q(V_H - \omega)Q$, which is rewritten [7]

$$Q(V_H - \omega)Q = -\frac{1}{4\epsilon^2} \left[ \nabla V_H \cdot \nabla + (V_H - \omega)^2 \right] + \xi(r)\sigma \cdot L,$$

for spherically symmetric potential $V_H$. The spin-orbit coupling term, the last term,

$$\delta V = \xi(r)\sigma \cdot L$$

can give finite contribution to the XMCD, whereas the first two terms give no contribution to the XMCD. We obtain multiple scattering XMCD formula at K-edge

$$\Delta I_0 = \Delta I_{0\text{atom}} - 2\pi \text{Im} \left[ \rho_{\uparrow}^1(k^\dagger)\delta \rho_{\downarrow}^1(k^\dagger) \exp(2i\delta_{\dagger}^{A\dagger})Z_{1,11}^\dagger - (\uparrow \text{ spin} \rightarrow \downarrow \text{ spin}) \right], \quad (38)$$

Here it is convenient for us to separately calculate the K-edge XMCD, atomic XMCD $\Delta I_{0\text{atom}}$ and multiple-scattering (MS)-XMCD (the second term of eq.(38)). Of course we expect no atomic XMCD in the case where the X-ray absorbing atom is nonmagnetic. In contrast MS-XMCD is finite even in those cases if some of nearby atoms are magnetic. The spin-dependent radial integrals are defined by use of $A(\omega; r)$ which is independent of X-ray polarization

$$\rho_{\uparrow}^1(k^\dagger) = \int R^\dagger_1(k^\dagger r)g_{1s}(r)A(r)r^2 dr,$$

$$\delta \rho_{\downarrow}^1(k^\dagger) = \int R^\dagger_1(k^\dagger r)\xi(r)g_{1s}(r)g_{1s}(r')A(r')r^2 dr^2 dr', \quad (39)$$

where $g_{Al}$ is the radial part of the propagator at the X-ray absorption site A,

$$g_{Al}(r, r') = \sum_L g_{Al}(r, r')Y_L(\hat{r})Y_L^*(\hat{r}').$$

For K-edge XMCD, main frame of one-electron relativistic XMCD theory still works. We can, however, explicitly use optical potentials for excited photoelectrons.

5. Concluding Remarks

In this paper we derive a new many-body XMCD theory based on relativistic quantum electrodynamics. Our discussion is separately given for spherical core (K-edge) and nonspherical cores (L$_2$ and L$_3$ edges), because the relativistic effects is essential to split L$_{23}$ shell into sub levels L$_2$ and L$_3$ for the latter. In K-edge excitation the relativistic effects on photoelectrons are essential to give rise to finite XMCD. These characteristic features are already observed in the previous XMCD theories, although the optical potential cannot be taken into account in those one-electron theories [7, 8].

The present theoretical framework enables us to take the relativistic many-body effects into account such as radiation field screening and degenerate effects of core levels, which are explicitly investigated here. The radiation field screening is also important near core thresholds as well as plasmon excitation region [27], as observed in MARPE analyses [22].
The radiation field screening provides energy dependent effective electron-photon interaction operator $A^\pm(\omega; r)Y_{1,\pm1}(\hat{r})$. One of remarkable features of the radial part $A^\pm(\omega; r)$ depends on circular polarization when the X-ray absorbing atom is spin-polarized, and also photon energy $\omega$. It strongly deviates from $r$ only near threshold.

Near degenerate effects are incorporated in the present theoretical framework. In the $L_2$ and $L_3$ edge XMCD, they split each of the degenerate sub levels. In XMCD from light elements like 3d transition metals, inter sub level mixing with the same quantum number $\mu$ should be taken into account. The radiation field screening and the near degenerate effects both contribute to strong deviation from the branching ratio, and also can give rise to different XMCD spectra from the simple rule (33). These many-body effects can be incorporated in the framework of multiple scattering theory developed so far. Both of the effects are not so influential in K-edge XMCD spectra. Other optical field effects can naturally be incorporated based on this relativistic QED theory as pointed out in our previous paper [28]. Detailed numerical calculations will be demonstrated in the forthcoming paper.

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References

[1] L. Hedin, Physica B158, 344 (1989)
[2] L. Campbell, L. Hedin, J. J. Rehr, W. Bardyszewski, Phys. Rev. B 65, 064107 (2002).
[3] T. Fujikawa, J. Phys. Soc. Jpn. 62, 2155 (1999).
[4] T. Fujikawa, J. Synchrotron Radiation 8, 76 (2001).
[5] T. Fujikawa, H. Arai, Recent Res. Devel. Physics 4, 657 (2003).
[6] H. Wende, Rep. Prog. Phys. 67, 2105 (2004).
[7] Ch. Brouder, M. Aloani, K. H. Bennemann, Phys. Rev. B 54, 7334 (1996).
[8] T. Fujikawa, S. Nagamastu, J. Elect. Spect. Relat. Phenom. 129, 55 (2003)
[9] A. Ankudinov, J. J. Rehr, Phys. Rev. B56, R1712 (1997).
[10] H. Ebert, V. Popescu, D. Ahlers, Phys. Rev. B 60, 7156 (1999).
[11] J. Schwitalla, H. Ebert, Phys. Rev. Lett., 80, 4586 (1998).
[12] A. Scherz, H. Wende, K. Baberschke, J. Minar, D. Bena, H. Ebert, Phys. Rev. B66, 184401 (2002).
[13] A. L. Ankudinov, A. I. Nevvizhskii, J. J. Rehr, Phys. Rev. B 67, 115120 (2003).
[14] C-O. Almbladh, M. Bergersson, J. Elect. Spect. relat. Phenom. 137-140, 393 (2004)
[15] Y. Onodera, J. Elect. Spect. relat. Phenom. 136, 85 (2004).
[16] T. Fujikawa, J. Elect. Spect. Relat. Phenom. 149, 61 (2005).
[17] T. Fujikawa, Physica Scripta T115, 35 (2005).
[18] B. Bezzerides, D. F. DuBois, Ann. Phys. 70, 10 (1972).
[19] W. Greiner, *Relativistic Quantum Mechanics*, Springer, Berlin, 1990.
[20] F. Gesztesy, H. Grosse, B. Thaller, Ann. Inst. Henri Poincare 40, 159 (1984).
[21] T. Fujikawa, H. Arai, J. Elect. Spect. Relat. Phenom. 149, 61 (2005).
[22] H. Arai, T. Fujikawa, Phys. Rev. B 72, 075102 (2005).
[23] C-O. Almbladh, L. Hedin, *Handbook on Synchrotron Radiation*, Vol. 1 b, (North Holland, 1983) ed. E. E. Koch, pp. 607-904.
[24] H. Ebert, *Spin-orbit influenced spectroscopies of magnetic solids*. Lecture Notes in Physics Vol. 466. (Springer, 1996) ed. by H. Ebert and G. Schütz, pp. 159
[25] L. Hedin, J. Michaels, J. Inglesfield, Phys. Rev. B 58, 15565 (1998).
[26] T. Fujikawa, L. Hedin, Phys. Rev. B40, 11507 (1989).
[27] W. Schattke, Prog. Surf. Sci. bf 54, 211 (1997).
[28] T. Fujikawa, H. Arai, AIP Conference Proceedings 882, *X-ray Absorption Fine Structure-XAFS 13*, p.75.