Theoretical Study of $L$-edge Resonant Inelastic X-ray Scattering in La$_2$CuO$_4$ on the Basis of Detailed Electronic Band Structure

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We study theoretically resonant inelastic x-ray scattering (RIXS) at the Cu $L_3$-edge in a typical parent compound of high-$T_c$ cuprate superconductors La$_2$CuO$_4$ on the basis of a detailed electronic band structure. We construct a realistic and precise tight-binding model by employing the maximally-localized Wannier functions derived from a first-principles electronic structure calculation, and then take account of the Coulomb repulsion between $d$ electrons at each Cu site. The antiferromagnetic ground state is described within the Hartree-Fock approximation, and take account of electron correlations in the intermediate states of RIXS within the random-phase approximation (RPA). Calculated RIXS spectra agree well with the experimentally observed features including low-energy magnon excitation, $d$-$d$ excitations, and charge-transfer excitations, over a wide excitation-energy range. In particular, we stress the importance of photon polarization dependence: the intensity of magnon excitation and the spectral structure of $d$-$d$ excitations depend significantly not only on the polarization direction of incident incoming photons but also that of outgoing photons. It is demonstrated that the single-magnon excitation intensity is maximized when the polarization directions of incoming and outgoing photons are perpendicular to each other.

1. Introduction

Resonant inelastic x-ray scattering (RIXS) provides a powerful optical method of observing elementary excitations in solids. Particularly, recent tremendous progress in energy-momentum resolution and theoretical understanding is promoting RIXS to one of major techniques of measuring various electronic and magnetic excitations.$^{1,2}$ Among RIXS phenomena, RIXS at the transition-metal edges is attracting much interest, which
is much suitable for elucidating electronic excitations in strongly correlated transition-metal compounds including the high-$T_c$ cuprate superconductors and various magnetic materials. It is notable that RIXS can provide us a variety of electronic excitation spectra, depending on which absorption edge of transition metal is utilized. At the $K$-edge in the hard x-ray regime, an inner-shell $1s$ electron is promoted to conduction $p$ bands. Accompanied with this promotion, strongly correlated $d$ electrons near the Fermi level are excited to screen the created inner-shell $1s$ hole. Thus correlated $d$-electrons are \textit{indirectly} excited. In this case, electronic excitations should conserve the total spin moment of the $d$-electron system, and therefore are restricted only to charge-orbital excitation processes or to generation processes of even-number magnons. In fact, charge-transfer excitations\textsuperscript{3,4}, $d-d$ orbital excitations\textsuperscript{5} and two-magnon excitations\textsuperscript{6} are observed in transition-metal compounds through $K$-edge RIXS. On the other hand, at the $L$-edge in the soft x-ray regime, an inner-shell $2p$ electron is promoted to correlated conduction $d$ bands. Thus correlated $d$-electrons are \textit{directly} excited. Since the spin and orbital angular momenta of the $2p$ states polarize each other due to strong spin-orbit coupling, the $d$ electrons can be excited not only in the charge-orbital channel but also in the spin channel. In application to high-$T_c$ cuprate superconductors, in which the spin moment is induced on the $d_{x^2-y^2}$ orbital, it had been believed that spin-flip scattering is not allowed in $L$-edge RIXS\textsuperscript{7,8}. Actually, more recently Ament and collaborators verified that spin-flip excitation is indeed allowed when the spin moments point parallel to the basal plane\textsuperscript{9}. In fact, magnon excitation is clearly observed in copper oxides where the spin moments are aligned along the basal plane\textsuperscript{10–14}. Magnon excitation is observed persistently even in doped metallic cuprates\textsuperscript{15–18} and $L$-edge RIXS promises to be a new technique of elucidating the pairing glue in high-$T_c$ superconductivity. The observed energy dispersion of the magnon peak agrees well with neutron scattering experiments\textsuperscript{10–12,14,15}.

In our present work, we discuss theoretically RIXS at the transition-metal $L$-edge. Intensive theoretical studies have been performed so far to analyze the $L$-edge RIXS in strongly correlated transition-metal compounds\textsuperscript{9,19–23}. In most of precedent studies, simplified effective models such as impurity Anderson models, finite-size cluster models, or Heisenberg models have been adopted to describe the electronic structure or the magnetic ground state, and the energy window and the number of momentum points allowed for calculation are inevitably restricted. Heisenberg antiferromagnetic superexchange couplings are often treated as tunable parameters to fit to experimental data,
and microscopic quantitative grounds for the values of coupling parameters are lacking. Therefore, it will be meaningful to develop another approximate but useful calculations without the above drawbacks, for analyzing experimental data in detail.

In the present study, we present a microscopic theoretical formulation of RIXS at the \(L\)-edge and apply it to a typical parent compound of high-\(T_c\) superconductors \(\text{La}_2\text{CuO}_4\). To describe the electronic structure of \(\text{La}_2\text{CuO}_4\) precisely, we use maximally localized Wannier functions (MLWF) derived from first-principles electronic structure calculation,\(^{24}\) and determine the antiferromagnetic ground state within the Hartree-Fock (HF) approximation. Electron correlations in the intermediate states are treated within the random-phase approximation (RPA). Our approach is based on perturbation expansion in Coulomb interaction, and a natural extension of our previous theoretical formulation of \(K\)-edge RIXS.\(^{25,26}\) It is approximate one but applicable to realistic and complex electronic structures such as multi-orbital systems. Similar formulation is already developed in Ref. 27.

The article is constructed in the following way: In § 2, we present our Hamiltonian and theoretical formulation to calculate RIXS spectra. In § 3, we present calculated RIXS spectra of single-magnon and \(d-d\) excitations, and their dependences on polarization direction and scattering angles, and compare some of them with experimental data. In particular, we shall see the intensity of magnon excitation and the spectral structure of \(d-d\) excitations depend significantly not only on the polarization direction of incident photons but also that of outgoing photons. In § 4, some discussions and remarks on our formulation and results are given. In § 5, the article is concluded with brief comments.

2. Formulation of RIXS

2.1 Hamiltonian

To discuss the RIXS process microscopically, we use the following form of Hamiltonian:

\[
H = H_{n.f.} + H_{2p} + H_{2p-d} + H_x,
\]

where \(H_{n.f.}\) describes the correlated electrons near the Fermi level, and \(H_{2p}\) and \(H_x\) describe the inner-shell \(2p\) electrons and the dipole transition by x-rays, respectively. \(H_{2p-d}\) is the Coulomb interaction between the \(2p\) and transition-metal \(d\) electrons (Cu-3\(d\) electrons in the case of \(\text{La}_2\text{CuO}_4\)). We present details of each term in the following.
To construct the Hamiltonian part $H_{n,f}$ for La$_2$CuO$_4$, firstly we perform first-principles band structure calculation assuming the paramagnetic state.\(^{28}\) To express the electronic orbital bases and scattering geometry, we take the coordinate system where the principal axes of nearest-neighbor Cu-O bonds are parallel along the cartesian axes (see Fig 1(a)). Then we perform tight-binding fitting to the obtained energy bands near the Fermi level by using the \texttt{wannier90} code\(^{24}\) where we take five $d$ orbitals at each Cu, and three $p$ orbitals at each O site. Thus we include 17 MLWF’s in the unit cell, since there are one Cu and four O sites in the unit cell. The orbital bases are defined in terms of the coordinate axes in Fig. 1(a), and the spin states are specified with respect to the $z$-axis. Thus we obtain a tight-binding model to fit the 17 bands near the Fermi level (See Appendix A for details). Adding the on-site Coulomb interaction part, we have the Hubbard-type Hamiltonian $H_{n,f}$ in the following form:

$$
H_{n,f} = \sum_{ii'} \sum_{\ell} \sum_{\ell'} \sum_{\sigma} t_{\ell,\ell'} (\mathbf{r}_i - \mathbf{r}_{i'}) a^\dagger_{i\ell\sigma} a_{i'\ell'\sigma} + \frac{1}{2} \sum_{\ell_1,\ell_2,\ell_3,\ell_4} \sum_{\ell_1'\sim\ell_4} \sum_{\sigma\sigma'} I_{\ell_1,\ell_2;\ell_3,\ell_4} (\mathbf{r}_i) a^\dagger_{i\ell_1\sigma} a^\dagger_{i\ell_2\sigma} a_{i\ell_3\sigma'} a_{i\ell_4\sigma'}
$$  

(2)

where $a^\dagger_{i\ell\sigma}$ and $a_{i\ell\sigma}$ are the electron creation and annihilation operators for orbital $\ell$ with spin $\sigma$ at site $i$. Throughout the present study, we always work with the electron representation not with the hole representation. ‘t.m.’ in the summation with respect to $i$ means summing only over transition-metal sites. $I_{\ell_1,\ell_2;\ell_3,\ell_4} (\mathbf{r}_i) \equiv I_{\ell_1,\ell_2;\ell_3,\ell_4}$ is the on-site Coulomb integral at transition-metal (i.e., Cu) sites. In the summation with respect to $\ell$, ‘@$\mathbf{r}_i$’ at the top means orbital $\ell$ should lie on the site $\mathbf{r}_i$. One-particle energy at orbital $\ell$ is given by $\varepsilon_\ell \equiv t_{\ell,\ell} (\mathbf{r} = 0)$. We modify the one-particle energy $\varepsilon_\ell$ for Cu-$d$ orbitals, to obtain a realistic level scheme of the local Cu-$d$ orbitals and $d$-$d$ excitation energies, as explained in Appendix A. Hereafter we use the following convention for later discussions: if $\ell$ denotes a $d$ orbital at a Cu site (e.g., $\ell = xy$), then $a_{i\ell\sigma} \equiv d_{i\ell\sigma} = d_{i\zeta}$, if $\ell$ denotes a $p$ orbital (e.g., $\ell = x$) at an O site, then $a_{i\ell\sigma} \equiv p_{i\ell\sigma}$, and so on. We expect that confusion between Cu-$p$ and O-$p$ orbitals will not occur, since the O-$p$ orbitals do not appear explicitly in the following discussions. Here we introduce the values of on-site Coulomb interaction $I_{\ell_1,\ell_2;\ell_3,\ell_4}$ at each Cu site in the form of Slater-Condon integrals (see Ref. 29 for the definition of Slater-Condon integrals and their relation to $I_{\ell_1,\ell_2;\ell_3,\ell_4}$): $F^0(d,d) = 6$ eV, $F^2(d,d) = 11.5$ eV, $F^4(d,d) = 7.4$ eV. The values of $F^2(d,d)$ and $F^4(d,d)$ are taken from Ref. 30, and $F^0(d,d)$ is determined to reproduce the insulating gap about 2.2 eV.\(^{31}\) Our choice of these Coulomb integrals corresponds approximately to $U \sim 7.5$ eV, $U' \sim 5-6$ eV, and $J \sim 0.6-1.2$ eV, where $U$, $U'$ and $J$ are the intra-orbital...
and inter-orbital Coulomb repulsions and the Hund’s coupling, respectively. For $H_{n.f.}$, we determine the antiferromagnetic ground state with the spin moments $m \parallel [110]$ within the HF approximation (see Appendix A about details of HF calculation).

For the $2p$ electrons, we assume completely localized $2p$ orbitals at each transition-metal site (Cu site in the present case of La$_2$CuO$_4$):

$$H_{2p} = \sum_{i} \sum_{m,\sigma} \varepsilon_{2p}(r_i) p_{i\sigma}^\dagger p_i^\sigma + \sum_{mm'} \sum_{\sigma\sigma'} \xi_{2p}(r_i) l_{mm'} \cdot s_{\sigma\sigma'} p_{i\sigma}^\dagger p_{i\sigma'}^\dagger,$$

where $\varepsilon_{2p}(r_i) \equiv \varepsilon_{2p}$ is the one-particle energy of the $2p$ state, $p_{i\sigma}^\dagger$ and $p_{i\sigma}$ are the creation and annihilation operators of $2p$ electrons with spin $\sigma$ and angular momentum $m$ ($m = -1, 0, 1$) at transition-metal site $i$, respectively. The second term of the right-hand side of eq. (3) is the spin-orbit coupling. $l_{mm'}$ are the matrix elements of orbital angular momentum, and $s_{\sigma\sigma'}$ are related to the Pauli matrices as $s = \sigma/2$. $H_{2p}$ is straightforwardly diagonalized, and the $2p$ eigenstates are characterized by the total angular momentum $J$ and its $z$ component $M$, where $J = 1/2, 3/2$ and $M = -J, -J+1, ..., J-1, J$. The energy levels consist of two kinds of levels as a result from splitting due to the spin-orbit coupling: $\varepsilon_{2p,J=1/2} = \varepsilon_{2p} - \xi_{2p}$ and $\varepsilon_{2p,J=3/2} = \varepsilon_{2p} + \xi_{2p}/2$. The former (latter) is two-fold (four-fold) degenerated. In the present case of Cu, we take $\varepsilon_{2p} = -936$ eV with respect to the Fermi level, and $\xi_{2p} = 13.3$ eV, which causes about 20 eV energy splitting between the $L_2$ and $L_3$ edges. The diagonalized eigenstates are expressed as

$$|J, M\rangle = \sum_{m=1,0,-1} \sum_{\sigma=\uparrow,\downarrow} |m, \sigma\rangle u_{m\sigma;JM}.$$  (4)

Specifically, for the $J = 1/2$ doublet,

$$|J = 1/2, M = 1/2\rangle = -\sqrt{\frac{1}{3}} |m = 0, \uparrow\rangle + \sqrt{\frac{2}{3}} |m = 1, \downarrow\rangle$$  (5)

$$|J = 1/2, M = -1/2\rangle = \sqrt{\frac{2}{3}} |m = -1, \uparrow\rangle - \sqrt{\frac{1}{3}} |m = 0, \downarrow\rangle,$$  (6)

and for the $J = 3/2$ quartet,

$$|J = 3/2, M = 3/2\rangle = |m = 1, \uparrow\rangle$$  (7)

$$|J = 3/2, M = 1/2\rangle = \sqrt{\frac{2}{3}} |m = 0, \uparrow\rangle + \sqrt{\frac{1}{3}} |m = 1, \downarrow\rangle$$  (8)

$$|J = 3/2, M = -1/2\rangle = \sqrt{\frac{1}{3}} |m = -1, \uparrow\rangle + \sqrt{\frac{2}{3}} |m = 0, \downarrow\rangle$$  (9)

$$|J = 3/2, M = -3/2\rangle = |m = -1, \downarrow\rangle.$$  (10)
$H_{2p-d}$ is given by

$$H_{2p-d} = \sum_i^{\text{t.m.}} \sum_{\ell \ell'} \sum_{mm' \sigma_1 \sigma_2} V_{2p-d}(r_i; m \sigma_1, \ell \sigma_2, \ell' \sigma_3, m' \sigma_4) p_{m \sigma_1}^\dagger d_{\ell \sigma_2}^\dagger d_{\ell' \sigma_3} p_{m' \sigma_4},$$

(11)

where $V_{2p-d}(r_i; \cdots)$ is the on-site Coulomb interaction between the $2p$ and $d$ orbitals at transition-metal site $r_i$. $\ell$ and $\ell'$ denote the $d$ orbitals: $\ell, \ell' = xy, yz, xz, x^2 - y^2, 3z^2 - r^2$. For convenience in later discussions, we define the following matrix elements:

$$V_{2p-d}(r_i; J, M, \zeta, \zeta', J'M') \equiv \sum_{mm' \sigma_1 \sigma_2} u_{m \sigma_1;JM}^* V_{2p-d}(r_i; m \sigma_1, \ell \sigma_2, \ell' \sigma_3, m' \sigma_4) u_{m' \sigma_2;J'M'}. \quad \text{(12)}$$

For numerical calculations on La$_2$CuO$_4$, we take $F^0(p, d) = F^2(p, d) = 1$ eV at Cu sites, but this interaction is almost irrelevant to spectral weights for the case of La$_2$CuO$_4$ as we see later.

$H_x$ describes resonant $2p-d$ dipole transition induced by x-rays:

$$H_x = \sum_i^{\text{t.m.u}} \frac{1}{N} \sum_{k, q} \sum_{\ell, m} w_{\ell, m}(r_i; q, e) \alpha_{qe} d_{k+q}^\dagger p_{k+m} + \text{h.c.}, \quad \text{(13)}$$

where $N$ is the number of unit cells, the summation in $i$ with ‘t.m.u’ means it is restricted to transition-metal sites in the unit cell. $d_{k+q}^\dagger [p_{k+m}]$ is the creation [annihilation] operator of transition-metal $d_\ell [2p_m]$ electrons in the momentum representation, and $\alpha_{qe}$ is the annihilation operator of a photon with momentum $q$ and polarization $e$. We assume the matrix elements of $w_{\ell, m}(r_i; q, e)$ are given in the form:

$$w_{\ell, m}(r_i; q, e) = -\frac{e}{m_e} \sqrt{\frac{2\pi}{|q|}} e^{i q \cdot r_i} (d_\ell |e \cdot p|2p_m)$$

(14)

$$\approx -i e \sqrt{2\pi |q|} e^{i q \cdot r_i} \langle d_\ell |e \cdot r|2p_m \rangle$$

in natural units ($c = \hbar = 1$), $m_e$ and $e$ are the mass and charge of an electron, respectively. $r_i$ is the transition-metal site where the x-rays are absorbed or emitted, and we assume that $w_{\ell, m}(r_i; q, e)$ does not vanish only when both of the orbitals $2p_m$ and $d_\ell$ lie on the site $r_i$. $\langle d_\ell |e \cdot r|2p_m \rangle$ can be calculated using atomic wave functions. For convenience in later discussions, we define

$$w_{\zeta,JM}(r_i; q, e) \equiv w_{\ell \sigma, JM}(r_i; q, e) \equiv \sum_{m=1,0,-1} w_{\ell, m}(r_i; q, e) u_{m \sigma; JM}, \quad \text{(15)}$$

where $\zeta$ is orbital-spin unified index: $\zeta \equiv (\ell, \sigma)$. 

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Fig. 1. (Color online) (a) Crystal structure of La$_2$CuO$_4$ and MLWF for the Cu-$d_{x^2-y^2}$ state. (b), (c) and (d) Definition of the scattering geometry. $q$ and $q'$ are the momentum vectors of the incoming and outgoing photons, respectively. $\theta$, $\phi$ and $\psi$ [$\theta'$, $\phi'$ and $\psi'$] are the Bragg, azimuthal and polarization angles, respectively, for incoming [outgoing] photons. In (c), the angle between transferred momentum $Q$ and the $z$-axis is approximately given by $\delta \approx (\theta - \theta')/2$. In (d), $e$ and $e'$ are the polarization vectors of the incoming and outgoing photons, respectively. The polarization angle is measured with respect to the scattering plane, i.e., $\psi = 0$ [$\psi = \pi/2$] means that the polarization direction is parallel [perpendicular] to the scattering plane.

2.2 RIXS intensity

RIXS intensity can be obtained by calculating the number of photons generated in different states from the incident-photon state per unit time. To do this, we employ the Keldysh perturbation theory as in Ref. 32. The present formulation of $L$-edge RIXS is a straightforward extension of our previous formulation on $K$-edge RIXS. The RIXS intensity is generally expressed by the diagram (I) in Fig. 2, if assuming that only a single electron-hole pair remains in the final state. The analytic expression of RIXS intensity is obtained from the diagram (I) of Fig. 2 as:

$$W(q, e; q', e') = \frac{1}{N} \sum_{k_1} \int_{-\infty}^{\infty} \frac{d\omega_1}{2\pi} \sum_{a_1a_2} G_{a_1}^+(k_1)G_{a_2}^-(k_1 + Q) \left\{ \sum_{i} \sum_{\zeta\zeta'} \sum_{J'J} \sum_{M=-J}^{J} \sum_{M'=-J'}^{J'} \right\}$$
Fig. 2. (I) RIXS intensity represented within the Keldysh perturbative formulation. The wavy lines and shaded rectangular represent the photon propagators and electron scattering vertex function $F(r_i; q, q')$, respectively. A pair of oriented solid lines represent the off-diagonal elements of the Keldysh Green’s function, and connect the upper normally-time-ordered and lower reversely-time-ordered branches. (II) Approximate expansion for the scattering vertex function $F(r_i; k_1; q, q')$: (a) $F^{(0)}(r_i; k_1; q, q')$ for ‘0th-order process’ (fluorescence-like), (b) $F^{(p)}(r_i; q, q')$ for ‘p-process’, (c) $F^{(d)}(r_i; q, q')$ for ‘d-process’. The filled triangle and square are the three-point and four-point vertex functions to be renormalized by electron correlations, respectively. In (b), the dashed line represents the core-hole potential $V_{2p-d}$. Thick solid lines represent the propagator of the inner-shell $2p$ electrons. (III) RPA diagrams for the three-point and four-point vertex functions $\Lambda_{\xi_1,\xi_3;\xi_2,\xi_4}(Q)$ and $\Gamma_{\xi_1,\xi_3;\xi_2,\xi_4}(Q)$ ((a) and (b), respectively), where empty squares represent the antisymmetrized bare Coulomb interaction $\Gamma^{(0)}_{\xi_1,\xi_3;\xi_2,\xi_4}$ among the $d$ electrons at transition-metal sites.

$$w_{\zeta,JM}(r_i; q, e)w_{\zeta',J'M'}^*(r_i; q', e')F_{\xi,JM,\xi';J'M';a_1,a_2}(r_i; k_1; q, q')^2, \quad (16)$$
where $G^\pm_a(k)$ is the Keldysh Green’s function, $a_{1,2}$ are indices for the diagonalized bands, $\zeta = (\ell, \sigma)$, $\zeta' = (\ell', \sigma')$, $\sum_{\zeta\zeta'} = \sum_{\ell\ell'} \sum_{\sigma\sigma'}$, and $k_1 = (\omega_1, k_1)$. $q$ and $q'$ are the four-momenta of the incoming and outgoing photons, respectively: $q = (\omega, q)$, $q' = (\omega', q')$. $e$ and $e'$ are the unit vectors pointing along the polarization direction of the absorbed and emitted photons, respectively. $Q$ is the energy and momentum loss of the photon: $Q = q - q' = (\omega - \omega', q - q') \equiv (\Omega, Q)$. $F_{\zeta JM, \zeta' J'M'; a_1, a_2}(r_i; k_1; q, q')$ is the scattering vertex function expressed using only the ordinary causal electron Green’s functions and electron-electron interaction. At this stage, we omit $\omega_1$ dependence of $F_{\zeta JM, \zeta' J'M'; a_1, a_2}(r_i; k_1; q, q')$, i.e., $F_{\zeta JM, \zeta' J'M'; a_1, a_2}(r_i; k_1; q, q') = F_{\zeta JM, \zeta' J'M'; a_1, a_2}(r_i; k_1; q, q')$, because it is justified within the following approximation for $F_{\zeta JM, \zeta' J'M'; a_1, a_2}(r_i; k_1; q, q')$. Within the HF approximation, the Green’s functions $G^\pm_a(k)$ are given by

\begin{align}
G^+_a(k_1) &= 2\pi i n_a(k_1) \delta(\omega_1 - E_a(k_1)), \\
G^-_a(k_1) &= -2\pi i [1 - n_a(k_1)] \delta(\omega_1 - E_a(k_1)),
\end{align}

where $E_a(k_1)$ is the energy of diagonalized band $a$, and $n_a(k_1)$ is the electron occupation density i.e., the Fermi distribution function, at momentum $k_1$ in band $a$: $n_a(k_1) = 1/(\exp[E_a(k_1)/T] + 1)$. Substituting eqs. (17) and (18) into eq. (16), we have

\[
W(q, e; q', e') = \frac{2\pi}{N} \sum_{k_1} \sum_{a_1 a_2} n_{a_1}(k_1) [1 - n_{a_2}(k_1 + Q)] \delta(\Omega + E_{a_1}(k_1) - E_{a_2}(k_1 + Q)) \times \prod_{i} \sum_{\zeta \zeta'} \sum_{J J'} \sum_{M = -J}^{J} \sum_{M' = -J'}^{J'} w_{\zeta JM}(r_i; q, e) w_{\zeta' J'M'}(r_i; q', e') \times F_{\zeta JM, \zeta' J'M'; a_1, a_2}(r_i; k_1; q, q').
\]

For calculation of $F_{\zeta JM, \zeta' J'M'; a_1, a_2}(r_i; k_1; q, q')$, we use perturbation expansion with respect to electron-electron interactions. There are three possible major contributions to $F_{\zeta JM, \zeta' J'M'; a_1, a_2}(r_i; k_1; q, q')$. The first is the zeroth-order term represented by the diagram (II)-(a) in Fig. 2. This diagram presents the main contribution from fluorescence processes, where a valence $d$ electron goes down to the $2p$ state without interacting with other electrons. We refer to this contribution as ‘0th-order process’. The second originates from the screening of the $2p$ core hole. Within the Born approximation with respect to the core-hole potential $V_{2p-d}$, this process is expressed by the diagram (II)-(b) in Fig. 2. We refer to this contribution as ‘$p$-scattering process’ or ‘$p$-process’.

\[
F_{\zeta JM, \zeta' J'M'; a_1, a_2}(r_i; k_1; q, q')
\]
third describes the scattering processes involving both the excited conduction $d$ electron and valence $d$ electrons. This contribution is expressed by the diagram (II)-(c) in Fig. 2. We refer to this contribution as ‘$d$-scattering process’ or ‘$d$-process’. Of course, in higher-order contributions, more complex diagrams can appear, which cannot simply be classified to ‘$p$-process’ or ‘$d$-process’. Nevertheless, this classification turns out to be convenient for microscopic analysis of RIXS spectra. Thus, we obtain the following approximate expression for the scattering vertex function:

$$ F_{ζJM,ζ',J'M';a_1,a_2}(r_i;k_1;q,q') = F_{ζJM,ζ',J'M';a_1,a_2}^{(0)}(r_i;k_1;q,q') $$

$$ - \sum_{ζ_{12}} u_{ζ_{12}}^*(k_1 + Q) u_{ζ_{12}}(k_1) [F_{ζJM,ζ',J'M';ζ_{12}}^{(p)}(r_i;q,q') $$

$$ + F_{ζJM,ζ',J'M';ζ_{12}}^{(d)}(r_i;q,q') ] , $$

(20)

where $u_{ζ,a}(k)$ is the diagonalization matrix of the HF Hamiltonian given by eq. (A-3). $ζ_n$ is orbital-spin unified index: $ζ_n = (ζ_n,σ_n)$, and $∑_{ζ_n} = Σ_{ζ_n}Σ_{σ_n}$, where $ζ_n$ represents $d$ orbitals at transition-metal sites. For the antiferromagnetic ordered state, the energy bands are doubly folded. Therefore, in addition to $ζ_n$, a two-valued index is necessary to specify which of doubled bands each state is on. But we suppress it for simplicity of notation. Contributions from the above three processes are given by

$$ F_{ζJM,ζ',J'M';a_1,a_2}^{(0)}(r_i;k_1;q,q') = δ_{JJ'}δ_{MM'} u^*_{d_{ζ}(i),a_2}(k_1 + Q) u_{d_{ζ'}(i),a_1}(k_1) $$

$$ \left[ ω + \bar{ε}_{2p_j}(r_i) - E_{a_1}(k_1 + Q) \right] , $$

(21)

$$ F_{ζJM,ζ',J'M';ζ_{12}}^{(p)}(r_i;q,q') = \sum_{ζ_{ζζ'}} V_{2p-j}(r_i;JM,ζ_3;ζ_4,J'M') Λ_{ζ_{ζζ'}}(Q) $$

$$ \times [ ω + \bar{ε}_{2p_j}(r_i) - E_{a_1}(k_1) [ ω + \bar{ε}_{2p_j}(r_i) - E_{a_1}(k_1) ] ] , $$

(22)

$$ F_{ζJM,ζ',J'M';ζ_{12}}^{(d)}(r_i;q,q') = δ_{JJ'}δ_{MM'} \sum_{ζ_{ζζ'}} Λ_{ζ_{ζζ'}}(Q) \sum_{a_{ζζ'}} \sum_{k} \frac{1}{N} \sum_{a} [ 1 - n_a(k) ] $$

$$ \times u^*_{d_{ζ}(i),a}(k) u_{d_{ζ'}(i),a}(k) $$

$$ \left[ ω + \bar{ε}_{2p_j}(r_i) - E_{a_1}(k) \right] [ ω + \bar{ε}_{2p_j}(r_i) - E_{a_1}(k) ] , $$

(22)

$$ F_{ζJM,ζ',J'M';ζ_{12}}^{(d)}(r_i;q,q') = δ_{JJ'}δ_{MM'} \sum_{ζ_{ζζ'}} Λ_{ζ_{ζζ'}}(Q) \sum_{a_{ζζ'}} \sum_{k} \frac{1}{N} \sum_{a} [ 1 - n_a(k) ] $$

$$ \times u^*_{d_{ζ}(i),a_3}(k + Q) u_{ζ_3,ζ_4}(k + Q) u^*_{ζ_4,ζ_1}(k) u_{d_{ζ'}(i),a_4}(k) $$

$$ \left[ ω + \bar{ε}_{2p_j}(r_i) - E_{a_1}(k + Q) \right] [ ω + \bar{ε}_{2p_j}(r_i) - E_{a_1}(k + Q) ] $$

$$ \frac{1 - n_{a_1}(k)}{ω + \bar{ε}_{2p_j}(r_i) - E_{a_1}(k) - Ω + E_{a_1}(k + Q) + iε} - \frac{n_{a_1}(k)}{Ω + E_{a_1}(k) - E_{a_1}(k + Q) + iε} , $$

(23)
where $\Lambda_{\zeta_2,\xi_4;\zeta_1,\xi_1}(Q)$ and $\Gamma_{\zeta_2,\xi_4;\zeta_3,\xi_1}(Q)$ are the three-point and four-point vertex functions, which are represented by the filled triangle and square in Fig. 2 (II) (b) and (c), respectively. Index $d_\zeta(i) = d_{\ell\sigma}(i)$ denotes the $d_\ell$ state at transition-metal site $\mathbf{r}_i$ with spin $\sigma$. $\epsilon_{2p_j}(\mathbf{r}_i) \equiv \epsilon_{2p_j}(\mathbf{r}_i) + i\Gamma_{2p}$, where $\Gamma_{2p}$ is the damping rate of the $2p$ core hole and set to 0.3 eV in the present study. Summations in $i$ with ‘t.m.u.’ at the top means that $\mathbf{r}_i$ should be restricted only to transition-metal sites in the unit cell. $\epsilon$ in eq. (23) ensures the causality, i.e., that an electron-hole pair is created only after the resonant transition of a $2p$ electron to $d$ states. $\epsilon$ has the physical meaning of the damping of the excited electron-hole pair. In our numerical calculations, we set $\epsilon = 20$ meV.

The vertex functions introduced above are renormalized by electron correlations. We take account of electron correlations within RPA. RPA for $\Lambda_{\zeta_2,\xi_4;\zeta_1,\xi_1}(Q)$ and $\Gamma_{\zeta_2,\xi_4;\zeta_3,\xi_1}(Q)$ is represented diagrammatically in Fig. 2 (III) (a) and (b), respectively. The analytic expressions for these diagrams are

$$
\Lambda_{\zeta_2,\xi_4;\zeta_1,\xi_1}(Q) = \delta_{\zeta_2\zeta_3} \delta_{\xi_4\xi_1} - \sum_{\zeta_2'\zeta_3'} \sum_{\xi_4'\xi_1'} \Lambda_{\zeta_2',\xi_4';\zeta_1,\xi_1}(Q) \chi_{\zeta_2,\xi_4;\zeta_3',\xi_1'}(Q) \Gamma_{\zeta_2',\xi_4';\zeta_1,\xi_1}^{(0)},
$$

$$
\Gamma_{\zeta_2,\xi_4;\zeta_3,\xi_1}(Q) = \Gamma_{\zeta_2,\xi_4;\zeta_3,\xi_1}^{(0)} - \sum_{\zeta_2'\zeta_3'} \sum_{\xi_4'\xi_1'} \Gamma_{\zeta_2',\xi_4';\zeta_3,\xi_1}(Q) \chi_{\zeta_2,\xi_4;\zeta_3',\xi_1'}(Q) \Gamma_{\zeta_2',\xi_4';\zeta_3,\xi_1}^{(0)},
$$

where $\Gamma_{\zeta_1,\zeta_2;\zeta_3,\zeta_4}^{(0)}$ is the antisymmetrized bare Coulomb interaction given by $\Gamma_{\zeta_1,\zeta_2;\zeta_3,\zeta_4}^{(0)} = I_{\ell_1,\ell_2;\ell_3,\ell_4} \delta_{\sigma_1\sigma_4} \delta_{\sigma_2\sigma_3} - I_{\ell_1,\ell_2;\ell_3,\ell_4} \delta_{\sigma_1\sigma_3} \delta_{\sigma_2\sigma_2}$. $\chi(Q)$ is the polarization function calculated by

$$
\chi_{\zeta_3,\zeta_2;\xi_1,\xi_1}(Q) = \frac{1}{N} \sum_{k} \sum_{a,a'} u_{\zeta_3,a}(k) u^*_{\xi_1,a}(k) u_{\zeta_2,a'}(k + Q) u^*_{\xi_1,a'}(k + Q) \chi_{a,a'}(k; Q),
$$

$$
\chi_{a,a'}(k; Q) = \frac{n_{a'}(k + Q) - n_a(k)}{\Omega + E_a(k) - E_{a'}(k + Q) + i\epsilon},
$$

where $\epsilon$ is interpreted as the damping rate of the excited electron-hole pair near the Fermi level, as already introduced above. Solving eqs. (24) and (25), we can determine $\Lambda_{\zeta_2,\xi_4;\zeta_1,\xi_1}(Q)$ and $\Gamma_{\zeta_2,\xi_4;\zeta_3,\xi_1}(Q)$ within RPA.

To resolve into the contribution from each process of the 0th-order, $p$-scattering and $d$-scattering, we introduce the process-resolved spectra as follows:

$$
W^{(0)}(q, e; q', e') = \frac{2\pi}{N} \sum_{k_1} \sum_{a_1 a_2} n_{a_1}(k_1)[1 - n_{a_2}(k_1 + Q)] \delta(\Omega + E_a(k_1) - E_{a_2}(k_1 + Q)) \times \sum_{i} \sum_{\zeta_2 \zeta_3} \sum_{J J'} \sum_{M' = -J}^{J} \sum_{M'' = -J'}^{J'} w_{\zeta_2,JM}(\mathbf{r}_i; q, e) w^*_{\zeta_1,J'M''}(\mathbf{r}_i; q', e').
$$
Further to resolve orbital-excitation processes involved in the 0th-order, \( p \)-scattering processes, we introduce the orbital-spin-resolved spectra as follows:

\[
W^{(p)}(q, e; q', e') = \frac{2\pi}{N} \sum_{k_1} \sum_{a_1 a_2} n_{a_1}(k_1)[1 - n_{a_2}(k_1 + Q)]\delta(\Omega + E_{a_1}(k_1) - E_{a_2}(k_1 + Q))
\times \left| \sum_{i} \sum_{J} \sum_{\zeta, \zeta'} \sum_{J'} w_{\zeta, J, M}(r_i; q, e) w^*_{\zeta', J', M'}(r_i; q', r') \right|^2,
\]

\[
W^{(d)}(q, e; q', e') = \frac{2\pi}{N} \sum_{k_1} \sum_{a_1 a_2} n_{a_1}(k_1)[1 - n_{a_2}(k_1 + Q)]\delta(\Omega + E_{a_1}(k_1) - E_{a_2}(k_1 + Q))
\times \left| \sum_{i} \sum_{J} \sum_{\zeta, \zeta'} \sum_{J'} w_{\zeta, J, M}(r_i; q, e) w^*_{\zeta', J', M'}(r_i; q', r') \right|^2,
\]

These are obtained from eq. (19) by keeping only one of \( F^{(0)}_{\zeta, J, M; \zeta', J', M'}(r_i; k_1; q, q') \), \( F^{(p)}_{\zeta, J, M; \zeta', J', M'}(r_i; q, q') \) and \( F^{(d)}_{\zeta, J, M; \zeta', J', M'}(r_i; q, q') \) and setting the rest two to zero in eq. (20).

Further to resolve orbital-excitation processes involved in the 0th-order, \( p \)-scattering and \( d \)-scattering processes, we introduce the orbital-spin-resolved spectra as follows:

\[
W^{(0)}_{\zeta, J, M; \zeta', J', M'}(r_i; k_1; q, q') = \left| \sum_{i} \sum_{J} \sum_{\zeta, \zeta'} w_{\zeta, J, M}(r_i; q, e) w^*_{\zeta', J', M'}(r_i; q', r') \right|^2.
\]

These processes are obtained from eq. (19) by setting only one of \( F^{(0)}_{\zeta, J, M; \zeta', J', M'}(r_i; k_1; q, q') \), \( F^{(p)}_{\zeta, J, M; \zeta', J', M'}(r_i; q, q') \) and \( F^{(d)}_{\zeta, J, M; \zeta', J', M'}(r_i; q, q') \) and setting the rest two to zero in eq. (20).
overall consistency, the factor $\epsilon$ transitions. This naive view is not correct, as explained next. We should note that, for eq. (19) describes only simple band-to-band transitions and fails to describe local $\zeta$ vanish only in the case where both of $\zeta$ and $\zeta_2$ reside on atomic site $r_i$. Thus summation in $r_i$ does not appear in eq. (31). On the other hand, in eqs. (32) and (33), summation with respect to $r_i$ is necessary, since $\zeta_1$ and $\zeta_2$ need not reside on the site $r_i$ where x-ray absorption and emission occur. All of the above formulae are valid also for general cases including several transition-metal atoms.

Here we should note that the total RIXS intensity $W(q, e; q', e')$ does not equal the sum of the resolved intensities, e.g., $W(q, e; q', e') \neq W^{(0)}(q, e; q', e') + W^{(p)}(q, e; q', e') + W^{(d)}(q, e; q', e')$, $W^{(p)}(q, e; q', e') \neq \sum_{\zeta_1, \zeta_2} W^{(p)}(q, e; q', e')$, $W^{(d)}(q, e; q', e') \neq \sum_{\zeta_1, \zeta_2} W^{(d)}(q, e; q', e')$, and so on. This is because the total summed spectrum $W(q, e; q', e)$ contains interference terms such as $F^{(0)}(r_i; k_1; q, q')F^{(d)*}(r_i; q, q')$, while resolved spectra $W^{(0)}(q, e; q', e')$ and $W^{(d)}(q, e; q', e')$ contain only $|F^{(0)}(r_i; k_1; q, q')|^2$ and $|F^{(d)}(r_i; q, q')|^2$, respectively. Nevertheless these resolved spectra are useful to take microscopic insights into the mechanism of RIXS, as we shall see later.

For numerical calculation of eq. (19), we use the Lorentzian expression for the $\delta$-function:

$$\delta(\Omega + E_{a_1}(k_1) - E_{a_2}(k_1 + Q)) \to \frac{1}{\pi} \frac{\epsilon}{[\Omega + E_{a_1}(k_1) - E_{a_2}(k_1 + Q)]^2 + \epsilon^2}.$$  

This function possesses poles at $\Omega = E_{a_2}(k_1 + Q) - E_{a_1}(k_1) \pm i\epsilon$, which correspond to the transition from band $a_1$ to band $a_2$. Therefore, at a first glance, one might consider that eq. (19) describes only simple band-to-band transitions and fails to describe local $d$-$d$ transitions. This naive view is not correct, as explained next. We should note that, for overall consistency, the factor $\epsilon$ should equal the damping rate of the excited electron-
hole pair, already introduced above. The position of the pole $\Omega = E_{a_2}(k_1 + Q) - E_{a_1}(k_1) \pm i\epsilon$ is modified to a non-trivial position by the RPA correction. The modified poles describe bound states between the excited electron and hole in the final state. As a result, we shall see not only charge-transfer excitations but also magnon excitation and local $d$-$d$ excitations can be described within our HF-RPA calculation on the basis of electronic bands.

For later discussions, we define the following quantity,

$$P^{J}_{\zeta\zeta'}(q, e; q', e') \equiv \left| \sum_{M=-J}^{J} w_{\zeta,JM}(r_i; q, e) w^{*}_{\zeta',JM}(r_i; q', e') \right|^2 \propto \left| \sum_{M=-J}^{J} \langle d_\zeta | e \cdot r | 2p_{JM} \rangle \langle 2p_{JM} | e' \cdot r | d_{\zeta'} \rangle \right|^2,$$

where $\zeta = (\ell, \sigma)$, $\zeta' = (\ell', \sigma')$, and $\ell$ and $\ell'$ lie on transition-metal site $r_i$. We should note that $\zeta$ [$\zeta'$] represents the orbital and spin of the $d$ electron which is initially promoted from a $2p$ state [finally decays down to the empty $2p$ state], and this electron could be different in general from the electron left above $E_F$ [removed below $E_F$] in the final state at $t = +\infty$. Nevertheless, we shall see $P^{J}_{\zeta\zeta'}(q, e; q', e')$ is useful for understanding the dependence of RIXS spectra on the scattering geometry.

### 3. Numerical Results

#### 3.1 Overall spectral structure

Throughout our present study, we set the incident photon energy at the Cu-$L_3$ edge (see Appendix B for absorption spectra), and set the azimuth angles as $\phi = \phi' = 0$. Firstly, we present a typical calculated result of RIXS spectrum within our theoretical framework (see the thick solid curve in Fig. 3). The spectrum consists of three main features: magnon excitation at low energies up to 400 meV, $d$-$d$ orbital excitations around 1.7-2.1 eV, and the charge-transfer excitations between 3-9 eV, which are semi-quantitatively consistent with experimental spectra.\(^{34}\)

The origin of each feature is clarified by using the process-resolved spectra (see § 2.2, and eqs. (28), (29) and (30)). The low-energy $d$-$d$ and magnon excitation weights originate solely from the $d$-process. We should note that, in our electronic band approach, the $d$-$d$ excitations are described as bound states of electron and hole on the bands. Therefore $d$-$d$ excitations are not contributed from the 0th-order process but from the $d$-process. The 0th-order process contributes only above 2.2 eV excitation energy to the RIXS weight, since the insulating gap is 2.2 eV. On the other hand, high-energy (above
3 eV) part is contributed from both the 0th-order process and d-process. The p-process, in which the d electrons are excited by screening the inner-shell 2p core hole, is negligible in the present case. As intuitively understood by the local picture, the Cu-d shell is completely filled with 10 electrons in the intermediate state, and the core-hole cannot be screened by the Cu-d electrons. In this point, L-edge RIXS substantially differs from K-edge RIXS. In K-edge RIXS, screening of the inner-shell 1s core hole is the essential process.\textsuperscript{25} Thus the Slater-Condon integrals between the 2p and 3d states, $F^0(p,d)$ and $F^2(p,d)$, are not significant parameters in the present Cu L-edge case. For the same reason, $G^1(p,d)$ and $G^3(p,d)$ are not significant.

3.2 Magnon excitation

Here we focus on the low-energy feature below 0.5 eV. As we have mentioned, magnon (spin-wave) mode appears below about 350 meV, and is dispersive as shown in Fig. 4(a). The theoretical dispersion of the magnon is quite consistent with experimental one in quantitative level as shown in Fig. 4(b). This magnon mode originates from spin-flip processes in the $d_{x^2-y^2}$ orbital. Here note that we have started not from a Heisenberg spin model but from an electron band model to derive the magnon spectrum. To fit
Fig. 4. (Color online) (a) Low-energy part of calculated RIXS spectra is depicted along the symmetry lines in the Brillouin zone. (b) Gray-level map of the low-energy RIXS intensity. The scattering geometry for calculation is $\theta = \theta' = \pi/4$ and $\pi \rightarrow \sigma' \ (\psi = 0, \ \psi' = \pi/2)$. The plots are experimental data of magnon excitation energy, which are read from Refs. 10 and 14. Experimental data contain those of $\theta + \theta' = 90^\circ$ (for small $|Q|$) and $130^\circ$ (for large $|Q|$).

well to the experimental magnon dispersion, Heisenberg-model approaches require not only nearest-neighbor exchange $J$ but also long-range ones. The exchange parameters are often used as fitting parameters. On the other hand, in our band approach, effects of the long-range magnetic correlations are taken into account through the inter-site hopping parameters, which are determined by the first-principles band calculation. It is notable that the magnon intensity should increase divergently towards $Q = 0$. This divergence is not a result from ordinary elastic processes, since we have already excluded...
Fig. 5. (Color online) Polarization dependence of the low-energy part of calculated RIXS spectrum. $\theta = \theta' = \pi/4$, and in-plane momentum transfer of photons is set to $Q = q - q' = (\pi/2, 0)$. Initial incoming photons are in $\pi$ polarization (i.e., $\psi = 0$) in (a) and in $\sigma$ polarization (i.e., $\psi = \pi/2$) in (b).
3.3 d-d excitations

Here we focus on the d-d excitations around 2 eV energy loss. In Fig. 6, a calculated spectrum for a typical scattering geometry is compared with the experimental data read from Ref. 34. Two-peak structure is well reproduced by the present calculation, although the peak positions depend on the modification of the completely-filled Cu-d levels (see Appendix A). In that scattering geometry, the low-energy peak around 1.7 eV are attributed mainly to the d-d transition from \( d_{xy} \) to \( d_{x^2-y^2} \), while the high-energy peak around 2.2 eV is to the d-d transition from \( d_{yz} \) to \( d_{x^2-y^2} \) (Note that we are working with the electron representation not with the hole one). The transition from \( d_{xz} \) to \( d_{x^2-y^2} \) is absent in that scattering geometry. The interval between the two peaks is somewhat overestimated. We consider that this overestimation is ascribed to the band structure calculation (and subsequent Wannier fitting and Hartree-Fock calculation), since we retained the energy level splitting between the \( d_{xy} \) and \( d_{yz}/xz \) levels in modifying the completely filled Cu-d levels (see Appendix A). In Fig. 6, we should note that the peaks are not contributed only from spin-conserved excitations but also from spin-flipped excitations. In particular, the spin-conserved and spin-flipped transitions from \( d_{xy} \) to \( d_{x^2-y^2} \) almost evenly occur. Energy positions of d-d excitation peaks do not significantly depend on momentum transfer, reflecting their localized nature (Momentum-transfer dependence is not shown).

The d-d excitation spectrum significantly depends on the scattering geometry. In the right panels of Fig. 7, the d-d excitation spectra are displayed for various Bragg angles with \( \theta + \theta' = \pi/2 \). For \( \pi \to \sigma' \), d-d excitation intensity monotonically increases with increasing \( \theta \) (left panel of Fig. 7(a)). For \( \sigma \to \pi' \), intensity of the 1.7 eV [2.2 eV] peak decreases [increases] drastically with increasing \( \theta \) (left panel of Fig. 7(b)). These behaviors seem well correlated with \( P_{(x^2-y^2 \sigma)(\ell \sigma')}^J=3/2}(q, e; q', e') \): As seen in Fig. 6, the 1.7 eV peak originates mainly from the d-d transition \( xy \to x^2 - y^2 \), and the 2.2 eV peak originates from the d-d transition \( yz \to x^2 - y^2 \). For \( \pi \to \sigma' \), \( P_{(x^2-y^2 \sigma)(xy \sigma)}^J=3/2} \) and \( P_{(x^2-y^2 \sigma)(yz \sigma)}^J=3/2} \) both increase with increasing \( \theta \) (right panel of Fig. 7(a)). For \( \sigma \to \pi' \), \( P_{(x^2-y^2 \sigma)(xy \sigma)}^J=3/2} \) decreases and \( P_{(x^2-y^2 \sigma)(yz \sigma)}^J=3/2} \) increases with increasing \( \theta \) (right panel of Fig. 7(b)). In the left panels of Fig. 8, the d-d excitation spectra are displayed for various polarizations of the incoming and outgoing photons. The dependence on polarization can roughly be understood in the same manner as above. For example,
Fig. 6. (Color online) A typical $d$-$d$ excitation spectrum around 2 eV. Thick and thin solid curves denote the calculated results of total and spin-orbital-resolved RIXS spectra, respectively. For the calculated results, polarization of photons is set as $\psi = \psi' = \pi/2$ ($\sigma \rightarrow \sigma'$). For the weight from $xy \rightarrow x^2 - y^2$, four curves ($xy \uparrow \rightarrow x^2 - y^2 \uparrow$, $xy \uparrow \rightarrow x^2 - y^2 \downarrow$, $xy \downarrow \rightarrow x^2 - y^2 \uparrow$, $xy \downarrow \rightarrow x^2 - y^2 \downarrow$) almost evenly contribute and their curves are overlaid (Note that we are working with the electron representation not with the hole one). Circles are experimental data read from Ref. 34 (incident incoming photons are in $\sigma$ polarization, but polarization of final outgoing photons is not discriminated in the experiment).

when the incident photon is in $\pi$ polarization ($\psi = 0$), intensity of the 1.7 eV [2.2 eV] peak increases [decreases] drastically with increasing $\psi'$ (left panel of Fig. 8(a)). This behavior is understood well by noticing that $P_{(x^2-y^2 \sigma)(xy \sigma)}^{J=3/2}$ increases and $P_{(x^2-y^2 \sigma)(yz \sigma)}^{J=3/2}$ decreases with increasing $\psi'$ (right panel of Fig. 8(a)).

4. Discussions

In this section, we present some remarks on $L$-edge RIXS, our formulation and calculated results.

As we have seen, in $L$-edge RIXS, the $d$-$d$ excitations play a major role in the RIXS weight. This is in strong contrast to the case of $K$-edge RIXS. In the case of $K$-edge RIXS, the process of screening the created 1s hole by the $d$ electrons is dominant, where the $d$ electrons are scattered isotropically due to the strongly localized 1s core hole and usually prohibited to change their orbital state. In those processes, the $d$ electrons
conserve their orbital angular momentum. This means that the orbital-diagonal $d$-$d$ excitations are dominant in $K$-edge RIXS. As a result, completely filled $d$ orbitals in the initial state are completely filled still in the final state of RIXS, and completely empty $d$ orbitals are empty still in the final state. Therefore we can construct a good effective theory by neglecting completely filled or empty $d$ orbitals, when we describe $K$-
Fig. 8. (Color online) Dependence of the $d$-$d$ excitation spectrum (left panels) and $P_{(x^2-y^2)\sigma}(\ell';\sigma') (q,e; q', e')$ (right panels) on polarizations of incoming and outgoing photons. In the right panels, $P_{(x^2-y^2)\sigma}(\ell';\sigma') (q,e; q', e')$ is shown for $\ell' = xy, yz, xz, 3z^2-r^2$. Empty and filled symbols are for the spin-conserved ($\sigma = \sigma'$) and spin-flipped ($\sigma = -\sigma'$) components, respectively. In (a) [in (b)], the incident incoming photons are in $\pi$ [$\sigma$] polarization, i.e., $\psi = 0$ [$\psi = \pi/2$]. The Bragg angles are $\theta = \theta' = \pi/4$ in the both cases.

edge RIXS. In fact, orbital excitations between different $d$ orbitals seem inactive in most cases of $K$-edge RIXS, and we can take only active $d$ orbitals, e.g., the $d_{x^2-y^2}$ orbital in the case of cuprates with the tetragonal or octahedral coordination. On the other hand, in $L$-edge RIXS, orbital states of $d$ electrons can change in the final state. This is because the $d$ electrons can exchange their orbital angular momentum into spin angular momentum and vice versa, mediated by the $2p$ states in which spin and orbital angular
momenta are coupled. Therefore, to analyze $L$-edge RIXS spectra over a wide-energy range, we should include $d$ orbitals which are initially completely filled or completely empty, in addition to partially filled $d$ orbitals. In this sense, $L$-edge RIXS is essentially a multi-orbital phenomenon, and can involve much more complex excitation processes than $K$-edge RIXS.

The $p$-process, where the $2p$ core hole is screened by the Cu-$d$ electrons, is almost ineffective in the present case of Cu $L$-edge RIXS. This is because the narrow Cu-$d$ band is completely filled in the intermediate state of RIXS, and is in great contrast to the case of $K$-edge RIXS. However, we should note that the $p$-process can be effective in other transition-metal compounds whose transition-metal $d$ bands are broad (i.e., localization is weak) and are not completely filled in the intermediate state.

As we have seen in § 3.2, the magnon intensity becomes divergent towards $Q = 0$. Very recently, Igarashi and Nagao found that such divergence essentially appears around $Q = 0$ as a result from broken symmetry.\(^{35}\) According to them, this divergence originates from anisotropic terms of the scattering amplitude which are a natural result from the long-range ordering, and is not reproduced within the so-called fast collision approximation (FCA). Although it is beyond the scope of the present work and not straightforward to clarify the analytic relation between our present calculation and theirs, such anisotropic terms are included within the HF approximation in our present calculation. Our calculation suggests that this divergent behavior should survive for realistic values of core-hole life time. Such divergent behavior around $Q = 0$ is a substantial difference between RIXS and neutron scattering, and deserves to be searched for carefully, although the measurement should be performed at low temperatures well below the Néel temperature and the inelastic weight around $Q = 0$ may be difficult to distinguish from the elastic one experimentally.

Note that the multi-magnon processes are beyond the present theoretical approach. $n$-magnon generation processes are represented by diagrams in which the upper and lower branches are connected by $2n$ lines, which are omitted in Fig. 2(I). Inclusion of the multi-magnon excitation processes is not feasible for the present complex electronic structure and remains an interesting future work.

In § 3.3, we have interpreted the dependence of the $d$-$d$ excitation spectrum on the scattering geometry by using the square of the product of the dipole-transition matrix, $P^{I}_{\xi\zeta'}(q, e; q', e')$ (see eq. (35)). We should note that such interpretation is not always valid, since RIXS intensity is not determined only by the dipole-transition matrix.
elements. Analysis based on $P_{\zeta\zeta'}^J(q, e; q', e')$ will become less effective for systems where orbitals are strongly hybridized with each other due to low crystal symmetry. In general, the $d$ electron which is initially promoted from a $2p$ state can be quite different from the $d$ electron remaining above $E_F$ in the final state, as a result from the intermediate scattering processes and orbital hybridization.

5. Conclusion

We have discussed the Cu $L_3$-edge RIXS for a typical parent compound of high-$T_c$ cuprate superconductors La$_2$CuO$_4$ on the basis of the first-principles electronic bands. We consider that the advantages of our approach are: it can reproduce RIXS features in the wide-energy range, including the low-energy magnon spectrum, intermediate-energy $d$-$d$ excitations and high-energy charge-transfer excitations, consistently with experiments. It is applicable to relatively complex three-dimensional multi-orbital systems. Finite size effects are absent. Therefore it is useful for analyzing experimental data for a wide variety of transition-metal compounds. Disadvantages are that the ground state needs to be described accurately within the Hartree-Fock approximation, and multi-magnon weights are not included at all.

In conclusion, we would like to stress the importance of photon polarization dependence: the intensity of magnon excitation and the spectral structure of $d$-$d$ excitations depend significantly not only on the polarization direction of incident incoming photons but also that of outgoing photons. Polarization of scattered photons is not discriminated so far in most of experiments.$^{36)}$ A full knowledge of the both polarizations of incoming and outgoing photons could become crucial to correctly assign RIXS spectral weights to magnetic and orbital excitation processes.

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Appendix A: Hartree-Fock Approximation

By fitting to the first-principles electronic structure of the nonmagnetic state, we obtain transfer integrals and one-particle energy levels. We take about 2000 transfer integrals to fit 17 bands near the Fermi energy using the 17 Wannier orbitals (all of the Cu-$d$ and O-$p$ states are included). Some typical values of calculated transfer integrals are 1.346 eV between nearest-neighbor Cu-$d_{x^2-y^2}$ and in-plane O-$p_{x/y}$, and 0.623 eV
between nearest-neighbor in-plane O-$p_{x/y}$ orbitals. These values quantitatively agree with 1.3 eV and 0.65 eV in Ref. 37. One-particle energy levels are obtained for the Cu-$d$ orbitals as: $\varepsilon_{xy} = 6.81$ eV, $\varepsilon_{yz/\bar{z}x} = 7.12$ eV, $\varepsilon_{x^2-y^2} = 7.55$ eV, $\varepsilon_{3z^2-r^2} = 7.56$ eV (the Fermi level is about 9.53 eV). Only the $d_{x^2-y^2}$ state is partially filled, and the other $d$ orbitals are completely filled with electrons. Here we consider that these values do not reflect a realistic level scheme of the local Cu-$d$ orbitals: for example, $\varepsilon_{x^2-y^2} - \varepsilon_{yz/\bar{z}x} = 0.43$ eV will be too small. To reproduce the $d$-$d$ transition energies which were recently determined with great accuracy by $L$-edge RIXS,\(^{34}\) we modify the one-particle energy levels of the completely-filled Cu-$d$ orbitals in the following way: we subtract 1.40 eV from $\varepsilon_\ell$ for the $t_{2g}$ ($d\varepsilon$) orbitals and 1.65 eV for the $d_{3z^2-r^2}$ orbital, and as a result we obtain $\varepsilon_{xy} = 5.41$ eV, $\varepsilon_{yz/\bar{z}x} = 5.72$ eV, $\varepsilon_{x^2-y^2} = 7.55$ eV, $\varepsilon_{3z^2-r^2} = 5.91$ eV (the Fermi level is about 9.49 eV). Hereafter, we redefine $\varepsilon_\ell$ by the subtracted one-particle energy.

In Fig. A.1(a), we show the original electronic structure, the fitted bands using the 17 Wannier orbitals, and the bands obtained for the modified Cu-$d$ energy levels.

To describe the antiferromagnetic ground state, we apply the HF approximation to the tight-binding Hamiltonian $H_{n.f.}$. For the Coulomb integrals $I_{\ell_1,\ell_2;\ell_3,\ell_4}$, we introduce the following notation:

$$J_{\ell,\ell'} \equiv I_{\ell,\ell';\ell,\ell'}, \quad \text{(A.1)}$$

$$K_{\ell,\ell'} \equiv I_{\ell,\ell';\ell,\ell'}. \quad \text{(A.2)}$$

$J_{\ell,\ell'}$ and $K_{\ell,\ell'}$ are the so-called direct and exchange integrals, respectively. We assume spin polarization is induced only in the $d$ orbitals at each Cu site, and take mean fields only for the Cu-$d$ electrons. The mean-field Hamiltonian for $H_{n.f.}$ is

$$H_{n.f.}^{HF} = \sum_{i'i'} \sum_{\ell} \sum_{\ell'} \sum_{\sigma} \sum_{\sigma'} t_{\ell,\ell'} (\mathbf{r}_i - \mathbf{r}_{i'}) a_{i\ell\sigma}^\dagger a_{i'\ell'\sigma'} + \sum_{i} \sum_{\ell} \sum_{\ell'} \sum_{\sigma} \left[ \frac{J_{\ell,\ell'}}{2} \langle n_{i\ell} \rangle + \sum_{\ell' \neq \ell} \frac{K_{\ell,\ell'}}{2} \langle n_{i\ell'} \rangle \right] n_{i\ell}$$

$$- \sum_{i} \sum_{\ell} \left[ \frac{J_{\ell,\ell'}}{2} \langle m_{i\ell} \rangle + \sum_{\ell' \neq \ell} \frac{K_{\ell,\ell'}}{2} \langle m_{i\ell'} \rangle \right] \cdot \mathbf{m}_{i\ell} - \sum_{i} \sum_{\ell} \sum_{\ell'} \sum_{\sigma} \frac{1}{4} \left( \langle n_{i\ell} \rangle^2 - |\langle m_{i\ell} \rangle|^2 \right)$$

$$- \sum_{i} \sum_{\ell \neq \ell'} \frac{J_{\ell,\ell'}}{2} \langle n_{i\ell} \rangle \langle n_{i\ell'} \rangle + \sum_{i} \sum_{\ell \neq \ell'} \frac{K_{\ell,\ell'}}{4} \left( \langle n_{i\ell} \rangle \langle n_{i\ell'} \rangle + \langle m_{i\ell} \rangle \cdot \langle m_{i\ell'} \rangle \right), \quad \text{(A.3)}$$

where

$$n_{i\ell} = \sum_{\sigma} d_{i\ell\sigma}^\dagger d_{i\ell\sigma}, \quad \text{(A.4)}$$
\[ m_{\ell} = \sum_{\sigma \sigma'} d_{i\ell \sigma}^\dagger \sigma \sigma' d_{i\ell' \sigma'}, \quad (A-5) \]

using the Pauli matrix vector \( \sigma \). Within the HF theory, we should consider that the one-particle energy \( \varepsilon_{\ell} \) is already including the following energy shift from the bare one,

\[ \Delta_{\ell}^{HF} \equiv \frac{J_{\ell,\ell}}{2} \langle n_{i\ell} \rangle + \sum_{\ell' \neq \ell} \left( J_{\ell,\ell'} - \frac{K_{\ell,\ell'}}{2} \right) \langle n_{i\ell'} \rangle, \quad (A-6) \]

due to the electron-electron Coulomb interaction at transition-metal site \( r_i \). Therefore, before determining the magnetic ground state, we need to evaluate the bare one-particle energy by \( \varepsilon_{\ell}^{(0)} \equiv \varepsilon_{\ell} - \Delta_{\ell}^{HF} \), where \( \Delta_{\ell}^{HF} \) is evaluated from the expectation values of particle numbers \( \langle n_{i\ell} \rangle \)'s in the paramagnetic state using eq. (A-6). Note that \( \varepsilon_{\ell} \)'s here are the modified values mentioned above. For the Coulomb integrals given in \( \S\,2 \), the obtained values of \( \varepsilon_{\ell}^{(0)} \) are as follows: \( \varepsilon_{xy}^{(0)} = -39.69 \text{ eV} \), \( \varepsilon_{yz/xz}^{(0)} = -40.02 \text{ eV} \), \( \varepsilon_{x^2-y^2}^{(0)} = -38.86 \text{ eV} \), \( \varepsilon_{3z^2-r^2}^{(0)} = -40.06 \text{ eV} \). Maintaining these values of \( \varepsilon_{\ell}^{(0)} \), we determine the mean-fields \( \langle n_{i\ell} \rangle \) and \( \langle m_{i\ell} \rangle \) self-consistently. We assume the antiferromagnetic ordering with the spin moments pointing along [110], as observed in neutron scattering. As a result, we obtain 68 diagonalized energy bands (\( E_a(k), 1 \leq a \leq 68 \)) for the antiferromagnetic ground state (Note spin degeneracy and folding of the Brillouin zone). The \( d_{x^2-y^2} \) orbitals accommodate 1.27 electrons and take the spin moment of 0.69 \( \mu_B \) per Cu site, while the other Cu-\( d \) orbitals are completely filled with electrons. Figure A-1(b) shows the obtained density of states for the antiferromagnetic ground state.

**Appendix B: Resonant X-ray Absorption Spectrum**

Resonant x-ray absorption spectrum (XAS) is obtained by calculating the number of photons absorbed by the electronic system per unit time. Keldysh diagrammatic representation of XAS is presented in Fig. B-1(I), and the analytic expression is

\[ A(q, e) = \frac{1}{N} \sum_k \int \limits_{-\infty}^{\infty} dt \ e^{-i\omega t} \sum_i \sum_{\zeta \zeta'} \sum_J \sum_{M=\pm J} G_{2pJ_M(i)}^+(k, t) G_{2pJ_M(i)}^-(k+q, -t), \quad (B-1) \]

where \( q = (\omega, q) \) and \( G_{2pJ_M(i)}^+(k, t) \) and \( G_{2pJ_M(i)}^-(k+q, t) \) are the Keldysh Green’s functions for the \( 2pJ_M \) electrons at transition-metal site \( i \) and that for the transition-metal \( d \) electrons, respectively:

\[ G_{2pJ_M(i)}^+(k, t) = i n_{2pJ_M(i)} e^{-i\varepsilon_{2pJ}(r_i) t} = i e^{-i\varepsilon_{2pJ}(r_i) t} \quad (B-2) \]
Fig. A-1. (Color online) (a) Electronic band structure of the non-magnetic state for $\text{La}_2\text{CuO}_4$. Thick solid, thin solid, and dashed curves are the results of the band calculation, Wannier-function fitting, and the tight-binding model with modified Cu-$d$ levels (see the text for details), respectively. The Wannier-fitting curves are almost completely overlaid on the 17 curves of the band calculation result around the Fermi energy. (b) Density of states (DOS) for the antiferromagnetic ground state. Thick solid, thin dashed, and thin solid curves are the results of the total, $t_{2g}$ and $e_g$ partial DOS, respectively. The Fermi energy is set to zero in the both panels.

\[
G_{\zeta',\zeta}(\mathbf{k},t) = -i \sum_a u_{\zeta',a}(\mathbf{k}) u_{\zeta,a}^*(\mathbf{k}) [1 - n_a(\mathbf{k})] e^{iE_a(\mathbf{k})t}. \quad (B\cdot3)
\]

Thus eq. (B-1) is reduced to

\[
A(q,\mathbf{e}) = 2\pi \sum_i \sum_{\zeta'\zeta} \sum_J \sum_{M=-J} \bar{w}_{\zeta,JM}(\mathbf{r}_i; q, \mathbf{e}) \bar{w}_{\zeta',JM}^*(\mathbf{r}_i; q, \mathbf{e})
\]

\[
\times \frac{1}{N} \sum_\mathbf{k} \sum_a [1 - n_a(\mathbf{k})] u_{\zeta',a}(\mathbf{k}) u_{\zeta,a}^*(\mathbf{k}) \delta(\omega + \varepsilon_{2pJ}(\mathbf{r}_i) - E_a(\mathbf{k})). \quad (B\cdot4)
\]
Fig. B.1. (I) Diagrammatic expression of x-ray absorption intensity. Wavy line, thick solid line, and thin solid line represent the propagators for the photon, Cu-2p and Cu-3d electrons, respectively. The shaded triangle is the electron-photon interaction renormalized by the Coulomb interaction between the 2p and 3d electrons. (II) The vertex correction by the multiple scattering between the 2p and 3d electrons (Ladder approximation).

\[ \bar{w}_{\zeta,JM}(r_i; q, e) \] is the effective 2p-d dipole-transition matrix renormalized within the ladder approximation as in Fig. B.1(II):

\[
\bar{w}_{\zeta,JM}(r_i; q, e) = w_{\zeta,JM}(r_i; q, e) + i \sum_{\zeta''} \sum_{J''} \sum_{M'' = -J''} V_{2p-d}(r_i; J'M', \zeta; \zeta'', JM) \\
\times \bar{w}_{\zeta'',J'M'}(r_i; q, e) \frac{1}{N} \sum_{k} \int_{-\infty}^{+\infty} \frac{dz}{2\pi} G_{2pJ'M'(i)}(k, z) G_{\zeta'',\zeta'}(k + q, z + \omega) \\
= w_{\zeta,JM}(r_i; q, e) - \sum_{\zeta''} \sum_{J''} \sum_{M'' = -J''} V_{2p-d}(r_i; J'M', \zeta; \zeta'', JM) \\
\times \bar{w}_{\zeta'',J'M'}(r_i; q, e) \frac{1}{N} \sum_{k} \sum_{\alpha} u_{\zeta'',\alpha}^{*}(k) u_{\zeta',\alpha}^{*}(k) \frac{1 - n_{\alpha}(k)}{\omega + \varepsilon_{2pJ'}(r_i) - E_{\alpha}(k) + i\epsilon},
\]

where \( G_{2pJ'M'(i)}(k) \) and \( G_{\zeta'',\zeta'}(k) \) are the ordinary causal Green’s functions for the 2p,JM electrons at transition-metal site \( i \) and that for the transition-metal d electrons, respectively.

Calculated results of XAS for several values of the Coulomb interaction between the Cu-2p and Cu-3d orbitals are displayed in Fig. B-2. The main peak position shifts to the low-energy region, increasing the Coulomb interaction. The calculated spectral shape suggests a possibility that a small satellite peak can appear. For the calculations of RIXS spectra, we simply use the unrenormalized matrix elements \( w_{\zeta,JM}(r_i; q, e) \).
Fig. B-2. (Color online) Calculated x-ray absorption spectra (XAS) near the Cu $L_3$-edge. We show four cases of the Coulomb interaction between the Cu-2$p$ and Cu-3$d$ orbitals: $F^0(p, d) = F^2(p, d) = 0, 1, 2, 4$ eV. The Bragg angle is $\theta = \pi/4$, and the absorbed photon is in $\pi$ polarization ($\psi = 0$).

The photon energy for the main resonance absorption is changed by using renormalized $\bar{w}_{\zeta,J_M}(\mathbf{r}_i; q, \mathbf{e})$, but it can be re-adjusted to the observed value by shifting the inner-shell 2$p$ level.
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