Momentum dependence in K-edge resonant inelastic x-ray scattering and its application to screening dynamics in CE-phase La$_{0.5}$Sr$_{1.5}$MnO$_4$

T. F. Seman,$^1$ X. Liu,$^{2,3}$ J. P. Hill,$^2$ M. van Veenendaal,$^{4,5}$ and K. H. Ahn$^1$

$^1$Department of Physics, New Jersey Institute of Technology, Newark, New Jersey 07102, USA
$^2$Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory, Upton, New York 11973, USA
$^3$Beijing National Laboratory for Condensed Matter Physics, and Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
$^4$Department of Physics, Northern Illinois University, DeKalb, Illinois 60115, USA
$^5$Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA

We present a formula for the calculation of K-edge resonant inelastic x-ray scattering on transition metal compounds, based on a local interaction between the valence shell electrons and the 1s core hole. Extending a previous result, we include explicit momentum dependence and a basis with multiple core-hole sites. We apply this formula to a single-layered charge, orbital and spin ordered manganite, La$_{0.5}$Sr$_{1.5}$MnO$_4$, and obtain good agreement with experimental data, in particular with regards to the large variation of the intensity with momentum. We find that the screening in La$_{0.5}$Sr$_{1.5}$MnO$_4$ is highly localized around the core-hole site and demonstrate the potential of K-edge resonant inelastic x-ray scattering as a probe of screening dynamics in materials.

PACS numbers: 78.70.Ck, 71.27.+a, 75.47.Lx, 71.10.-w

I. INTRODUCTION

There has been a great interest recently in K-edge resonant inelastic x-ray scattering (RIXS) in particular in transition metal oxides, because of its unique advantages over other probes. In this spectroscopy, hard x-rays with energies of the order of 10 keV excite transition-metal 1s electrons into empty 4p levels, which decay back to the 1s levels. In addition to the elastic process, inelastic processes occur that result in low energy excitations of the order of 1 eV near the Fermi energy, the cross section of which is enhanced by the resonant condition. The K-edge RIXS spectrum provides information on the momentum dependence of the excitations, is sensitive to the bulk properties because of the high energy of hard x-rays, and directly probes valance-shell excitations because there is no core hole in the final states. Since early studies on nickel-based compounds K-edge RIXS has been a useful probe for novel excitations in transition metal oxides, in particular, high-T$_c$ cuprates.

Theoretically, it has been proposed that the K-edge RIXS spectrum reflects different aspects of the electronic structure depending on the size of the core-hole potential, $U_{\text{core}}$, between the 1s core hole and the 3d electrons, relative to the 3d band width. In the weak or strong limit of $U_{\text{core}}$, the ultra-short core-hole lifetime expansion is applicable and it has been shown that the K-edge RIXS spectrum corresponds to the dynamic structure factor, $S(q, \omega)$, in the intermediate case of $U_{\text{core}}$, numerical calculations show asymmetric electron-hole excitations and that the RIXS spectrum is substantially modified from $S(q, \omega)$.

One of the main conclusions of Ref. 14 is that the K-edge RIXS intensity for transition metal oxides essentially represents the dynamics of electrons near the Fermi energy, which screen the 1s core hole created by the x-ray. Tuning the incoming x-ray energy to the absorption edge allows an approximation in which the sum over the intermediate states is replaced with the single lowest-energy intermediate state. The study further showed that expanding K-edge RIXS intensity according to the number of final-state electron-hole-pair states is a fast-converging expansion where the one-electron-hole-pair states dominate, particularly for insulators. The calculation further shows that the electron excitation is from the unoccupied band throughout entire first Brillouin zone, reflecting the localized nature of the core-hole screening by electrons in real space. In contrast, the hole excitations are mostly from occupied states close to the gap to minimize the kinetic energy, particularly when the gap energy is smaller than the band width.

In Ref. 15, the focus was on the energy dependence of electron-hole excitations and the case of one-core-hole site per unit cell. The momentum dependence of the RIXS spectrum and the possibility of multiple core-hole sites within a unit cell were not considered explicitly. In the current paper, we derive a formula that includes the full momentum dependence as well as multiple core-hole sites within a unit cell in the tight-binding approach. The formula is expressed in terms of the intermediate states with a completely localized 1s core hole, and we show that the RIXS spectrum in reciprocal space can be readily compared with the screening cloud in real space.

As a specific example, we calculate the K-edge RIXS spectrum for La$_{0.5}$Sr$_{1.5}$MnO$_4$ and make a comparison with experimental results. This material has a layered perovskite structure, which includes two-dimensional MnO$_2$ planes with eight Mn sites per unit cell in the low-temperature spin, orbital, charge, and structure ordered state. Experimental results show a dramatic variation of the RIXS intensity in reciprocal space in spite of the fact that there is almost no change in the peak energy of the energy-loss feature. We find good agreement between theory and experiment. By varying the
parameter values, we find a correlation between the variation of the K-edge RIXS spectrum in reciprocal space and the size and shape of the screening cloud in real space. We further examine the periodicity of the K-edge RIXS spectrum.

The paper is organized as follows. Section II presents the derivation of the K-edge RIXS formula in the limit of a completely localized $1s$ core hole. We present the experimental results and the theoretical model for La$_{0.5}$Sr$_{1.5}$MnO$_4$ in Sec. III and Sec. IV, respectively. Section V presents the results of our calculations and comparison with experimental results. Section VI includes further discussion on our results and Sec. VII summarizes. Appendix A shows details of the K-edge RIXS formula derivation. Appendix B shows the RIXS formula in terms of eigenstates with and without the core hole. Appendix C includes the expression of the tight-binding Hamiltonian for La$_{0.5}$Sr$_{1.5}$MnO$_4$ in reciprocal space. We discuss the actual electron numbers at nominal “Mn$^{3+}$” and “Mn$^{4+}$” sites in La$_{0.5}$Sr$_{1.5}$MnO$_4$ in Appendix D. The programs used for our calculations are available online.

II. K-EDGE RIXS FORMULA IN THE LIMIT OF LOCALIZED $1S$ CORE HOLE

A. Derivation of the K-edge RIXS formula

The Kramers-Heisenberg formula is the starting point for the derivation of our K-edge RIXS formula:

$$I(\omega, \mathbf{k}, \mathbf{k'}, \epsilon, \epsilon') \propto \sum_f \sum_n \langle f | D^\dagger | n | \rangle \langle n | D | g \rangle |E_g + \hbar \omega - E_n + i \Gamma_n| \delta(E_g - E_n + \hbar \omega),$$

where $|f\rangle$, $|n\rangle$, and $|g\rangle$ represent the final, intermediate and initial states, $E_f$, $E_i$, and $E_g$ their energies, $\Gamma_n$ the inverse of the lifetime, $\hbar \omega$ the energy of incoming x-ray with wavevector $\mathbf{k}$, and $\hbar \omega$ the x-ray energy loss. $D^\dagger$ and $D$ are the electric multipole operators, which include the incoming and outgoing x-ray wavevectors and polarization vectors, $(\mathbf{k}, \epsilon)$ and $(\mathbf{k'}, \epsilon')$.

In general, the $1s$ core hole component of the intermediate eigenstates $|n\rangle$ can be chosen as a delocalized momentum eigenstate. In the limit of the $1s$ electron hopping amplitude approaching zero, the intermediate energy eigenstates with different core hole momenta become degenerate, and the appropriate linear combinations can be made to form intermediate energy eigenstates with a $1s$ core hole completely localized at a chosen site. Therefore, the state $|n\rangle$ can be chosen as $|n_{\mathbf{R}+\mathbf{d}}\rangle$, the intermediate energy eigenstate with the core hole at a site $\mathbf{R}+\mathbf{d}$, where $\mathbf{R}$ and $\mathbf{d}$ represent the lattice point and the relative position of core-hole site within the unit cell, respectively. The summation over intermediate states $\sum_n$ can then be written as three summations, $\sum_{\mathbf{R}} \sum_{\mathbf{d}} \sum_{n_{\mathbf{R}+\mathbf{d}}}$. We take the dipole approximation for the electric multipole operators $D^\dagger$ and $D$. By analyzing how the phases of the intermediate and final eigenstates change following a translation by the lattice vector $\mathbf{R}$, we find that the sum over $\mathbf{R}$ gives rise to conservation of crystal momentum. Under the appropriate experimental conditions, such as for the experiments reported in this paper in which the scattering plane is fixed with respect to the crystal and the incoming x-ray polarization vectors remain perpendicular to the scattering plane as shown in Fig. I, the polarization effect in the K-edge RIXS is a constant factor. We can then effectively remove the $4p$ creation and annihilation operators and replace the dipole operators by the core-hole creation and annihilation operators. This results in the following expression:

$$I(\omega, \mathbf{k}, \mathbf{k'}) \propto \sum_{\mathbf{K}} \sum_f \sum_{\mathbf{d}} \sum_{n_{\mathbf{d}}} e^{-i(k'-k) \cdot \mathbf{d}} \langle f | \mathbf{a}^\dagger_d | n_{\mathbf{d}} \rangle \langle n_{\mathbf{d}} | \mathbf{a}^\dagger_d | g \rangle |E_g + \hbar \omega - E_n - i \Gamma_n| \delta(E_g - E_n + \hbar \omega - i \Gamma_n)$

where $\mathbf{a}^\dagger_d$ is the creation operator of the $1s$ core-hole at site $\mathbf{d}$, $\mathbf{K}$ represents a reciprocal lattice vector, and $\mathbf{k}_f$ denotes the net momentum of the final state. Details of the derivation of the above formula are presented in Appendix A.

We make further approximations to simplify the numerical calculation of RIXS spectrum. First, we replace the sum $\sum_{n_{\mathbf{d}}}$ by a single term with $n_{\mathbf{d}} = n_{\mathbf{d}}^{\text{low}}$, that is, the lowest energy eigenstate with the core hole at a site $\mathbf{d}$. This is justified for two reasons. First, $\langle n_{\mathbf{d}}^{\text{low}} | \mathbf{a}^\dagger_d | g \rangle$ is largest for $n_{\mathbf{d}}^{\text{low}}$, the well-screened state. Second, the incoming x-ray energy is tuned to the absorption edge, which makes the lowest energy intermediate state the most probable, while higher energy intermediate states, in particular, the unscreened states are less likely to be excited by the incoming x-rays in a K-edge RIXS process. The lowest energy intermediate state $|n_{\mathbf{d}}^{\text{low}}\rangle$ is dominated by the single-pair electron-hole excitations, especially in insulators, because of the higher energies necessary for multiple-pair electron-hole excitations. We therefore consider single-pair final states $|\epsilon_{\mathbf{k}_f} \epsilon_{\mathbf{l}_h} \ell_{\mathbf{k}_h} \sigma\rangle$ with an electron with wavevector $\mathbf{k}_f$, band index $\ell_{\mathbf{k}_f}$, and energy $\epsilon_{\mathbf{k}_f}$, and a hole with wavevector $\mathbf{k}_h$, band index $\ell_{\mathbf{k}_h}$, and energy $\epsilon_{\mathbf{k}_h}$, both with spin $\sigma$. Finally, if the resonant energies $E_{n_{\mathbf{d}}} - E_g$
and core-hole lifetime broadenings $\Gamma_{\sigma,\alpha}$ are similar for different core-hole sites within the unit cell, then we can neglect the denominator in Eq. 2 for fixed incoming x-ray energy, because it becomes a constant factor in the overall K-edge RIXS spectrum. These approximations lead to the following formula, which we use for the numerical calculation of the K-edge RIXS spectrum.

$$I(\omega, Q) \propto \sum_{K} \sum_{L_e, k_c} \left| \sum_{l_h, k_h} e^{-iQ \cdot d} \langle l_e, k_c | l_h, k_h | \epsilon_d^{l_h} | \epsilon_{\text{low}}^{l_e} \rangle \langle n_{\text{low}}^{l_e} | \delta_{Q, 0} \rangle \right|^2 \times \delta(\epsilon_{l_e, k_c} - \epsilon_{l_h, k_h} + \hbar \omega) \delta(k_c - k_h + Q + K),$$

(3)

where $Q = k' - k$. This formula relates the K-edge RIXS spectrum to the response of the system to a localized charge. The reasonable approximations we have taken significantly reduce the time for numerical calculations, and therefore, this formula can be used with the density functional approach as well as the tight-binding approach. Details on how we numerically calculate $I(\omega, Q)$ with Eq. 3 are presented in Appendix B.

B. Periodicity of K-edge RIXS in reciprocal space

Understanding the periodicity of the K-edge RIXS spectrum is useful, for example, in determining where to probe in reciprocal space. Also, as we will show below, there is useful information in the momentum dependence. First, it should be noted that periodicity in reciprocal space is not inherent in inelastic x-ray scattering. For off resonance, an increase in transferred momentum changes the transition matrix elements, since higher order terms in the multipole expansion are included.

While the latter supports the two-dimensional character of the system, the former cannot be explained by dynamic structure factor measurements. The main focus in this paper is the intensity variation of the K-edge RIXS spectrum to the response of the system to a localized charge. The reasonable approximations we have taken significantly reduce the time for numerical calculations, and therefore, this formula can be used with the density functional approach as well as the tight-binding approach. Details on how we numerically calculate $I(\omega, Q)$ with Eq. 3 are presented in Appendix B.

III. EXPERIMENTAL RESULTS FOR $La_{0.5}Sr_{1.5}MnO_4$

Mn K-edge RIXS from $La_{0.5}Sr_{1.5}MnO_4$ was measured at the Advanced Photon Source on beamlines 30-ID and 9-ID at temperature $T = 20$ K, well below CE-type magnetic, charge, orbital, and structural ordering temperatures. The instrumental energy resolution was of about 270 meV (FWHM). As shown in Fig. 1, a single crystal grown in traveling solvent floating zone method is aligned so that when the x-ray wavevector transfer $Q$ is in the scattering plane, it has $Q_x = Q_y$ with the $x$ and $y$ axes along the Mn-O bond direction and the $z$ axis perpendicular to the MnO$_2$ plane. The scattering plane was fixed with respect to the crystal and the polarization of the incoming and outgoing x-rays was perpendicular to the scattering plane, so that the polarization factor is a constant factor in the RIXS formula, as assumed in the derivation of Eq. 3. Data taken either at a fixed sample angle, $\theta$, or a fixed detector angle, $2\theta$, are shown as connected dots in Fig. 2. The elastic peak has been subtracted from the data.

The main focus in this paper is the intensity variation of the 2 eV peak, which is known to arise from transitions between Mn 3$d$ $e_g$ bands from optical measurements. The intensity of the 2 eV peak increases rapidly from $Q_x = Q_y = 0$ to $Q_x = Q_y = \pm a$, where $a$ represent the average Mn-Mn distance within the MnO$_2$ plane, but is almost independent of $Q_z$. While the latter supports the two-dimensional character of the $e_g$ electrons confined within each MnO$_2$ layer, the former cannot be explained by dynamic structure factor $S(q, \omega)$. This, combined with the fact that there are eight core-hole sites per two-dimensional unit cell, makes the experimental results for $La_{0.5}Sr_{1.5}MnO_4$ an ideal case to test the validity of our theory.

IV. TIGHT BINDING HARTREE-FOCK HAMILTONIAN AND CORE-HOLE POTENTIAL FOR $e_g$ ELECTRONS IN $La_{0.5}Sr_{1.5}MnO_4$

$La_{0.5}Sr_{1.5}MnO_4$ has a layered two-dimensional perovskite structure with negligible hopping of the Mn 3$d$ $e_g$ electrons between the MnO$_2$ layers. This is consistent with the experimental observation of K-edge RIXS spectrum being independent of the momentum transfer perpendicular to MnO$_2$ layers.
experimental data, taken at 2θ = 68°, 2θ = 78°, and θ = 40° respectively, and Qₓ = Qᵧ = Hₓm 2a and Qz = Lm 2a. The elastic peaks are subtracted from data. Dashed line represents a momentum-independent peak, presumably from a O-Mn transition. Solid curves in gray scale represent the RIXS intensity calculated at Qₓ = Qᵧ = Hₓm 2a for the Mn-Mn transition for the parameter set with t₄ = 0.9 eV, added to the dashed line, as discussed in Sec. V D.

FIG. 2. (Color online) Experimental and theoretical K-edge RIXS intensities for Laₐ₀.₅Sr₁₅MnO₄ with CE-type charge-orbital-spin ordering. The symbols in panels (a), (b) and (c) represent the experimental data, taken at 2θ = 68°, 2θ = 78°, and θ = 40° respectively, and Qₓ = Qᵧ = Hₓm 2a and Qz = Lm 2a. The elastic peaks are subtracted from data. Dashed line represents a momentum-independent peak, presumably from a O-Mn transition. Solid curves in gray scale represent the RIXS intensity calculated at Qₓ = Qᵧ = Hₓm 2a for the Mn-Mn transition for the parameter set with t₄ = 0.9 eV, added to the dashed line, as discussed in Sec. V D.

FIG. 3. (Color online) In-plane structural layout of Mn ions for Laₐ₀.₅Sr₁₅MnO₄ in CE-type ordering. Red and blue arrows represent the t₂g spin alignment. a₁ and a₂ represent the primitive lattice vectors for CE-phase. a₁ and a₂ are primitive vectors for lattice without charge, orbital, and spin ordering. The rounded hexagon encloses the Mn ions in the basis.

We therefore consider a Hamiltonian for a single MnO₂ layer. Laₐ₀.₅Sr₁₅MnO₄ undergoes a structural and orbital ordering transition at 230 K, and a CE-type magnetic ordering transition at 110 K, schematically shown in Fig. 3 for the MnO₂ layer. In this figure, “Mn³⁺” and “Mn⁴⁺” are used to indicate the two sites not related by symmetry, rather than controversial charge ordering. The strong Hund’s coupling between the eₙ electron spin and the t₂g electron spin confines most of the eₙ electron hopping along the zigzag chain. The distortion of the oxygen octahedron surrounding the Mn ions splits the eₙ energy levels through the Jahn-Teller electron-lattice coupling.

Our tight-binding Hamiltonian considers the effective Mn 3d eₙ levels only, because the RIXS peak at around 2 eV is due to transitions between the bands from these levels. We note that these effective Mn levels are in fact linear combinations of atomic Mn 3d eₙ levels and atomic O 2p levels. Appendix D discusses this aspect in more detail, in particular, in relation to the electron numbers on the Mn ions.

Within this effective model, we define dᵢσ as the creation operator of the eₙ electron with the spin state σ = ↑, ↓ and orbital state ξ = 1 for (3z² - r²)/2 and ξ = 2 for √(x² - y²)/2 at the Mn site i = (mₓa, mᵧa), where mₓ and mᵧ are integers, as shown in Fig. 3. The electron hopping term is

\[
\hat{H}_{\text{hopping}} = -\frac{1}{2} \sum_{i,j \delta \xi \xi' \sigma} t_{ij}^{\xi \xi'} \left( d_{i \xi \sigma}^\dagger d_{j+\delta \xi' \sigma} + d_{j+\delta \xi' \sigma}^\dagger d_{i \xi \sigma} \right).
\]

(5)

The vector δ = ± δₓ, ± δᵧ represents the nearest neighbor sites of a Mn ion. The hopping matrices within the MnO₂.
around the “Mn sites and the following Jahn-Teller Hamiltonian term,

\[ \hat{H}_{\text{JT}} = -\beta \lambda \sum_{i,\sigma} \begin{pmatrix} \begin{pmatrix} d_{11\sigma}^i \\ d_{12\sigma}^i \end{pmatrix}^T \end{pmatrix}^{Q_{3i}} \begin{pmatrix} -Q_{2i} \\ -Q_{2i} \end{pmatrix} \begin{pmatrix} d_{11\sigma}^i \\ d_{12\sigma}^i \end{pmatrix}, \]  

(11)

where \( \lambda \) corresponds to the Jahn-Teller coupling constant. The isotropic \( Q_1 \) distortion interacts with the total \( e_g \) electron number through the following “breathing” electron-lattice Hamiltonian term, \( \hat{H}_{\text{br}} \).

\[ \hat{H}_{\text{br}} = -\beta \lambda \sum_{i,\sigma} \begin{pmatrix} \begin{pmatrix} d_{11\sigma}^i \\ d_{12\sigma}^i \end{pmatrix}^T \end{pmatrix}^{Q_{3i}} \begin{pmatrix} -Q_{2i} \\ -Q_{2i} \end{pmatrix} \begin{pmatrix} d_{11\sigma}^i \\ d_{12\sigma}^i \end{pmatrix}, \]  

(12)

where \( \beta \) represents the ratio between the strengths of the breathing and the Jahn-Teller coupling.

We also include the Hund’s coupling of the \( e_g \) electron spin state to the classical \( t_{2g} \) spin direction,

\[ \hat{H}_{\text{Hund}} = -J_H \sum_{i,\xi,\sigma'} S_{t_{2g}i} \cdot d_{2\sigma'}^i \tau_{\xi\sigma''} d_{\xi\sigma''}, \]  

(13)

where \( J_H \) represents the Hund’s coupling constant, \( S_{t_{2g}i} \) the \( t_{2g} \) spin vector ordered in CE-type structure and \( \tau \) is the Pauli matrix vector.

As in Ref. [31], we also include the 3d-3d on-site Coulomb interaction,

\[ \hat{H}_{\text{dd}}^{\text{HF}} = U \sum_i \sum_{(\eta,\sigma) \neq (\eta',\sigma')} \hat{n}_{i\eta\sigma} \hat{n}_{i\eta'\sigma'}, \]  

(14)

where \( \hat{n}_{i\eta\sigma} = d_{i\eta\sigma}^\dagger d_{i\eta\sigma} \) is the number operator and \( U \) represents the size of the 3d-3d Coulomb interaction. The index \( \eta = -, + \) represents the local orbital eigenstates of \( H_{\text{JT}} \) with lower and higher energies, respectively, chosen for the following Hartree-Fock approximation:

\[ \hat{H}_{\text{dd}}^{\text{HF}} = \sum_i \left( U_{i+\eta} d_{i+\eta}^\dagger d_{i+\eta} + U_{i-\eta} d_{i-\eta}^\dagger d_{i-\eta} \right), \]  

(15)

where \( U_{i+\eta} = U (\langle \hat{n}_{i+\eta} \rangle + \langle \hat{n}_{i-\eta} \rangle) \), etc. \( \text{[31]} \)

The total Hamiltonian for Mn 3d \( e_g \) electrons for calculations of K-edge RIXS initial and final states is then the sum of the terms described so far,

\[ \hat{H}_d = \hat{H}_{\text{hopping}} + \hat{H}_{\text{JT}} + \hat{H}_{\text{br}} + \hat{H}_{\text{Hund}} + \hat{H}_{\text{dd}}^{\text{HF}}, \]  

(16)

The CE type ordering of the \( t_{2g} \) spins and the lattice distortions associated with charge and orbital ordering give rise to the primitive lattice vectors \( a'_1 \) and \( a'_2 \) shown in Fig. 4.

The primitive reciprocal lattice vectors are \( b'_1 = (\frac{2\pi}{a'_2}, -\frac{2\pi}{a'_2}) \) and \( b'_2 = (\frac{2\pi}{a'_1}, \frac{2\pi}{a'_1}) \), and the first Brillouin zone is \( \Omega_{1BZ} = \{ k | -\frac{2\pi}{a'_2} < k_x + k_y \leq \frac{2\pi}{a'_2}, -\frac{2\pi}{a'_1} < k_x - k_y \leq \frac{2\pi}{a'_1} \} \).

In the intermediate state, we must also account for the presence of the core hole. The 1s-3d on-site Coulomb interaction is generally expressed as

\[ \hat{H}_{\text{sd}} = -U_{\text{core}} \sum_{i,\xi,\sigma,\sigma'} d_{i\xi\sigma}^\dagger \hat{a}_{\sigma'}^\dagger \hat{a}_{\sigma'} d_{i\xi\sigma}, \]  

(17)

where \( U_{\text{core}} \) represents the size of the 1s-3d Coulomb interaction, and \( \hat{a}_{\sigma'}^\dagger \) is the creation operator for a 1s core hole with spin \( \sigma' \) at site \( i \). As discussed in Sec. II A in the limit of vanishing 1s electron hopping amplitude, the K-edge RIXS
intermediate energy eigenstates can be chosen as states with a single completely localized 1s core hole, which can be found from
\[ \hat{H}_{\text{total},i_c} = \hat{H}_d + \hat{H}_{\text{ad},i_c}, \]
with
\[ \hat{H}_{\text{ad},i_c} = -U_{\text{core}} \sum_{\xi,\sigma} \xi_i^{\dagger} \xi_\sigma \xi_i^{\dagger} \xi_\sigma, \]
i_c representing the 1s core-hole site, and \( s_{i_c}^{\dagger} \), \( s_{i_c} \) = 1 being used. To calculate the K-edge RIXS spectrum, we need to represent the eigenstates of \( \hat{H}_{\text{total},i_c} \), as a linear combination of the eigenstates of \( \hat{H}_d \), as described in detail in Appendix B.

The expression of the Hamiltonian \( \hat{H}_d \) and \( \hat{H}_{\text{total},i_c} \) in reciprocal space for \( \text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4 \) is presented in Appendix C.

Each Hamiltonian term has one parameter. Some of the parameter values are chosen by modifying corresponding values for \( \text{LaMnO}_3 \) found in Ref. 31. The chosen parameter values are \( t_0 = 0.9 \text{ eV}, \lambda = 7.41 \text{ eV/Å}, \beta = 1.5, J_H |t_{\text{2g},i}| = 2.2 \text{ eV}, U = 3.5 \text{ eV}, \) and \( U_{\text{core}} = 4.0 \text{ eV} \). In addition, we vary \( t_0 \) and \( \lambda \) while maintaining the gap size around 2 eV to examine how the RIXS spectrum depends on the \( e_g \) electron hopping amplitude.

V. RESULTS FROM THEORY AND COMPARISON WITH EXPERIMENTS

A. Electronic density of states in the absence and in the presence of the core hole

We first present our results on energy eigenstates and eigenvalues of the Hamiltonians for a 16×16 Mn site cluster with periodic boundary conditions. The calculated density of states (DOS) is shown in Fig. 5(a) in the absence of a core hole. The occupied band mostly consists of the lower Jahn-Teller belongs parallel to the \( t_{\text{2g}} \) spins at \( \text{Mn}^{3+} \) sites, whereas the lowest empty band mostly consists of similar \( e_g \) levels at \( \text{Mn}^{4+} \) sites. The excitation between these two bands is responsible for the 2 eV RIXS peak, which is the focus of our comparison with experiment data. Due to spin degeneracy in CE-type antiferromagnetic ordering, the electronic DOS \( D_\downarrow(\varepsilon) \) for spin \( \downarrow \), is identical to that for spin \( \uparrow, D_\uparrow(\varepsilon) \).

We next analyze the Hamiltonian \( \hat{H}_{\text{total},i_c} \) in the presence of the core hole at site \( i_c \). The \( t_{\text{2g}} \) spin direction at \( i_c \) breaks the spin degeneracy in the DOS. The DOS \( D_{\downarrow}^{i_c=(0,0)}(\varepsilon) \) is displayed in Fig. 5(b), for the core hole site \( i_c = (0, 0) \) in Fig. 5, which is a \( \text{Mn}^{3+} \) site with \( t_{\text{2g}} \) spin \( \uparrow \). The core-hole potential pulls out bound states from the band continuum identified by vertical lines with circles on top in Fig. 5(b). The lowest bound state is at about \(-4 \text{ eV}\), that is, \( U_{\text{core}} \), below the lowest band with \( \text{Mn}^{3+} \) character. The second bound state is within the gap. The DOS for the band continuum is almost unchanged, except that the number of states within each band below and above the gap is reduced by one because of the bound states pulled out. By filling the states from the lowest energy with the same number of electrons in the intermediate states as in the ground state, as shown in Fig. 5(b), we obtain the lowest energy intermediate state, \( |n_{\text{int}}^{i_c} \rangle \). Therefore, the bound state below the lowest band is occupied and the bound state within the gap is empty in the intermediate state. \( D_{\downarrow}^{i_c=(0,0)}(\varepsilon) \) is almost identical to the DOS without a core hole in Fig. 5(a), because the electrons with spin \( \downarrow \) contribute very little to the screening of the core hole due to the strong Hund’s coupling.

The DOS \( D_{\uparrow}^{i_c=(a,0)}(\varepsilon) \), for the core hole at \( i_c = (a, 0) \) in Fig. 5, which is a \( \text{Mn}^{4+} \) site with \( t_{\text{2g}} \) spin \( \uparrow \), is shown in Fig. 5(c) and has similar features. The lowest bound state is
at around $-2$ eV, that is, $U_{\text{core}}$ below the band with the Mn$^{4+}$ site character, which is the lowest empty band. Again, the lowest bound state is filled and the bound state within the gap is empty for $\mathcal{S}^{\text{low}}(\delta_{\text{low}})$, as indicated in Fig. 6(c).

As a comparison, we carry out similar calculations for the parameter values of $t_0 = 1.5$ eV and $\lambda = 3.51$ eV/Å, “R” in (b) represents a resonant state, rather than a bound state. Note that a single state at the top of the lower band in (b) is empty.

FIG. 6. (Color online) Similar figures as Fig. 5 for $t_0 = 1.5$ eV and $\lambda = 3.51$ eV/Å. “R” in (b) represents a resonant state, rather than a bound state. Note that a single state at the top of the lower band in (b) is empty.

Understanding the distributions of the electrons and holes that are excited by the core hole is essential for the interpretation of RIXS spectrum. Excited electron and hole distributions with respect to the energy for the RIXS final state, $n_{\text{fin},\sigma}(\varepsilon)$ with $\varepsilon > \varepsilon_F$ and $n_{\text{fin},\sigma}^h(\varepsilon)$ with $\varepsilon < \varepsilon_F$, are defined as follows:

$$n_{\text{fin},\sigma}(\varepsilon) = \sum_{\epsilon_{l\kappa}>\epsilon_F} \sum_{m=1}^{N_\epsilon} \left| \langle 0 | b_{l\kappa\sigma}^\dagger c_{m\sigma}^\dagger | 0 \rangle \right|^2 \delta(\varepsilon - \epsilon_{l\kappa}) , \quad (20)$$

$$n_{\text{fin},\sigma}^h(\varepsilon) = \sum_{\epsilon_{l\kappa}<\epsilon_F} \sum_{m=1}^{N_\epsilon} \left| \langle 0 | b_{l\kappa\sigma}^\dagger c_{m\sigma} | 0 \rangle \right|^2 \delta(\varepsilon - \epsilon_{l\kappa}) , \quad (21)$$

where $\varepsilon_F$ represents the Fermi energy in the absence of the core hole, $\epsilon_{l\kappa}$ is the creation operator for the $m$-th lowest energy eigenstate of $\hat{H}_{\text{total}}$, with spin $\sigma$ and energy $\epsilon_{m\sigma}$, and $b_{l\kappa\sigma}^\dagger$ represents the creation operator for the eigenstate with wavevector $k$ and energy $\epsilon_{l\kappa}$ within the $l$-th lowest band of $\hat{H}_{\text{tot}}$, and $N_e$ represents total electron number. These are the electrons and holes that are moved by the scattering process. For example, $n_{\text{fin},\sigma}(\varepsilon)$ corresponds to the projection of occupied intermediate states to unoccupied initial states. The $\delta$-function makes this distribution represented with respect to the energy without the core hole.

Similar electron and hole distributions with respect to the energy for the RIXS intermediate state, $n_{\text{int},\sigma}(\varepsilon)$ and $n_{\text{int},\sigma}^h(\varepsilon)$, are defined in the same way as Eqs. (20) and (21), except that the energy $\delta$-function is replaced by $\delta(\varepsilon - \epsilon_{m\sigma})$. This difference also implies that we have $n_{\text{int},\sigma}(\varepsilon)$ for $\varepsilon < \varepsilon_F$ and $n_{\text{int},\sigma}^h(\varepsilon)$ for $\varepsilon > \varepsilon_F$, where $\varepsilon_F$ represents the Fermi energy in the presence of the core hole.

These excited electron and hole distributions are plotted in Figs. 6(a), 6(e), and 6(c) for $\sigma = \uparrow$. Similar distributions for spin $\downarrow$ state are less than 10% of those for spin $\uparrow$ state. The plots of $n_{\text{int},\sigma}(\varepsilon)$ and $n_{\text{int},\sigma}^h(\varepsilon)$ in the lower panels of Figs. 6(d), 6(e), and 6(c) show that the bound states in the intermediate state, marked in Figs. 6(b), 6(c), and 6(c), respectively, make the dominant contribution to the electron-hole excitations.

The plots of $n_{\text{fin},\sigma}(\varepsilon)$ and $n_{\text{fin},\sigma}^h(\varepsilon)$ in the upper panels of Figs. 6(d), 6(e), and 6(c) show that, while $n_{\text{fin},\sigma}(\varepsilon)$ resembles...
the DOS of the unoccupied band, \( n_{i\sigma}^h(\varepsilon) \) shows a peak at the top of the occupied band, in particular, in Fig. 4(e). This represents asymmetric screening dynamics between electrons and holes.

For the exceptional case of \( t_0 = 1.5 \) eV and a core hole at Mn\(^{3+}\) site, the comparison between Fig. 4(b) and the lower panel in Fig. 4(d) reveals that the occupied resonant state within the lower band marked by “R” and the empty state at the top of the occupied band in Fig. 4(b) make dominant contributions to \( n_{i\sigma}^\text{ex}(\varepsilon) \) and \( n_{i\sigma}^\text{hh}(\varepsilon) \). The resonant state is dominant for electron excitations because this state is pulled from the initially unoccupied bands, whereas the lowest bound state comes mostly from the initially occupied band. The delocalized state at the top of the occupied band predominantly contributes to the hole excitation, because it is occupied in the initial state and empty in the intermediate state, which results in hole excitation very close to the gap shown in the upper panel in Fig. 4(d).

We note that these results are consistent with the conclusions of Ref. 15, thus validating the present study.

C. Electron and hole excitations by the core hole represented in real space

In this subsection, we present the distribution of electrons and holes excited by the core hole in real space.

First, in the absence of the core hole, the electron number \( \langle n_{i\sigma}^\text{ex} \rangle \) is calculated for each spin state \( \sigma = \uparrow, \downarrow \) and orbital state \( \eta = +, - \) at each site \( i \) from the initial ground state \( |g\rangle \) of the Hamiltonian \( \hat{H}_2 \). The total \( e_\eta \) electron numbers calculated for our \( 16 \times 16 \) cluster in the absence of the core hole are 0.87 at the nominal Mn\(^{3+}\) site and 0.13 at the nominal Mn\(^{4+}\) site for the parameter set with \( t_0 = 0.9 \) eV, indicating a difference of 0.74 in charge density between these two sites. We note that these numbers should not be directly compared with the local density approximation theory results or resonant x-ray scattering results, because our effective Mn 3d \( e_\eta \) states are not pure atomic Mn orbital states but combinations of atomic Mn and O orbitals. A proper comparison is described in Appendix D which shows that the electron numbers in our model are consistent with local density approximation and resonant x-ray scattering results. It is found that most of these electrons occupy the lower Jahn-Teller level \( \eta = - \), approximately \( \sqrt{3}(x^2 - z^2)/2 \) or \( \sqrt{3}(y^2 - z^2)/2 \) orbital at the Mn\(^{3+}\) site and the \( (3z^2 - r^2)/2 \) orbital at the Mn\(^{4+}\) site, with spin parallel to \( \tau_{2g} \) spin at each site, consistent with the orbital ordering proposed in Ref. 15.

In the intermediate state, these electron numbers change to screen the core hole. The changes in electron number, that is, excited electron and hole numbers, are shown in Fig. 7 for \( t_0 = 0.9 \) eV and in Fig. 8 for \( t_0 = 1.5 \) eV, where the volumes of red and blue spheres are proportional to the excited electron and hole numbers, respectively. Note that these changes in electron and hole numbers are consistent with the excited electron and hole distributions along the energy axis reported in Figs. 5(d), 5(e), 6(d) and 6(e). The site with the largest electron number in each panel corresponds to the core-hole site. The gray solid and dashed lines in the background represent the zigzag chain with \( \tau_{2g} \) spin \( \uparrow \) and \( \downarrow \), respectively. For the \( t_0 = 0.9 \) eV case, Figs. 7(a) and 7(b) show that the excited electrons are mostly confined right at the core-hole site. The localization of the electrons in the intermediate state leads to the relatively broad electron distribution, \( n_{i\sigma}^\text{ex}(\varepsilon) \), along the energy axis in the upper panels of Figs. 5(d) and 5(e). Comparison of the largest solid red spheres in Figs. 7(a) and 7(b) shows that more screening electrons accumulate at the core-hole site when the core hole is created at the Mn\(^{4+}\) site (0.92 electron) than at the Mn\(^{3+}\) site (0.91 electron). This result can be understood from the orbital ordering pattern: Initially, the Mn\(^{4+}\) site has less \( e_\uparrow \) electrons on the site itself but more electrons at its nearest neighbor Mn sites along the zigzag chain with orbitals pointing toward the Mn\(^{4+}\) site compared to the Mn\(^{3+}\) site, which allows the core hole at Mn\(^{4+}\) sites to attract more electrons. Hole distribution in Figs. 7(a) and 7(b) show that these screening electrons are mostly from

---

FIG. 7. (Color online) Screening configuration in real space for \( t_0 = 0.9 \) eV with a core hole at (a) Mn\(^{3+}\), and (b) Mn\(^{4+}\) site. The volume of the red and blue spheres is proportional to the excited electron and hole numbers, respectively. The excited electron number at the core-hole site (the site with the largest red sphere) is 0.92 for (a) and 0.91 for (b).

FIG. 8. (Color online) Screening configuration in real space for \( t_0 = 1.5 \) eV with a core hole at (a) Mn\(^{3+}\), and (b) Mn\(^{4+}\) site, similar to Fig. 7. The excited electron number at the core-hole site is 0.91 for (a) and 0.91 for (b).
the nearest neighbors along the zigzag chain, accounting for about 90% of the total hole number. The results show that even though the hole excitation is not as localized as the electron excitation and \( n_{\text{fin}}^e(\varepsilon) \) is sharper along the energy axis than \( n_{\text{fin}}^t(\varepsilon) \) in Fig. 5(d) and 5(e), the holes are still tightly bound to the core-hole site forming an exciton-like electron-hole-pair state.

The situation changes for the case of large electron hopping \( t_0 = 1.5 \text{ eV} \). Figure 8(a) shows the electron-hole excitations for a core hole at a Mn\(^{3+}\) site. In this case, the hole distribution becomes delocalized, and only about 8% of the hole is localized within the nearest neighbors of the core-hole site, while the majority of the hole is delocalized along the zigzag chains with the same spin direction as the core-hole site, consistent with the result in Figs. 8(b) and 8(d). The hole number does not decay with the distance from the core-hole site, indicating qualitatively different screening dynamics. Even for the case with a core hole at a Mn\(^{4+}\) site, Fig. 8(b), the hole distribution spreads to further neighbors along the zig-zag chain, reflecting the tendency toward delocalization.

As we shall see, such screening patterns in real space can be related to the variation of the RIXS intensity in reciprocal space. This will be discussed in Sec. V E

D. Calculated K-edge RIXS spectrum and comparison with experimental data

We calculate the RIXS intensity, \( I(\omega, Q) \) according to Eq. 3. To make a comparison between the calculated results and the experimental data, we first examine the experimental data more closely. In addition to the momentum-dependent RIXS peak at around 2 eV, the experimental RIXS spectrum in Fig. 2 shows momentum-independent spectral weight, in particular above 3 eV. The shape of the experimental RIXS spectrum, particularly with small in-plane wavevector changes, such as \( Q_x = Q_y = -0.03 \times \pi \) in Fig. 2(a), indicates that the RIXS spectral weight above 3 eV may have the same origin as the 4–5 eV O 2p–Mn 3d transition observed in optical experiments in related manganites. Based on this assumption, we model the experimental RIXS spectrum with a momentum-independent peak, shown in dashed lines in Fig. 2 centered at 4.5 eV and with a half-width at half-maximum of 1.5 eV similar to the optical peak, and a momentum-dependent Mn 3d–3d peak around 2 eV, calculated from Eq. 3 using \( \hat{H}_d \) and \( \hat{H}_{\text{total}, \text{i}} \). Here, although it does not affect the results much, we use the RIXS intensity averaged over twin domains in the crystal with zigzag chains along the [110] and [110] directions, \( I_{\text{avg}}(\omega, (Q_x, Q_y)) = |I(\omega, (Q_x, Q_y)) + I(\omega, (-Q_x, Q_y))|/2 \). The results in Fig. 2 demonstrate a reasonable agreement between the calculated spectra shown in solid lines and the experimental data shown in symbols, considering the experimental noise. The 4.5 eV peak has a substantial tail even in the range of 1–3 eV. Such momentum-independent tails have also been observed in bilayer manganites.

To compare just the 2 eV peak between the theory and experiment, we subtract the 4.5 eV peak from the experimental data and plot the intensity, as a contour plot in the plane of energy and \( Q_x = Q_y = H_{\text{ex}} \frac{\pi}{a} \) in Fig. 10(a). This clearly shows the momentum dependence of the intensity of the 2 eV peak. The calculated RIXS intensity in Fig. 10(b) for \( t_0 = 0.9 \text{ eV} \) shows good agreement with experimental data. In contrast, in Fig. 10(b) we show the calculated RIXS spectrum for \( t_0 = 1.5 \text{ eV} \), which is not consistent with the experimental data.

E. Energy-integrated RIXS intensity in reciprocal space

To make a more quantitative comparison between theory and experiment, we integrate the spectrum of the 2 eV peak from 1 eV to 3 eV after subtracting 4.5 eV peak, for both theory and experiment. The results are shown in Fig. 11 along the diagonal direction in reciprocal space, in which the theoretical results for the various parameter sets, and the experimental data are normalized with respect to the maximum integrated intensity. The parameter sets used for the calculations are \((t_0, \lambda) = (0.1 \text{ eV}, 10.79 \text{ eV}/\AA), (0.9 \text{ eV}, 7.41 \text{ eV}/\AA), (1.1 \text{ eV}, 4.81 \text{ eV}/\AA), (1.32 \text{ eV}, 3.76 \text{ eV}/\AA), (1.35 \text{ eV}, 3.73 \text{ eV}/\AA), (1.50 \text{ eV}, 3.51 \text{ eV}/\AA), \) chosen to keep the peak at around 2 eV. All other parameter values are unchanged. The experimental data in Fig. 11 shows that the integrated RIXS intensity in-
The measured RIXS intensity, as well as the calculated RIXS

F. Periodicity of K-edge RIXS spectrum in reciprocal space for charge-orbital-spin ordered manganites

As mentioned in Sec. [11,12] in earlier studies of La$_2$CuO$_4$, it was shown that the observed K-edge RIXS spectrum reflects the periodicity of the lattice and is a function of the reduced wavevector $q$ within the first Brillouin zone, defined as $Q = q + K$, where $Q$ is the total x-ray wavevector change and $K$ is a reciprocal lattice vector. 

The experimental data presented in this paper clearly indicates that such periodicity is not present for La$_{0.5}$Sr$_{1.5}$MnO$_4$. The measured RIXS intensity, as well as the calculated RIXS intensity, seen in Figs. 9 and 11 increases continuously past the boundary of the first Brillouin zone at $(\frac{\pi}{a}, \frac{\pi}{a})$. As discussed in Sec. [11,12] the periodicity seen in Ref. 21 applies only to solids with one core-hole site per unit cell, such as La$_2$CuO$_4$. For solids with multiple core hole sites per unit cell due to the ordering of spin, charge, orbital or local lattice distortions, the periodicity in K-edge RIXS spectrum follows the periodicity of the lattice without ordering, like the square
Mn-site lattice in $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$, not the periodicity of the actual lattice with ordering. Our numerical calculations in Figs. 12 and 13 confirm such periodicity in $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$: Fig. 12 shows energy-integrated RIXS intensity calculated for the $t_0 = 0.9$ eV case in a larger region of reciprocal space of $-\frac{2\pi}{a} < Q_x \leq \frac{2\pi}{a}$ and $-\frac{2\pi}{a} < Q_y \leq \frac{2\pi}{a}$. The diamond around $(0,0)$ is the actual first Brillouin zone of the spin, charge and orbital ordered structure, whereas the outer square domain $-\frac{2\pi}{a} < Q_x \leq \frac{2\pi}{a}$ and $-\frac{2\pi}{a} < Q_y \leq \frac{2\pi}{a}$, denotes the first Brillouin zone of the lattice without ordering. It is evident that RIXS spectrum does not exhibit periodicity with respect to the actual primitive reciprocal lattice vectors, $b_1'$ and $b_2'$, shown in Fig. 12, but rather shows periodicity with respect to primitive reciprocal lattice vectors of the lattice without ordering, $b_1$ and $b_2$, shown in Fig. 12. Even though it is only a single data point, the experimental data at around $Q_y = 0.68 \times \frac{2\pi}{a}$ in Fig. 11 is consistent with such periodicity. Further experimental data for $|Q_x| > \frac{\pi}{a}$, $|Q_y| > \frac{\pi}{a}$ are required for the verification of this periodicity. We note that careful examination of the periodicity is only approximate. The small displacement of the $\text{Mn}^{3+}$ ions of 0.0265 Å along the diagonal direction from the ideal square lattice included in our calculations, makes the Mn sites deviate slightly from the exact square lattice. Figure 13 shows that, even for the $t_0 = 1.5$ eV case, the periodicity still does not follow the actual reciprocal lattice, even though the RIXS intensity oscillates more rapidly in reciprocal space.

We next provide a physical explanation of why the K-edge RIXS spectrum from charge-orbital ordered manganites follows the periodicity of the Brillouin zone with the absence of charge-orbital order. We first consider artificial doubling of the unit cell for a one-dimensional chain with interatomic distance $a$. In Fig. 14 thick (blue) lines, both solid and dashed, and solid lines, both thick (blue) and thin (red), show a schematic diagram of the band structure before and after the artificial unit cell doubling, respectively. The arrows between $1s$ and $4p$ bands represent the core hole creation and annihilation by x-rays. Due to the interaction with the core-hole, electron-hole pairs can be excited into the valence shell, as indicated by the arrows within the $3d$ band. Excitations with a transferred crystal wavevector $Q$ from the state 1 can be either an intraband transition to the state 2 shown in Fig. 14(a) or an interband transition to the state 3 shown in Fig. 14(b). However, the reduced Brillouin zone $[-\frac{\pi}{a}, \frac{\pi}{a}]$ is an artificial construction and should give equivalent results to the real Brillouin zone $[-\frac{\pi}{a}, \frac{\pi}{a}]$, in which the state $3'$ in Fig. 14(b) should be considered instead of the state 3. Therefore, the intraband and interband transitions correspond to wavevector transfers of $Q$ and $Q + K$, respectively, where $K = -\frac{\pi}{a}$, a reciprocal lattice vector of the doubled unit cell. This implies that they occur at two distinct wavevector transfers and should be distinguishable. The underlying reason is that not only the valence bands are backfolded due to the doubling of unit cell, but also the core level bands. An interband (intraband) transition in the valence band also leads to an interband (intraband) transition in the core level band, as shown in arrows in the $1s$ band in Fig. 14. We now consider real unit cell doubling due to charge-orbital order. For a finite but small charge-orbital order, the band structure would be modified mostly near the Brillouin zone boundary, as represented by the thin black dotted lines in the $3d$ bands in Fig. 14 and the RIXS that involves states far from the zone boundary, such as the states 1, 2 and 3, should not dramatically change from those in the absence of charge-orbital order. Therefore, the K-edge RIXS spectrum $I(\omega, Q)$ and $I(\omega, Q + K)$ would remain different even after charge-orbital ordering. Obviously, the situation becomes more complex when the charge-orbital order becomes stronger leading to a further mixing of the bands. However, the schematic figure explains why the periodicity for charge-orbital ordered manganites occurs with the Brillouin zone in the absence of such order.

VI. DISCUSSION

In this section, we discuss what insights the RIXS spectrum in reciprocal space can provide on the screening dynamics. Figures 15(a) and 15(b) show $n_h/n_h^{\text{max}}$, that is the hole density normalised to its maximum, versus distance $l$ from the core-hole site along the zig-zag chain for the case of core hole at a Mn$^{3+}$ and Mn$^{4+}$ site, respectively, in a semi-logarithmic plot. For $t_0 \leq 1.3$ eV of Fig. 15(a) and all $t_0$ of Fig. 15(b), the hole density decreases exponentially and thus can be fit to $n_h/n_h^{\text{max}} \propto \exp(-l/l_s)$, where $l_s$ can be interpreted as the size of the screening cloud. We find that the sizes of the screening clouds are approximately 0.4 and 0.5 interatomic distances for the Mn$^{3+}$ and Mn$^{4+}$ sites, respectively, for $t_0 = 0.9$ eV, and become larger, as $t_0$ increases, as shown along the horizontal axis in Fig. 15(c), which includes the result for $t_0 = 0.6$ eV additionally.

We next look for a correlation between the size of the screening cloud in real space and the features of the K-edge
The results indicate that the width of the RIXS peak can be a measure of the size of the exciton-like screening cloud in real space, and a measure of the ratio between the occupied band width and the hole binding energy.

Recently, K-edge RIXS spectra for bilayer manganites La$_2$-$_x$Sr$_{1+x}$Mn$_2$O$_7$ with $x = 0.36$ and 0.5 have been reported by Weber et al. Although not as pronounced as our results for single layered manganites, Ref. 33 shows an increase of the 2 eV peak intensity in A-type and CE-type antiferromagnetic LaSr$_2$Mn$_2$O$_7$, as the x-ray wavevector transfer increases from $(0,0,Q_z)$ to $(\frac{\pi}{a}, \frac{\pi}{a}, Q_z)$. In the context of our work above, such results can be interpreted as the formation of an exciton-like screening cloud in bi-layer manganites, the size of which is likely larger than that for the single-layer manganites discussed above, considering the less-pronounced increase of the 2 eV peak intensity.

Finally, we note that Semba et al. calculated the K-edge RIXS spectrum for LaMnO$_3$, based on the Keldysh-type Green’s function formalism. The results in Ref. 16 show about a 10% increase of the 2 eV peak from $(0,0,0)$ to $(1,0,0)$ in their choice of $x$ and $y$ axes, which are equivalent to $Q = (0,0,0)$ to $Q = (\frac{\pi}{a}, \frac{\pi}{a}, 0)$ in our notation. The results again can be interpreted as the formation of exciton-like screening clouds, consistent with our calculations, even though the core-hole state for the intermediate eigenstates is chosen as delocalized in Ref. 16. The periodicity of the RIXS spectrum discussed in Sec. II B and Sec. V F was also identified in Ref. 16 even though the association of such periodicity with the approximate square lattice of the core-hole sites was not specifically mentioned.

VII. SUMMARY

We have presented a formalism to calculate the K-edge RIXS spectra in transition metal oxides based on tight-binding Hamiltonians and a local 1s–3d Coulomb interaction, in which the choice of intermediate eigenstates with a completely localized 1s core hole allows for the interpretation of the data in terms of screening dynamics in real space. We have also found that the periodicity of K-edge RIXS spectrum follows the reciprocal lattice vectors of the lattice without the ordering of spin, charge, orbital, or local lattice distortions, rather than the reciprocal lattice vectors of the actual lattice with such ordering.

We have applied our formalism to the highly-momentum-dependent K-edge RIXS spectrum observed for La$_{0.5}$Sr$_{1.5}$MnO$_4$ in CE-type spin-orbital-structure ordering. It is found that the sharp increase of the 2 eV peak intensity from the center toward the corner of the first Brillouin zone of the lattice without ordering is an indication of a highly localized screening cloud in La$_{0.5}$Sr$_{1.5}$MnO$_4$ with a typical size of 0.4–0.5 Mn-Mn distances. We also showed that there exists a positive correlation between the width of the energy-integrated K-edge RIXS intensity peak in reciprocal space, the size of the exciton-like screening cloud in real space, and the ratio between occupied band width and hole binding energy.

The analysis in this paper was performed for the case of an intermediate strength core-hole potential, that is $U_{\text{core}}$ com-
parable to the $3d$ electron bandwidth. In fact, this is appropriate for most transition metal oxides and therefore the present approach should have general applicability. One of the important results is that this approach highlights the connection between K-edge RIXS and the impurity problem in strongly correlated electron systems, and we show that this technique is a new probe of momentum-dependent screening dynamics of localized impurities.

ACKNOWLEDGEMENTS

We thank D. Casa, D. Prabhakaran, A. T. Boothroyd and H. Ding for their invaluable support in experiments. The collaborations between T.R.S., K.H.A., and M.v.V. were supported by the Computational Materials and Chemical Sciences Network under Grants No.DE-FG02-08ER46540 and No.DE-SC0007091. K.H.A. was further supported by 2012 and 2013 Argonne X-ray Science Division Visitor Program. M.v.V. was supported by the US Department of Energy, Office of Basic Energy Sciences, Division of Materials Science and Engineering under Award No.DE-FG02-03ER46097 and NIU Institute for Nanoscience, Engineering, and Technology. The work at Brookhaven was supported by the US Department of Energy, Division of Materials Science, under Contract No. DE-AC02-98CH10886. Work at Argonne National Laboratory and use of the Advanced Photon Source was supported by the US DOE, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

Appendix A: RIXS formula derivation

As explained in Sec. II A, we get the following formula from the Kramers-Heisenberg formula, Eq. (1), in the limit of completely localized core hole,

$$I(\omega, \mathbf{k}, \mathbf{k}', \xi, \xi') \propto \sum_{\mathbf{K}} \sum_{f} \sum_{d} \sum_{n twisted} \frac{\langle f |D^\dagger |n_{\mathbf{R}+\mathbf{d}} \rangle \langle n_{\mathbf{R}+\mathbf{d}} |D |g \rangle}{E_g + \hbar \omega_k - E_{n_d} + i\Gamma_{n_d}} \delta(E_g - E_f + \hbar \omega),$$

where $|n_{\mathbf{R}+\mathbf{d}}\rangle$ represents the intermediate energy eigenstate with the core hole at a site $\mathbf{R} + \mathbf{d}$ within the unit cell at a lattice point $\mathbf{R}$. Further applying the dipole approximation to the K-edge scattering amplitude, we obtain

$$\langle f |D^\dagger |n_{\mathbf{R}+\mathbf{d}} \rangle \langle n_{\mathbf{R}+\mathbf{d}} |D |g \rangle = e^{-i(c' - k) \cdot \mathbf{K}} \times \langle f | \mathbf{r} \rangle \langle n_{\mathbf{R}+\mathbf{d}} | \mathbf{r} | g \rangle.$$  \hspace{1cm} (A1)

Two many-body states $|\Psi^f\rangle$ and $|\Psi^R\rangle$, which have total momentum $\hbar \mathbf{K}$ and identical wave functions in two different coordinate systems with the coordinates for $|\Psi^R\rangle$ shifted with respect to the coordinates for $|\Psi^0\rangle$ by $\mathbf{R}$, are related to each other by a phase factor $|\Psi^R\rangle = e^{-i\mathbf{R} \cdot \mathbf{K}} |\Psi^0\rangle$. Assuming that $|g\rangle$ and $|f\rangle$ have net momenta of zero and $\hbar \mathbf{k}_f$, respectively, we obtain the following relation $|\Psi^R\rangle$.

$$\langle f | \mathbf{r} \rangle \langle n_{\mathbf{R}+\mathbf{d}} | \mathbf{r} | g \rangle = e^{-i\mathbf{k}_f \cdot \mathbf{R}} \langle f | \mathbf{r} \rangle \langle n_{\mathbf{d}} | \mathbf{r} | g \rangle,$$

$$\langle n_{\mathbf{R}+\mathbf{d}} | \mathbf{r} | g \rangle = \langle n_{\mathbf{d}} | \mathbf{r} | g \rangle.$$  \hspace{1cm} (A2)

Therefore, the sum over lattice vectors $\mathbf{R}$ for the combined factor of $e^{-i(c' - k + k_f) \cdot \mathbf{R}}$ from Eqs. (A2–A3) leads to the conservation of the crystal momentum $\delta(c' - k + k_f + \mathbf{K})$, where $\mathbf{K}$ represents the reciprocal lattice vectors. This results in the following expression for the RIXS intensity,

$$\langle f | \mathbf{r} \rangle \langle n_{\mathbf{R}+\mathbf{d}} | \mathbf{r} | g \rangle = e^{-i\mathbf{k}_f \cdot \mathbf{R}} \langle f | \mathbf{r} \rangle \langle n_{\mathbf{d}} | \mathbf{r} | g \rangle.$$  \hspace{1cm} (A3)

Appendix B: Expression of the matrix elements in the K-edge RIXS formula in terms of eigenstates in the presence and absence of core hole

In general, we transform $\hat{H}_d$ and $\hat{H}_{total, i}$ into the reciprocal space as follows,

$$\hat{H}_d = \sum_{\mathbf{k}, \mathbf{k'}, \xi, \xi'} \sum_{\sigma} \sum_{\sigma'} \sum_{\mathbf{K}, \mathbf{K'}, \xi, \xi'} \sum_{\sigma} \hat{H}_d^{\mathbf{k}+\mathbf{K}, \xi, \mathbf{k'}, \xi', \sigma} \times \hat{d}_{\mathbf{k}+\mathbf{K}, \xi, \sigma}^\dagger \hat{d}_{\mathbf{k'}, \xi', \sigma},$$

\hspace{1cm} (B1)
and

\[ \hat{H}_{\text{total},i} = \sum_{k, k'} \sum_{\xi, \xi'} \sum_{\sigma} H_{k+\xi, k'+\xi', \xi, \sigma} \times d_{k+\xi, \sigma}^\dagger d_{k'+\xi', \sigma} \]  \hspace{1cm} (B2)

where \( k \) and \( k' \) represent vectors within the first Brillouin zone \( \Omega_{1BZ} \), \( K \) and \( K' \) the reciprocal lattice vectors within the extended “first Brillouin zone” \( \Omega_{EBC} \) defined by the core hole site \( i \). Spin states are represented by \( \sigma \), and orbital states by \( \xi \) and \( \xi' \).

From the eigenstates \( |l k \sigma \rangle \) of \( \hat{H}_d \) with the wavevector \( k \in \Omega_{1BZ} \) within the \( l \)-th lowest energy band, and the \( m \)-th lowest energy eigenstate \( |m \sigma \rangle \) of \( \hat{H}_{\text{total},i} \), we define \( \beta_{l k m \sigma} = \langle l k \sigma | m \sigma \rangle \).

In the RIXS formula Eq. (3), \( \langle n_{\text{low}}^d | \frac{1}{2}_{d} | g \rangle \) and \( \langle l c k_c l_h k_h \sigma | \frac{1}{2}_{d} | n_{\text{low}}^d \rangle \) are found from

\[ \langle n_{\text{low}}^d | \frac{1}{2}_{d} | g \rangle = \prod_{\sigma = \uparrow}^{\downarrow} \left| \begin{array}{cccc}
\beta_{1k_1 \downarrow} & \beta_{1k_1 \downarrow} & \cdots & \beta_{1k_1 \downarrow} \\
\beta_{1k_2 \downarrow} & \beta_{1k_2 \downarrow} & \cdots & \beta_{1k_2 \downarrow} \\
\vdots & \vdots & \ddots & \vdots \\
\beta_{1k_{N_k} \downarrow} & \beta_{1k_{N_k} \downarrow} & \cdots & \beta_{1k_{N_k} \downarrow}
\end{array} \right| \]

\[ \langle l c k_c l_h k_h \sigma | \frac{1}{2}_{d} | n_{\text{low}}^d \rangle = \prod_{\sigma = \uparrow}^{\downarrow} \left| \begin{array}{cccc}
\beta_{1k_1 \downarrow} & \beta_{1k_1 \downarrow} & \cdots & \beta_{1k_1 \downarrow} \\
\beta_{1k_2 \downarrow} & \beta_{1k_2 \downarrow} & \cdots & \beta_{1k_2 \downarrow} \\
\vdots & \vdots & \ddots & \vdots \\
\beta_{1k_{N_k} \downarrow} & \beta_{1k_{N_k} \downarrow} & \cdots & \beta_{1k_{N_k} \downarrow}
\end{array} \right| \times \left| \begin{array}{cccc}
\beta_{1k_1 \uparrow} & \beta_{1k_1 \uparrow} & \cdots & \beta_{1k_1 \uparrow} \\
\beta_{1k_2 \uparrow} & \beta_{1k_2 \uparrow} & \cdots & \beta_{1k_2 \uparrow} \\
\vdots & \vdots & \ddots & \vdots \\
\beta_{1k_{N_k} \uparrow} & \beta_{1k_{N_k} \uparrow} & \cdots & \beta_{1k_{N_k} \uparrow}
\end{array} \right| \]

where \( N_e \) represents the total electron number, \( N_k \) the number of \( k \)-points in \( \Omega_{1BZ} \), \( \ell_{h}^\text{max} \) the index for the highest occupied band, and \( \sigma = -\sigma \). In Eq. [B4], the set of band and momentum indices, \((l_h^\sigma, k_h^\sigma)\) and \((l_h^\sigma, k_h^\sigma)\), represent the occupied states right before and right after the hole state represented by \((l_h, k_h)\) when the eigenstates of \( \hat{H}_d \) are ordered according to the band index and momentum index \( \Omega_{1BZ} \).

**Appendix C: Expressions of the Hamiltonians in reciprocal space**

In the absence of the core hole, the Hamiltonian for a single layer of \( \text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4 \) has the following form in reciprocal space,

\[ \hat{H}_d = \sum_{\sigma, k \in \Omega_{1BZ}} d_{k \sigma} \left( H^{\text{d,nonint}}_{k \sigma} + H^{\text{d,HF}}_{k \sigma} \right) d_{k \sigma} \]  \hspace{1cm} (C1)

where

\[ d_{k \sigma} = (d_{k+K_1, 1, \sigma}^1, d_{k+K_1, 2, \sigma}^1, d_{k+K_2, 1, \sigma}^1, d_{k+K_2, 2, \sigma}^1, d_{k+K_3, 1, \sigma}^1, d_{k+K_3, 2, \sigma}^1, d_{k+K_4, 1, \sigma}^1, d_{k+K_4, 2, \sigma}^1, d_{k+K_5, 1, \sigma}^1, d_{k+K_5, 2, \sigma}^1, d_{k+K_6, 1, \sigma}^1, d_{k+K_6, 2, \sigma}^1, d_{k+K_7, 1, \sigma}^1, d_{k+K_7, 2, \sigma}^1, d_{k+K_8, 1, \sigma}^1, d_{k+K_8, 2, \sigma}^1) \]  \hspace{1cm} (C2)
with \( K_1, K_2, K_3, K_4, K_5, K_6, K_7, \) and \( K_8 \) representing \((0, 0), (\pi, 0), (0, \pi), (\pi, \pi), (\pi, -\pi), (\pi, -\pi), (\pi, -\pi), (\pi, -\pi)\), and \((\pi, -\pi)\), respectively,

\[
H_{k\sigma}^{\text{dd, nonint}} = \begin{pmatrix}
M_1 + W_{3u} & -G_\sigma & G_\sigma & W_{1x} + W_{3x} & W_2 & G_\sigma & G_\sigma & W_2 \\
-G_\sigma & M_2 + W_{3u} & W_{1x} + W_{3x} & G_\sigma & W_2 & G_\sigma & G_\sigma & W_2 \\
G_\sigma & W_{1x} + W_{3x} & M_1 + W_{3u} & -G_\sigma & W_2 & G_\sigma & G_\sigma & W_2 \\
W_{2x} & G_\sigma & G_\sigma & W_{2x} & M_5 + W_{3u} & G_\sigma & G_\sigma & W_1 + W_{3s} \\
G_\sigma & W_{2x} & W_{2x} & G_\sigma & M_6 + W_{3u} & W_{1x} + W_{3s} & G_\sigma & W_1 + W_{3s} \\
G_\sigma & W_{2x} & W_{2x} & G_\sigma & W_{1x} + W_{3s} & M_7 + W_{3u} & -G_\sigma & M_8 + W_{3u} \\
W_{2x} & G_\sigma & G_\sigma & W_{2x} & W_1 + W_{3s} & W_1 + W_{3s} & G_\sigma & W_2 \\
G_\sigma & W_{2x} & W_{2x} & G_\sigma & W_{2x} & G_\sigma & W_{2x} & W_{2x} \\
G_\sigma & W_{2x} & W_{2x} & G_\sigma & W_{2x} & G_\sigma & W_{2x} & W_{2x}
\end{pmatrix},
\]

\[
M_j = \left[ \frac{\hbar}{2} \{ \cos(k_x + K_{j,z}) + \cos(k_y + K_{j,y}) \} \right] \frac{\sqrt{3J_0}}{2} \{ \cos(k_x + K_{j,z}) - \cos(k_y + K_{j,y}) \} \}
\]

At Mn\(^{3+}\) sites in the \( x/y \) directional legs of the zigzag chain in Fig. 5

\[
\tan \theta_1 = \pm \frac{Q_{3u} + Q_{3h} - \sqrt{(Q_{3h} + Q_{3s})^2 + 4Q_{2s}^2}}{2Q_{2s}}
\]

At Mn\(^{4+}\) sites, \( \theta_1 = 0 \). The matrix for the number operator in reciprocal space is necessary to evaluate \( U_{i_n,\sigma} \) and its element is given below.

\[
\left( \hat{n}_{i_n,\eta} \right)_{2(j-1)+\xi,2(j'-1)+\xi'} = e^{-i (K_j - K_{j'}) \cdot i_n} (R_{i_n,\eta})_{\xi,\xi'}
\]

We find the eigenstates and eigenenergies of the 16 \( \times \) 16 matrix \( H_{k\sigma}^{\text{dd, HF}} \) at chosen set of \( k \) points through the Hartree-Fock iterative calculations, which are used to find the electronic DOS in the absence of the core hole shown in Figs. 5(a) and 6(a).

The Hamiltonian in the presence of the core hole at a site \( i_c \) for \( N \times N \) cluster model of La\(_{0.5}\)Sr\(_{1.5}\)MnO\(_4\), with \( N \) multiple of 4, is presented below.

\[
\hat{H}_{\text{total},i_c} = \sum_{\sigma, k, k' \in \Omega_{1BZ}} \sum_{\eta, \bar{\eta}} U_{i_n, \sigma} d_{i,k}^{\dagger} H_{k\sigma}^{\text{dd, nonint}} \delta_{kk'} + H_{k\sigma}^{\text{dd, HF}}
\]

\[
\hat{H}_{k\sigma}^{\text{dd, HF}} = \sum_{\eta, \bar{\eta}} U_{i_n, \sigma} d_{i,k}^{\dagger} H_{k\sigma}^{\text{dd, HF}}
\]

\[
\begin{align*}
R_{i_n,-} &= \begin{pmatrix}
\cos^2 \theta_{i_n} & \cos \theta_{i_n} \sin \theta_{i_n} \\
\cos \theta_{i_n} \sin \theta_{i_n} & \sin^2 \theta_{i_n}
\end{pmatrix}, \\
R_{i_n,+} &= \begin{pmatrix}
\sin^2 \theta_{i_n} & -\cos \theta_{i_n} \sin \theta_{i_n} \\
-\cos \theta_{i_n} \sin \theta_{i_n} & \cos^2 \theta_{i_n}
\end{pmatrix}.
\end{align*}
\]

\( \theta_1 \) is defined from the lower (−) and upper (+) Jahn-Teller eigenstate,

\[
d_{i,-, \sigma} = d_{i,1\sigma} \cos \theta_1 + d_{i,2\sigma} \sin \theta_1,
\]

\[
d_{i,+ , \sigma} = -d_{i,1\sigma} \sin \theta_1 + d_{i,2\sigma} \cos \theta_1.
\]

\[
\hat{n}_{i, \eta, \sigma} = \sum_{k, k' \in \Omega_{1BZ}} d_{k, \sigma}^{\dagger} n_{i, \eta, k' \sigma} d_{k', \sigma},
\]

where \( n_{i, \eta, k' \sigma} = \frac{1}{2} \{ \delta_{kk'} \} \).

With \( \eta = +, - \) at \( j, j' = 1, 2, \ldots, 8 \), and \( \xi, \xi' = 1, 2 \). For the evaluation of \( U_{i_n, \sigma} \), the number operator in reciprocal space is necessary, shown below.
where

$$\left( e^{i\mathbf{k}\sigma} \right)_{2j-1+\xi,2j-1+\xi'} = e^{-i(\mathbf{k}-\mathbf{k}')\cdot \mathbf{r}} e^{-i(K_j-K_{j'})\cdot (\mathbf{R}_{\eta\xi})} \ ,$$

(E22)

Eigenvectors and eigenvalues are found for the $2N^2 \times 2N^2$ matrix of $H_{\text{total,}\xi}$ for each spin direction $\sigma$ in the presence of the core hole, through the Hartree-Fock iterative calculations. When necessary, the Pulay mixing method is used to reach a convergence.\(^{21,22}\) The eigenstates and eigenergies in the absence of the core hole for the same cluster are found by setting $U_{\text{core}} = 0$ and repeating the Hartree-Fock iterative calculations. The two sets of eigenstates and eigenvalues give $\varepsilon_{\xi\mathbf{k}\sigma}$, $\varepsilon_{\mu\mathbf{k}\sigma}$, and $\beta_{\mathbf{k}\mathbf{n}\sigma}$, which are used for the K-edge RIXS spectrum calculations of La$_{0.5}$Sr$_{1.5}$MnO$_4$.

Appendix D: Electron numbers at Mn$^{3+}$ and Mn$^{4+}$ sites

In this Appendix, we discuss the electron numbers on Mn ions. In our effective Hamiltonian, the state created by $d_{\mathbf{k}\sigma}$ is a hybridized state of atomic Mn 3d orbital and surrounding atomic O 2p orbitals. Therefore, $e_g$ electron numbers of 0.87 and 0.13 found for “Mn$^{3+}$” and “Mn$^{4+}$” sites in our effective Hamiltonian do not represent the actual numbers on Mn ions, which can be measured by resonant x-ray scattering. For a proper comparison we carry out an analysis in terms of atomic Mn 3d and O 2p orbitals, similar to Ref.\(^{43}\). In the basis of $|d^4\rangle$ and $|d^4L\rangle$, where $d^0$ and $L$ represent the presence of $n$ electrons in atomic Mn 3d level and a hole in the ligand O 2p level of $e_g$ symmetry, the Hamiltonian for the states with one $e_g$ electron is

$$H_{\text{one } e_g} = \begin{pmatrix} 0 & 2t_{dp} \\ 2t_{dp} & \Delta \end{pmatrix} \ ,$$

(D1)

where $t_{dp}$ represents the O 2p – Mn 3d electron hopping amplitude and $\Delta$ is the energy difference between Mn 3d and O 2p levels. Similarly, the Hamiltonian for the states with zero $e_g$ electron is

$$H_{\text{zero } e_g} = \begin{pmatrix} 0 & 2t_{dp} \\ 2t_{dp} & \Delta - U_{\text{atomic}} \end{pmatrix} \ ,$$

(D2)

in the basis of $|d^3\rangle$ and $|d^4L\rangle$, where 3d–3d Coulomb interaction $U_{\text{atomic}}$ is included to account for one less 3d electrons in $|d^4L\rangle$ than in $|d^3\rangle$.

The lower energy eigenstates of $H_{\text{one } e_g}$ and $H_{\text{zero } e_g}$,

$$|\text{one } e_g \text{ electron} \rangle = \mu_1|d^3\rangle + \nu_1|d^4L\rangle \ ,$$

$$|\text{zero } e_g \text{ electron} \rangle = \mu_0|d^3\rangle + \nu_0|d^4L\rangle \ ,$$

(D3)

(D4)

correspond to the states with one and zero electron in hybridized $e_g$ levels considered in our effective Hamiltonian $H_{\tilde{d}}$. Therefore, $|\text{one } e_g \text{ electron} \rangle$ state has $\mu_1|\mu_1|^2 + 5|\nu_1|^2$ electrons in atomic Mn 3d levels, whereas $|\text{zero } e_g \text{ electron} \rangle$ state has $3|\mu_0|^2 + 4|\nu_0|^2$ electrons in atomic Mn 3d levels. Therefore, $n_{e_g}$ electrons in the hybridized $e_g$ levels obtained from $H_{\tilde{d}}$ corresponds to $n_{\text{atomic } Mn}$ electrons on the atomic Mn 3d levels, defined as

$$n_{\text{atomic } Mn} = n_{e_g}(4|\mu_1|^2 + 5|\nu_1|^2) + (1 - n_{e_g})(3|\mu_0|^2 + 4|\nu_0|^2) .$$

(D5)

For typical values of $t_{dp} = 1$ eV, $\Delta = 4$ eV, $U_{\text{atomic}} = 7$ eV, and $n_{e_g} = 0.87$ and 0.13 obtained for $e_g$ levels around “Mn$^{3+}$” and “Mn$^{4+}$” sites for $t_0 = 0.9$ eV case, we find $n_{\text{atomic } Mn}$ = 4.10 and 3.84 for nominal Mn$^{3+}$ and Mn$^{4+}$ ions,\(^{23,24}\) and the difference is only about 0.26, which is much smaller than the difference of 0.74 between $n_{e_g}$’s and is consistent with 0.15–0.3 suggested by resonant x-ray scattering at the Mn K-edge and bond valance sum method.\(^{23,24}\)
We note that unlike the three-dimensional manganites, the degeneracy of the $e_g$ levels are broken even without the $Q_2$ or $Q_3$ distortions because of the layered crystal structure. So, we should consider $\hat{H}_{JT}$ as the effective Hamiltonian that includes not only the effect of the oxygen octahedron but also the crystal field of farther ions.

We also note that the Fourier transform of electron number change shown in Fig. 7(a) and 7(b) has a maximum at $(\pm \pi a, \pm \pi a)$, consistent with the point in reciprocal space with maximum integrated RIXS intensity. However, such correspondence does not apply to $t_0 = 1.5$ eV case, indicating further study is required to establish the exact relation between RIXS intensities in reciprocal space and screening in real space.

We use the relation $\langle f | R | n^{+d} \rangle = \langle n^{+d} | R | g \rangle = 0$.

In other words, from the $N_e/2 \times N_e/2$ part of the matrix of $\beta_{lkm\sigma}$ with $m = 1, \ldots, N_e/2$ and $\varepsilon_{lkm} < \varepsilon_F$, the row corresponding to $k = k_h$ and $l = l_h$ is replaced by the row corresponding to $k = k_e$ and $l = l_e$ in the matrix of $\beta_{lkm\sigma}$.

We use the relation $\langle f | R | n^{+d} \rangle = \langle n^{+d} | R | g \rangle = 0$.

In other words, from the $N_e/2 \times N_e/2$ part of the matrix of $\beta_{lkm\sigma}$ with $m = 1, \ldots, N_e/2$ and $\varepsilon_{lkm} < \varepsilon_F$, the row corresponding to $k = k_h$ and $l = l_h$ is replaced by the row corresponding to $k = k_e$ and $l = l_e$ in the matrix of $\beta_{lkm\sigma}$.

P. Pulay, Chem. Phys. Lett. 73 (2), 393 (1980).

P. Pulay and R.-F. Liu, J. Phys. Chem. 94 (14), 5548 (1990).

M. A. van Veenendaal, H. Eskes, and G. A. Sawatzky, Phys. Rev. B 47, 11462 (1993).

We use the relation $\langle f | R | n^{+d} \rangle = \langle n^{+d} | R | g \rangle = 0$.

In other words, from the $N_e/2 \times N_e/2$ part of the matrix of $\beta_{lkm\sigma}$ with $m = 1, \ldots, N_e/2$ and $\varepsilon_{lkm} < \varepsilon_F$, the row corresponding to $k = k_h$ and $l = l_h$ is replaced by the row corresponding to $k = k_e$ and $l = l_e$ in the matrix of $\beta_{lkm\sigma}$.

P. Pulay, Acta Crystallogr. Sect. B: Struct. Sci. 47, 192 (1991); I. D. Brown, ibid. 48, 553 (1992).