Theoretical Study of Resonant Inelastic X-ray Scattering Spectrum in Nickelates

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Abstract. We examine theoretically the Resonant Inelastic X-ray Scattering (RIXS) spectra on nickelates by using numerically exact diagonalization techniques on the two-band Hubbard model. Other spectra such as the dynamical charge correlation function are examined to discuss what excitations appear in the RIXS. We demonstrate that the spectra which appear upon doping in the dynamical charge correlation function and the RIXS are originated from only high spin states, in contrast to the optical conductivity where the spectrum comes from both high and low spin states.

The two-dimensional nickelate \( \text{La}_{2-x}\text{Sr}_x\text{NiO}_4 \) has received special attention as a reference system of high-\( T_c \) cuprates. The undoped nickelate \((x = 0)\) has the charge gap in the optical conductivity. Upon doping of holes, a broad spectrum appears in the gap. Three of the present authors have examined theoretically the optical conductivity in the Hubbard model with \( \text{e}_g \)-orbital bands and shown that the spectrum in the gap comes from the excitations to the low spin states as well as those due to the antiferromagnetic spin background disturbed by holes [1]. The Ni \( K \)-edge resonant inelastic X-ray scattering (RIXS) is another experiment to extract the information of the charge excitations. In particular, one can examine the momentum resolved charge excitations with RIXS [2, 3, 4]. It is interesting to clarify whether the excitations seen in the optical conductivity can also occur in RIXS. In this study, we examine theoretically the RIXS spectra in undoped and doped Nickelates by using numerically exact diagonalization techniques on the Hubbard model with \( \text{e}_g \)-orbital bands. We also calculate other spectra such as the dynamical charge correlation function and demonstrate that spectra which appear upon doping in the dynamical charge correlation function and the RIXS are originated from only high spin states, in contrast to the optical conductivity where the spectrum comes from both high and low spin states.

The Hubbard model of \( \text{e}_g \) orbital bands is written as,

\[
H = \sum_{\langle i,j \rangle, \sigma, \mu, \nu} \left( t_{ij}^\mu \hat{c}_{i,\mu,\sigma}^\dagger \hat{c}_{j,\nu,\sigma} + \text{h.c.} \right) + U \sum_{i,\mu} n_{i,\mu,\uparrow} n_{i,\mu,\downarrow} + U' \sum_i N_{i,u} N_{i,v} + K \sum_{\langle i,j \rangle, \sigma, \sigma'} \hat{c}_{i,u,\sigma}^\dagger \hat{c}_{i,v,\sigma'} \hat{c}_{j,u,\sigma'} \hat{c}_{j,v,\sigma} + K \sum_i \left( \hat{c}_{i,u,\uparrow}^\dagger \hat{c}_{i,u,\downarrow} \hat{c}_{i,v,\uparrow} \hat{c}_{i,v,\downarrow} + \text{h.c.} \right),
\]

(1)
where $u$ and $v$ denote $3z^2 - r^2$ and $x^2 - y^2$ orbitals, respectively, $n_{i,\mu,\sigma} = c_{i,\mu,\sigma}^\dagger c_{i,\mu,\sigma}$ and $N_{i,\mu} = n_{i,\mu,\uparrow} + n_{i,\mu,\downarrow}$. The parameters $U$, $U'$, and $K$ are the intra-orbital and inter-orbital Coulomb repulsions and the exchange interaction, respectively, with $U = U' + 2K$. The parameter $t_{ij}^{\mu\nu}$ is the hopping matrix element between orbital $\mu$ at site $i$ and $\nu$ at $j$. In a two-dimensional system defined in the $xy$ plane, the hopping matrix elements between neighboring sites are given by $t_{ij}^{\mu\nu} = - t$, $t_{ij}^{\mu\nu} = - t/3$, and $t_{ij}^{\mu\nu} = + (\pm t)/\sqrt{3}$ in the $x(y)$ direction [1].

We take $U/t = 14$ and $K/t = 2$ with $t \sim 0.3$ eV, which are the same values used in Ref. [1].

In the Ni $K$-edge RIXS, the emission of a photon with a dipole transition between Ni 4$p$ and Ni 1$s$ states occurs resonantly by tuning the energy of incoming photon to Ni $K$ absorption edge. In the intermediate state, we introduce Coulomb interaction between $3d$ and 1$s$-core holes [5], given by $H_c = U_c \sum_{i,\mu,\sigma,\sigma'} n_{i,\mu,\sigma} n_{i,\mu,\sigma'}$, where $n_{i,\mu,\sigma}$ is the number operator of 1$s$-core hole. By assuming that the 4$p$ photo-electron enters into the bottom of the 4$p$ bands, the RIXS spectrum for Ni $K$-edge is expressed as,

$$ I(\Delta K, \Delta \omega) = \sum_f \left| \langle f | D_{f,K}^\dagger G(\omega_i) D_K | 0 \rangle \right|^2 \delta (\Delta \omega - E_f + E_0), $$

(2)

where $\Delta K = K_f - K_i$ and $D_K = \sum_{\sigma} e^{iK_{i\sigma}} s_{i\sigma} + H.c.$ with the creation operator $s_{i\sigma} (p_{i\sigma}^\dagger)$ of 1$s$-core hole (4$p$ electron). $K_{i\sigma}$ is the wave vector of the incoming (outgoing) photon with energy $\omega_i (\omega_f)$, and $\Delta \omega = \omega_i - \omega_f$. $G^{-1}(\omega_i) = \omega_i + i\Gamma - H_c - H_{1s,4p}$, where $H_{1s,4p}$ is composed of the energy separation $\varepsilon_{1s-4p}$ between the Ni 1$s$ level and the bottom of the 4$p$ band, and $\Gamma$ is the inverse of relaxation time in the intermediate state. $|0\rangle$ is the ground state with energy $E_0$ and $|f\rangle$ is the final state of RIXS with energy $E_f$. We use $\Gamma/t = 1$ and $U_c/t = 14$.

We use the Lanczos-type exact diagonalization technique on up to $\sqrt{3} \times \sqrt{3}$-unit-cell cluster under periodic boundary conditions. We will show the results for the eight-unit-cell cluster in the following. The spectrum $I(\Delta K, \Delta \omega)$ is calculated by using a modified version of the conjugate-gradient method together with the Lanczos technique.

Figures 1 and 2 show the RIXS spectra calculated in half-filled and two-hole doped cases, respectively. The spectra above $\Delta \omega/t \sim 12$ in Fig. 1 are associated with the excitations across the charge gap scaled by $\sim U$, i.e., the Mott gap excitations. The center of gravity of the spectrum at $\Delta K = (\pi, \pi)$ is higher in energy than those at other momenta. This result suggests that the momentum dependence of the spectra along the $(\pi, \pi)$-direction may appear in undoped

![Figure 1](image1.png)  
**Figure 1.** The RIXS Spectrum on the eight-unit-cell cluster of the two-band Hubbard model in the half-filled case. The $\delta$-functions are convoluted with a Lorentzian broadening of 0.2$t$.

![Figure 2](image2.png)  
**Figure 2.** The same as Fig. 1 but in the two-hole doped case.
Nickelate. Note that the experimental data have revealed a weakly dispersive feature along the ($\pi, 0$)-direction [2].

In Fig. 2, the spectral structures at $\Delta \omega/t \sim 18$ are due to the excitations across the Mott gap. The energy position of the spectrum is shifted in a higher energy region upon doping, which is a similar behavior to that in the single-band Hubbard model [6]. The spectra below $\Delta \omega/t \sim 5$ are associated with intra-band excitations because the energy positions of the spectra depend on the hopping parameter $t$. The energy region in which spectra appear upon doping is consistent with the experimental data [3, 4]. In the optical conductivity [1], the spectra appear all over the gap upon doping, and those above $\omega/t \sim 5$ come from the excitations to the low spin states.

In order to discuss what excitations occur in RIXS, we first examine a fundamental spectrum for the charge excitation, i.e., the dynamical charge correlation function expressed as,

$$N(q, \omega) = \sum_n |\langle n | N_{q,\mu}(0) | 0 \rangle|^2 \delta(\omega - E_n + E_0), \quad (3)$$

where $N_{q,\mu} = \sum_\nu e^{-i q \cdot r} N_{\nu,\mu}$. Figure 3 shows the calculated spectrum in the two-hole doped case, together with components for each orbital, where the $\nu$-component is calculated by replacing the operator $\sum_\mu N_{q,\mu}$ with $N_{q,\nu}$. The spectra of the excitations across the Mott gap are much smaller in intensity than the RIXS spectra because the excitations in RIXS can be enhanced through the tuning of the energy of the incident photon. On the other hand, the spectra related to the intra-band excitations is similar in shape to the RIXS spectra. In Fig. 3, we also find that the structures at $\omega/t \sim 5$ with $q = (\pi, \pi)$ and $(\pi, 0)$ are mainly reproduced by the $x^2 - y^2$ component and that at $\sim 2.5$ with ($\frac{\pi}{2}, \frac{\pi}{2}$) by both $x^2 - y^2$ and $3z^2 - r^2$.

Next we examine the single particle excitation spectrum, which is expressed as,

$$A_\mu(k, \omega) = \sum_n |\langle n | c_{k,\mu,\sigma}(0) | 0 \rangle|^2 \delta(-\omega - E_n + E_0) + \sum_n |\langle n | c^1_{k,\mu,\sigma}(0) | 0 \rangle|^2 \delta(\omega - E_n + E_0), \quad (4)$$

where $c_{k,\mu,\sigma}$ is the Fourier transform of $c_{1,\mu,\sigma}$. Figure 4 shows $A_\mu(k, \omega)$ in the two-hole doped case. The peaks at $\omega/t \sim 10.5, 14.5, \text{ and } 19$ are characterized by $3A_2$ (high spin), $1E$ (low spin), and $1A_1$ (low spin) states at the site where an electron is added, respectively, and peaks at $\omega/t \sim 25$ are given by the triply occupied states [1]. Comparing $N(q, \omega)$ with the particle-hole...
excitations, we find that the excitations in energy region below $\omega/t \sim 6$ in $N(q, \omega)$ correspond to convolutions of peaks below the Fermi level in $A_\mu(k, \omega)$ and those characterized by high spin states above the Fermi level. The structures at $\omega/t \sim 5$ with $q = (\pi, \pi)$ and $(\pi, 0)$ in Fig. 3, which dominantly consist of the $x^2 - y^2$ component, correspond to excitations from the (0,0) state at $\omega/t \sim 4$ to $(\pi, \pi)$ and $(\pi, 0)$ states at $\omega/t \sim 10.5$ in Fig. 4 (a), respectively. Similarly, the structure at $\omega/t \sim 2.5$ with $(\pi, \pi)$ in Fig. 3 can be explained with excitations from the $(\pi, \pi)$ state at $\omega/t \sim 8$ to $(\pi, \pi)$ and/or $(\pi, 0)$ states at $\omega/t \sim 10.5$ in Fig. 4 (a) and (b). The results suggest that only high spin states contribute to spectra which appear upon doping in $N(q, \omega)$, as well as the RIXS.

In order to confirm that excitations related to only high spin states occur in $N(q, \omega)$, we introduce the projection operator $P$ for excluding low spin states and doubly occupied states in any orbitals, which is expressed as,

$$P = \prod_i \left[ 1 + \frac{1}{2} N_i (N_i - 1) \left( S_{i,\uparrow} \cdot S_{i,\downarrow} - \frac{1}{4} \right) \right] (1 - n_{i,\uparrow}\uparrow n_{i,\downarrow}\downarrow) (1 - n_{i,\downarrow}\downarrow n_{i,\uparrow}\uparrow), \quad (5)$$

where $N_i = \sum_{\mu,\sigma} n_{i,\mu,\sigma}$ and $S_{i,\mu,\sigma} = \frac{1}{2} \sum_{\alpha,\beta} c_{i,\mu,\alpha}^\dagger \sigma_{\alpha,\beta} c_{i,\mu,\beta}$ with $\sigma$ the Pauli matrix, and calculate a spectrum $\bar{N}(q, \omega)$ defined as $\bar{N}(q, \omega) = \sum_n |\langle n | P \sum_{\mu} N_{q,\mu}|0\rangle|^2 \delta(\omega - E_n + E_0)$. The result is shown in Fig. 5. The dominant structures in $N(q, \omega)$ also appear in $\bar{N}(q, \omega)$. This fact indicates that the excitations occur within high spin states. Thus, we conclude that only high spin states contribute to excitations which occur upon doping in the dynamical charge correlation function and the RIXS, in contrast to the optical conductivity.

In summary, we have examined theoretically the RIXS spectra by using numerically exact diagonalization techniques on the two-band Hubbard model. We have also calculated the dynamical charge correlation function and single particle excitation spectra and demonstrated that the spectra which appear upon doping in the dynamical charge correlation function and the RIXS are originated from only high spin states, in contrast to the optical conductivity where the spectrum comes from both high and low spin states.

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