Optical responses of photoexcited states in the one-dimensional ionic Hubbard model

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Abstract. Photoinduced optical responses are studied in the one-dimensional ionic Hubbard model with the nearest-neighbor repulsion $V$. For $V=0$, carriers introduced by photoirradiation move freely both in the Mott insulator phase and in the band insulator phase, giving rise to a Drude peak in the optical conductivity spectrum. The carriers in the Mott insulator phase remain conducting for $0 < V < 2t$ because their kinetic energy overcomes the binding energy. By contrast, the electrons and the holes in the band insulator phase are bound to form excitons for $V > 0$, which do not contribute to the charge transport unless the excitation energy allows them to be separated. The dependence of the Drude weight in the lowest-energy photoexcited state on $V$ and the system size is investigated for both phases. Implications to experimental studies of halogen-bridged metal-complex chains are discussed.

1. Introduction
Halogen-bridged metal-complex chains, known as MX chains, have attracted considerable attention of many physicists and chemists because of the variety of electronic phases [1]. Their ground states depend on the metal element. In the Ni complexes, they are Mott insulators due to large on-site Coulomb repulsion. In the Pd complexes, they are charge-density-wave (CDW) insulators due to relatively large electron-phonon interactions. Recent experiments on their photoinduced optical properties show a distinct difference between these insulators. In the Ni complexes, the optical conductivity shows a Drude-like low-energy component just after the photoexcitation, suggesting that the photoinduced state is metallic [2]. The Pd complexes remain insulating with a finite optical gap even after the photoexcitation [3]. In this theoretical study, we discuss the origin of this difference in these optical responses. The one-dimensional (1D) ionic Hubbard model with the nearest-neighbor repulsion $V$ [4], which is called the 1D extended ionic Hubbard model in this paper, is employed to describe the electronic property of the MX chains. By using the exact diagonalization method, we calculate optical conductivity spectra and Drude weights for the ground and photoexcited states. Our results indicate that the photoinduced metallic property of the Ni complexes is caused by doublons and holons in the Mott insulator background. In the CDW phase of the Pd complexes, even weak nearest-neighbor repulsion can bind electrons and holes introduced by the photoexcitation.
2. One-dimensional extended ionic Hubbard model

The 1D extended ionic Hubbard model is defined as

\[ H = -t \sum_{\sigma} (c_{l+1,\sigma}^\dagger c_{l,\sigma} + c_{l,\sigma}^\dagger c_{l+1,\sigma} + U n_{l,\uparrow} n_{l,\downarrow} + V \sum_l n_l n_{l+1} + \Delta \sum_l (-1)^l n_l , \]  

where \( c_{l,\sigma}^\dagger \) (\( c_{l,\sigma} \)) is the creation (annihilation) operator of an electron with spin \( \sigma \) at site \( l \), \( n_{l,\sigma} = c_{l,\sigma}^\dagger c_{l,\sigma} \), and \( n_l = n_{l,\uparrow} + n_{l,\downarrow} \). The parameter \( t \) denotes the nearest-neighbor transfer integral, \( U \) the on-site repulsion strength, \( V \) the nearest-neighbor repulsion strength, and \( \Delta (> 0) \) a half of the level difference between the neighboring orbitals.

This model is useful to describe both the CDW phase and the Mott insulator phase. Equation (1) with \( \Delta = 0 \) is the 1D extended Hubbard model, which has been used for studies of 1D Mott insulators [5]. In the CDW phase, displacement of the halogen (X) atoms leads to alternating electron levels at the metal (M) sites (figure 1), which corresponds to a finite \( \Delta \). Here we note that \( \Delta \) is a parameter of this model, not a dynamical variable of the lattice displacement [6]. Thus we can treat a CDW insulator as a band insulator.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{schematic.png}
\caption{Schematic electronic structure of the CDW phase. \( \bullet \) (\( \bigcirc \)) denotes a metal (halogen) ion. Because of the displacements of halogen ions, the energy levels at the metal sites alternate. The difference between the unoccupied and doubly occupied energy levels is \( 2\Delta \).}
\end{figure}

In order to clarify the photoinduced optical response of the system, we calculate the optical conductivity spectrum for the optically allowed, first excited state \( |\psi_{1\text{opt}}\rangle \) with energy \( E_{1\text{opt}} \) given by

\[ \Re[\sigma_1(\omega)] = D_1 \delta(\omega) - \frac{1}{N\omega} \Im \left[ \langle \psi_{1\text{opt}} | \hat{j} \frac{1}{\omega + i\epsilon + E_{1\text{opt}} - \hat{H}} \hat{j} | \psi_{1\text{opt}} \rangle - \langle \psi_{1\text{opt}} | \hat{j} \frac{1}{\omega + i\epsilon - E_{1\text{opt}} + \hat{H}} \hat{j} | \psi_{1\text{opt}} \rangle \right] , \]

where \( D_1 \) is the Drude weight of \( |\psi_{1\text{opt}}\rangle \) calculated as

\[ D_1 = \frac{-\pi}{N} \langle \psi_{1\text{opt}} | \hat{K} | \psi_{1\text{opt}} \rangle - \frac{2\pi}{N} \sum_{n\neq1\text{opt}} \frac{|\langle \psi_{1\text{opt}} | \hat{j} | \psi_{1\text{opt}} \rangle|^2}{E_n - E_{1\text{opt}}} . \]

Here \( \hat{K} \) is the kinetic term of the Hamiltonian (1), and \( \hat{j} \) is the current operator defined as \( \hat{j} = it \sum_{l,\sigma} (c_{l+1,\sigma}^\dagger c_{l,\sigma} - c_{l,\sigma}^\dagger c_{l+1,\sigma}) \). We treat the half-filled \( N \)-site chains and impose the periodic boundary condition for \( N=4n \) and the anti-periodic boundary condition for \( N=4n+2 \). The Lanczos diagonalization method is used.

3. Results

3.1. Optical conductivity

In this subsection, we illustrate the deference between the optical conductivity spectrum of the Mott insulator and that of the band insulator by setting \( V = 0 \) at first. Effects of finite \( V \)
will be discussed in the next subsection. The optical conductivity spectra of the ground and photoexcited states in the Mott insulator phase are shown in figure 2 (a). In the ground state, the spectrum has an optical gap, above which the absorption is caused by creation of a doublon and a holon in a continuum. In the photoexcited state, a considerable amount of the spectral weight is transferred from the holon-doublon continuum to the Drude component and another low-energy component. The absorption above the optical gap survives the photo-carrier doping, but it is weakened especially near the optical gap because the photoexcitation significantly alters the electron correlation. The low-energy component below the optical gap is due to the transition between nearly degenerate, odd- and even-parity states [7].

Figure 2 (b) shows the optical conductivity spectra of the ground and photoexcited states in a band insulator. In the ground state, the spectrum has an optical gap, above which the absorption is caused by creation of an electron and a hole in a continuum. In the photoexcited state, a small amount of the spectral weight is transferred from the lowest-energy part of the continuum to the Drude component. The absorption above the optical gap is robust except for its lowest-energy part because the photoexcited electron and the hole are only weakly correlated with the other electrons.

Figure 2. Optical conductivity of the ground state $\sigma(\omega)$ and of the excited state $\sigma_1(\omega)$, (a) for the Mott insulator phase ($U/t = 6, V/t = 0$, and $\Delta/t = 0$), and (b) for the band insulator phase ($U/t = 1$, $V/t = 0$, and $\Delta/t = 3$). 12-site rings are used and the broadening factor $\epsilon$ is set to $0.1t$ in this calculation.

3.2. Drude weight
For the Mott insulator phase, the Drude weight of the lowest-energy photoexcited state $D_1$ is shown in figure 3 as a function of the nearest-neighbor repulsion strength $V$. For $V < 2t$, the doublon and the holon are unbound to contribute to the metallic conductivity [8]. The Drude weight $D_1$ decreases very slowly with the system size $N$ (figure 4). With increasing $N$, the density of the carriers becomes low and $D_1$ should decrease. In the present calculations up to $N=14$, the large $N$ behavior cannot be derived. If it is fitted to the exponential function $D_1 = \text{const.} \times \exp(-N/\xi)$ [9, 10], the localization length $\xi$ is estimated to be comparable with the system size used in the calculations. Indeed the fitting to a power function $D_1 \sim N^{-\alpha}$ seems to be more appropriate. For a fixed system size, $D_1$ initially increases with $V$ for $V < 2t$, whose mechanism is unclear. For $V > 2t$, the doublon and the holon are bound together [8]. The neutral pair would not contribute to the conduction at zero energy. Indeed, $D_1$ decreases
quickly with $N$ (figure 4), which is well fitted to the exponential function with a small localization length.

![Figure 3](image-url) **Figure 3.** Drude weight of the lowest-energy photoexcited state $D_1$, as a function of $V$, for the Mott insulator with $U/t=20$, $\Delta=0$ and different $N$.

![Figure 4](image-url) **Figure 4.** $D_1$, as a function of $N$, for the Mott insulator with $U/t=20$, $\Delta=0$ and different $V$. Solid lines are fits to the exponential function $D_1 = \text{const.} \times \exp(-N/\xi)$. The localization length $\xi$ for $V/t = 0$ ($V/t = 6$) is 6.9 (1.4).

For band insulators, $D_1$ is shown in figure 5 as a function of $V$. For any $N$, $D_1$ monotonically decreases with $V$ because the electron and the hole are bound to form an exciton with an infinitesimally small $V$ [11]. Only at $V=0$, $D_1$ decreases very slowly with $N$, implying the metallic behavior (figure 6). Because the fitted localization length $\xi$ is close to the largest system size used in the calculations, the carriers are actually free to contribute to the metallic conductivity for $V=0$ only. For $V > 0$, $D_1$ exponentially decreases with $N$, whose localization length becomes short with increasing $V$ (figure 6).

The effect of the nearest-neighbor repulsion $V$ is different between in Mott insulators and in band insulators. In a band insulator, an infinitesimally small $V$ can bind an electron and a hole to form an exciton. However, in a Mott insulator, a small $V$ cannot bind a doublon and a holon. In the half-filled extended Hubbard model, the energy of the photoexcited state is given by $U - 4t$ if the doublon and the holon are unbound [8]. The doublon and the holon have an effective transfer integral of $t$, and their kinetic energies $-2t$ are summed up in addition to the cost of double occupancy $U$. If the doublon and the holon are bound together, the energy of the photoexcited state is given by $U - V - 4(t^2/V)$ [8]. Although they gain the binding energy $V$, the effective transfer integral of the pair is much reduced to $2t^2/V$ because the doublon and the holon need to be separated once to move together. Thus their binding requires $V > 2t$, where the Drude weight decreases with $V$.

4. **Summary and discussion**

The optical conductivity spectra and the Drude weights are calculated for the ground and photoexcited states in the one-dimensional extended ionic Hubbard model at half filling. The exact diagonalization method is employed for systems with up to 14 sites. Photoexcitations introduce doublons and holons into Mott insulators, and electrons and holes into band insulators. Without nearest-neighbor repulsion, the effective transfer integrals of these carriers are different as a function of the optical gap. Those of doublons and holons are given by $t$. Because of
the spin-charge separation in the purely one-dimensional systems, the spin fluctuations do not affect the motion of these carriers. This is in contrast to the two-dimensional system, where the quantum spin fluctuations are necessary for the carriers to move around, recovering the antiferromagnetic spin correlation. The effective transfer integrals of electrons and holes are given by $t^2/(2\Delta)$ in the large $\Delta$ limit, so that they decrease with increasing optical gap.

The effect of nearest-neighbor repulsion on doublons and holons are quite different from that on electrons and holes. Because the doublon-holon pair has a much smaller effective transfer integral of $2t^2/V$ than the doublon or the holon, they gain the kinetic energy by unbinding for $V < 2t$. In this case, they can contribute to the metallic conduction. The relations for $V < 2t$ and for $V < 2t$ are suggested to hold in the copper-oxide chains and the Ni complexes, respectively, from the comparisons between their optical conductivity spectra and their photoconductivity spectra [11]. By contrast, the electron-hole pair has an effective transfer integral comparable with that of the electron or the hole, so that even small $V$ binds the electron and the hole together. The resultant neutral exciton does not contribute to the conduction.

These results are for the lowest-energy photoexcited states. When the energy of photoexcitation is large enough for the bound carriers to be separated, we expect finite photoconductivity. Thus the energy dependence of the pump light is important for the optical responses of the photoexcited states. In the experiment [2], the energy of the pump light 1.55eV is larger than the energy to create an exciton 1.3eV. In the halogen-bridged metal complexes, the effect of lattice fluctuations would also be important. Because the Pd complexes have the CDW order, they are much more sensitive to the lattice fluctuations than the Ni complexes in the Mott insulator phase. The low-energy optical responses in the Pd complexes are therefore easily suppressed by both the lattice fluctuations and the formation of excitons.

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