Interband absorption in a strongly correlated half-filled band Hubbard chain: Effect of long-range Coulomb interaction

S. K. Lyo
Sandia Laboratories, Albuquerque, New Mexico 87115
(Received 24 March 1978)

We study the effect of a weak long-range Coulomb interaction on the interband absorption in a strongly correlated half-filled-band Hubbard chain such as low-dimensional charge-transfer organic salts by introducing a small nearest-neighbor Coulomb repulsion (U_1) to the Hubbard model. A long-range interaction gives rise to an attractive potential well between the doubly occupied site and the hole and distorts the interband absorption line shape for transitions to the upper Hubbard band. Also, it leads to formation of, and additional transitions to, a bound excitonic state. With an increasing value of U_1, the intensity leaks gradually from the former transitions to the latter, while the total intensity is conserved.

I. INTRODUCTION

It seems that the electronic correlation is quite strong in some of the narrow-band low-dimensional charge-transfer organic salts such as chloranil-alkali salts or TCNQ (tetracyanoquinodimethane) compounds (e.g., alkali-TCNQ)[1,2] although the coupling strength in the latter systems is yet an unsettled question in a strict sense.[3] In these systems the charge transfer is usually complete[4] and there is one excess electron per acceptor (i.e., TCNQ) site. The strength of the on-site Coulomb interaction (U_0) is deduced from the activation energy of the dc conductivity or the position of the interband absorption peak. One expects that important information about band structure can be extracted from optical-absorption measurement. If the strength of the electronic correlation is larger than the bandwidth (defined as "unity" hereafter), the many-body aspect of the problem should be treated carefully. The conventional single-particle approach is not justified in general.

Recently Lyo and Gallinar[5] studied the inter-band absorption in a unidimensional, strongly correlated (i.e., $U_0 \gg 1$) half-filled Hubbard band[6] using a rigorous perturbation method. In such a system the Coulomb screening is not as efficient as in metals and it is proper to consider the effect of a long-range Coulomb interaction. For simplicity we consider the effect of a weak nearest-neighbor Coulomb repulsion ($U_1 \ll U_0$) on the inter-band absorption at low temperatures ($T \ll k_B^{-1}U_0$; k_B is Boltzmann's constant). It is found that, for a finite value of U_1, the absorption line shape becomes asymmetric and significantly distorted, although the total intensity is unaffected. It is also found that with an increasing value of U_1, the doubly occupied site (to be defined as "particle") and the hole form a sharper local (i.e., molecular) state and "steals" the intensity gradually from the absorption band of the extended states. In particular, for the antiferromagnetic ground state, the particle-hole bound state is formed for $U_1 > \frac{1}{2}$ and below the bottom of the absorption band of the extended states. The absorption band of the latter states extends from a photon energy $\hbar\omega = U_0 - 1$ to $\hbar\omega = U_0 + 1$, with a width equal to twice the hole bandwidth, and has a significantly distorted line shape for a finite U_1 and for all spin configurations.

In the Sec. II we set up the formulation for the interband absorption using U_0^{-1} as a perturbation parameter. In Sec. III the line shape is evaluated for antiferromagnetic, ferromagnetic, and random spin configurations. The paper is concluded in Sec. IV.

II. FORMULATION

The Hamiltonian is given by

$$H = H_0 + V \tag{1a}$$

with

$$H_0 = U_0 \sum_i n_{i\uparrow} n_{i\downarrow} + U_1 \sum_i n_i n_{i+1},$$
$$V = -t \sum_{i\sigma} (c^\dagger_{i+1\sigma} c_{i\sigma} + c^\dagger_{i\sigma} c_{i+1\sigma}) \tag{1b}$$

Here $c^\dagger_{i\sigma}$ ($c_{i\sigma}$) creates (destroys) a state of spin σ at site i, $n_{i\sigma}$ ($= c^\dagger_{i\sigma} c_{i\sigma}$) is the number operator and $n_i = n_{i\uparrow} + n_{i\downarrow}$. We assume that U_0 and U_1 are both positive and $U_0 - U_1 \gg t$, where t is the transfer integral. The real part of the conductivity is given by[7]

$$\sigma_R(\omega) = \frac{\pi e^2 \tanh(\beta\hbar\omega/2)}{\Omega\omega}\,\phi(\omega), \tag{2a}$$

with

$$\phi(\omega) = \int_{-\infty}^{\infty} \frac{d\tau}{2\pi\hbar}\, e^{i\omega\tau}\phi(\tau), \tag{2b}$$

where e and Ω are the electronic charge and the volume of the sample, respectively, and $\beta = (k_B T)^{-1}$. The correlation function $\phi(\tau)$ is given by

$$\phi(\tau) = \langle v(\tau) v(0) + v(0) v(\tau) \rangle . \tag{3}$$

The velocity operator is given by

$$v = \frac{ita}{\hbar} \sum_{j\sigma} (c^{\dagger}_{j+1\sigma} c_{j\sigma} - c^{\dagger}_{j\sigma} c_{j+1\sigma}), \tag{4}$$

where a is the lattice constant. Note that we are concerned only with charge-transfer absorption. The angular brackets in (3) represent the canonical thermodynamic average and $v(\tau)$ is in the Heisenberg representation.

To the lowest order in t/U_0 the correlation function $\phi(\omega)$ can be written in the form[5]:

$$\phi(\omega) = (1/\pi) \mathrm{Im} \langle vGv \rangle_c , \tag{5}$$

where Im indicates the imaginary part of the quantity that follows and the full Green's function is given by

$$G = \frac{1}{\hbar\omega - i0 - H} = g + gVg + \ldots , \tag{6}$$

where

$$g = \frac{1}{\hbar\omega - i0 - H_0} . \tag{7}$$

The subscript c in (5) indicates that only the connected graphs (to be defined below) are included. The thermodynamic average is taken with respect to the antiferromagnetic ground state at zero temperature and random spin configuration at high temperatures. Inserting (6) in (5) and designating the nth-order contribution in V as $\phi_n(\omega)$, the connected graphs for $\phi_n(\omega)$ represent processes wherein a particle and a hole are created by the velocity operator from states consisting of one excess electron per site, make a total of n steps by successive operations of the n transfer operators V without running into each other and then recombine at a suitable site by the other velocity operator, recovering the initial spin configuration. We are, thus, ignoring those higher-order [in $t/(U_0 - U_1)$] virtual processes with more particle-hole creations and recombinations. In the following, three spin configurations are considered: antiferromagnetic, random, and ferromagnetic configurations. The latter can be achieved by applying an external magnetic field.

To compute $\phi_n(\omega)$, assume that the particle and the hole approach each other to the neighboring sites $m+1$ times in the course of the above-described nth-order excursion. One then has, from (5) to (7),

$$\phi_n(\omega) = \frac{2N}{\pi} \mathrm{Im} \left(\frac{ta}{\hbar}\right)^2 \sum_m g_1 (g_0 t)^{n-m} (g_1 t)^m W_{n,m} . \tag{8}$$

The free Green's function g is given by $g_1 = [\hbar\omega - i0 - (U_0 - U_1)]^{-1}$ when the particle and the hole are nearest neighbors and by $g_0 = (\hbar\omega - i0 - U_0)^{-1}$ otherwise. N is the number of lattice sites and n is even. $W_{n,m}$ is the average number of such excursions. It is seen that the particle and hole attract each other with the potential energy U_1 at neighboring sites. One then expects the possibility of formation of bound states.

Define $\Omega_{n,m}$ as the average number of subclass graphs where the hole is fixed at its original site and only the particle moves. These subclass graphs contain $n/2$ forward-going steps and $n/2$ backward-going steps. One now replaces k_1 of the forward steps of the particle by backward steps of the hole, as well as k_2 of the backward steps of the particle by forward steps of the hole, the relative motion between the hole and the particle remaining the same for arbitrary k_1 and k_2. However, in this case, the final position of the hole (where the recombination occurs by the velocity operator) is at $k = k_2 - k_1$ steps away from the original site. The recombination then occurs at this final site by the other velocity operator. It is readily seen that the original spin configuration can be restored only if one has an antiferromagnetic spin arrangement from the original site of the hole (say $x = 0$) to the $(k+1)$ st site. This probability is given by

$$P(k) = p^{|k|+1} , \tag{9}$$

where $p = 1$, $p = \frac{1}{2}$ and $p = 0$, respectively, for antiferromagnetic, random, and ferromagnetic spin configurations. One then has

$$W_{n,m} = A_n \Omega_{n,m} , \tag{10}$$

where

$$A_n = \sum_{k_1=0}^{n/2} \sum_{k_2=0}^{n/2} P(k_1 - k_2) \binom{n/2 \quad n/2}{k_1 \quad k_2} , \tag{11}$$

where $\binom{n}{k} = n!/[(n-k)!\,k!\,]$. The quantity A_n has been obtained by Lyo and Gallinar[5] by using a random walk generating function and is given by

$$A_n = p \int_0^1 dx\, Q(x, p) (2x)^n , \tag{12}$$

where

$$Q(x, p) = \frac{1}{\pi(1 - x^2)^{1/2}} \frac{1 - p^2}{2p[(1+p)^2/4p - x^2]} . \tag{13}$$

Inserting (10) and (12) in (8), one obtains

$$\phi(\omega) = \frac{2N}{\pi} \left(\frac{ta}{\hbar}\right)^2 p \times \int_0^1 dx\, Q(x, p) \times \mathrm{Im} \left(\sum_{\substack{n=0 \\ n=\mathrm{even}}}^{\infty} g_1 \sum_m (g_0 t')^{n-m} (g_1 t')^m \Omega_{n,m} \right), \tag{14}$$

where $t' = 2tx$.

The quantity in the large parentheses in (14) is identical to the diagonal element of the Green's function:

$$G'(\omega) = \langle 0, 1 | \frac{1}{\hbar\omega - i0 - H_0 - H'} | 0, 1 \rangle \tag{15}$$

where $|0, 1\rangle$ designates an antiferromagnetic state vector with the hole at $x = 0$ and the particle at $x = 1$. The operator H' transfers only the particle between adjacent sites with a matrix elements given by $t' = 2tx$, while the particle-hole recombination is forbidden. The absorption is then proportional to the thermal average of the local density of particle-hole states. One can readily evaluate (15), using a forward-going self-energy summation method employed by Brinkman and Rice[8]: The Green's function $G'(\omega)$ is written as

$$G'(\omega) = \frac{1}{\hbar\omega - (U_0 - U_1) - \Sigma(\omega)} . \tag{16}$$

The self-energy $\Sigma(\omega)$ is given by (z is the coordination number, i.e., $z = 2$)

$$\Sigma(\omega) = (z-1)t'^2[g_0^{-1} - \Sigma(\omega)]^{-1} . \tag{17}$$

The factor $(z-1)$ represents the number of forward-going paths at each lattice point. Setting $4t \equiv 1$, and defining $u \equiv \hbar\omega - U_0$, one finds

$$\Sigma(\omega) = \tfrac{1}{2}[u - \mathrm{sgn}(u)(u^2 - x^2)^{1/2}] . \tag{18}$$

The line-shape function for the inter-band transition is then found from (2), (14)–(16), and (18), and is evaluated in Sec. III.

III. INTERBAND ABSORPTION

Designating the contributions from the cut $x \geq |u|$ in (18) by a superscript b, one finds from (16)

$$\mathrm{Im}\, G'^{b}(\omega) = \frac{2(x^2 - u^2)^{1/2}}{(u + 2U_1)^2 - u^2 + x^2}, \quad x \geq |u| \tag{19}$$

and

$$\sigma_R^b(\omega) = \sigma_0 \Theta(1 - |u|) \int_{|u|}^{1} \frac{Q(x, p)(x^2 - u^2)^{1/2}}{(u + 2U_1)^2 - u^2 + x^2}\, dx , \tag{20}$$

where $\Theta(x)$ is a unit step function and

$$\sigma_0 = e^2 a^2 tpN/\hbar U_0 \Omega . \tag{21}$$

The absorption band for σ_R^b extends from $\hbar\omega = (U_0 - 1)$ to $(U_0 + 1)$ and its width equals twice the hole band width. This absorption is due to the excitation of electrons into the upper Hubbard band.

An additional contribution to the absorption (to be designated by a superscript a) is obtained from a pole in the region $0 \leq x \leq -u$:

$$\mathrm{Im}\, G'^{a}(\omega) = 2\pi\delta[u + 2U_1 - (u^2 - x^2)^{1/2}], \quad x < -u \tag{22}$$

or, equivalently,

$$\mathrm{Im}\, G'^{a}(\omega) = 4\pi(u + 2U_1)\xi(u)\delta(x^2 - x_0^2) , \tag{23}$$

where

$$x_0 = [-4U_1(u + U_1)]^{1/2} \tag{24}$$

and

$$\xi(u) = \begin{cases} 1, & -2U_1 < u < -U_1 \\ 0, & \text{otherwise} \end{cases} . \tag{25}$$

Using (2), (14), (15), and (23), one finds

$$\sigma_R^a(\omega) = \frac{\pi\sigma_0}{x_0} Q(x_0, p)(u + 2U_1)\xi(u)\Theta(1 - x_0) . \tag{26}$$

This absorption arises from transitions to local particle-hole states, as is seen from the behavior $\sigma_R^a \propto \delta(u + U_1)$ in the limit $U_1 \gg 1$.

The absorption is then given by the sum of σ_R^b and σ_R^a found in (20) and (26), respectively. The integrated absorption is defined by

$$I^{a,b} = \int \sigma_R^{a,b}(\omega)\, du . \tag{27}$$

It is shown in Appendix A that the total integrated absorption satisfies a sum rule:

$$I_{\text{total}} = I^a + I^b = \tfrac{1}{2}\sigma_0\pi . \tag{28}$$

This follows also directly from (2) and (3) for a general weak long-range interaction, if one uses the relationship $\int \phi(\omega)\, d\omega = \phi(\tau = 0)/\hbar$. The integrated intensity I^a is given by (Appendix A):

$$I^a = \begin{cases} \dfrac{\sigma_0\pi}{2}\left(1 - \dfrac{p+1}{8U_1^2}\right), & U_1 \geq \tfrac{1}{2} \\ \dfrac{\sigma_0}{8U_1^2}\left[\dfrac{1-p^2}{2p}\sin^{-1}2U_1 - 2\left(\dfrac{(1+p^2)}{4p} - 4U_1^2\right)\tan^{-1}\left(\dfrac{1-p}{1+p}\,\dfrac{2U_1}{(1-4U_1^2)^{1/2}}\right)\right], & 0 \leq U_1 \leq \tfrac{1}{2} \end{cases} \tag{29}$$

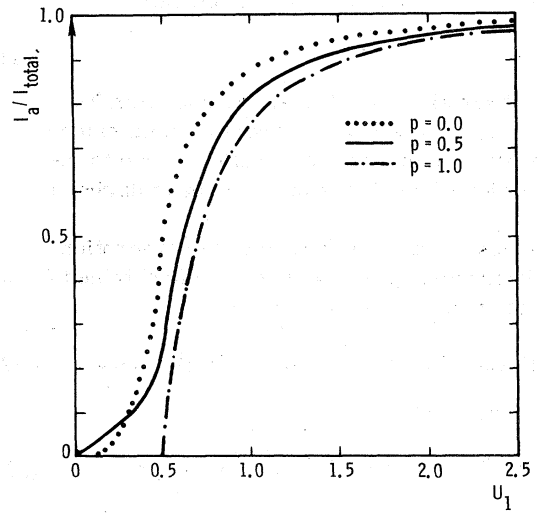

FIG. 1. Plot of the ratio I_a/I_{total} vs U_1.

It is seen from (26) and (29) that, as U_1 becomes larger (i.e., $U_1 \gg \frac{1}{2}$), the absorption band for σ_R^a splits off the absorption band of σ_R^b, takes up most of the intensity, and becomes resonant at $u = -U_1$ with a sharp width $\sim 1/4U_1$. For a small value of U_1, one has

$$I^a = \frac{4\sigma_0 U_1}{3}\left(\frac{1-p}{1+p}\right), \quad U_1 \ll \tfrac{1}{2}.$$

In Fig. 1, we plot I^a/I_{total} as a function of U_1.

For the antiferromagnetic ground state ($p=1$), I^a vanishes and no local state is formed for $U_1 < \frac{1}{2}$. Using $Q(x, 1) = \delta(1 - x - 0)$, one finds from (20) and (26),

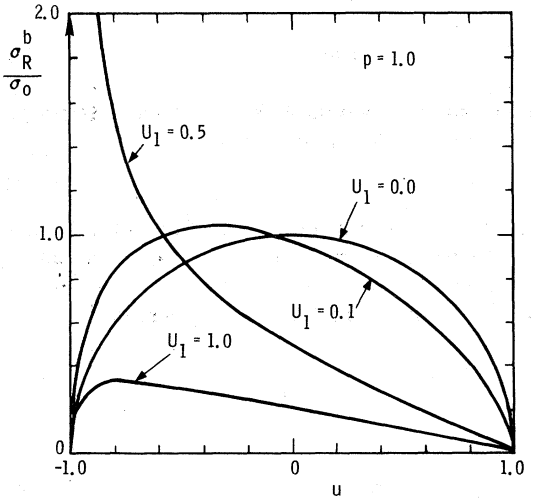

FIG. 2. Plot of the line-shape function for the antiferromagnetic ground state for several values of U_1.

$$\sigma_R^a(\omega) = \tfrac{1}{2}\pi\sigma_0[1 - 1/(2U_1)^2]\delta(u + U_1 + 1/4U_1)\Theta(U_1 - \tfrac{1}{2}), \quad p = 1 \quad (30a)$$

and

$$\sigma_R^b(\omega) = \frac{\sigma_0(1-u^2)^{1/2}\Theta(1-|u|)}{(u+2U_1)^2 - u^2 + 1}, \quad p = 1. \quad (30b)$$

At $U_1 = \frac{1}{2}$, a sharp local absorption emerges from the bottom of the absorption band of σ_R^b. In Fig. 2 the absorption line shape of σ_R^b is shown for the antiferromagnetic spin configuration for several values of U_1. For $U_1 = 0$, the line shape is symmetric with a maximum at $u = 0$. As U_1 grows, the peak moves to the left. At $U_1 = \frac{1}{2}$, the peak diverges as $(u+1)^{-1/2}$. As U_1 becomes larger than $\frac{1}{2}$, the intensity starts to leak out and the height of the peak decreases. Note that the line shape is significantly distorted even for a small value $U_1 = 0.1$.

For a random spin configuration with $U_1 = 0$, the line shape is symmetric with a logarithmic divergence[5] at $u = 0$. For a finite value of U_1, the divergence is replaced by a finite peak for σ_R^b and the line shape behaves in a similar way as in the antiferromagnetic case: With U_1 increasing, the position of the peak moves toward the bottom of the band and at $U_1 = \frac{1}{2}$ it diverges as $\sigma_R^a \propto (1+u)^{-1/2}$. The height of the peak decreases as U_1 increases further, while the intensity leaks out continually to σ_R^a-absorption. According to (26) the latter is nonvanishing only for $-(U_1 + U_m) \leq u \leq -U_1$ where U_m is the smaller of $1/4U_1$ and U_1. Note that σ_R^a diverges at its upper edge as $(u+U_1)^{-1/2}$ for all values of U_1 and as $(u + U_1 + 1/4U_1)^{-1/2}$ at its lower edge for $U_1 \geq \frac{1}{2}$.

IV. CONCLUSION

We have examined the effect of a long-range Coulomb interaction on the interband absorption in a strongly correlated half-filled Hubbard band by introducing a small ($U_1 \ll U_0$) nearest-neighbor Coulomb repulsion to the Hubbard Hamiltonian. The long-range Coulomb interaction gives rise to an effective attractive potential well between the particle and the hole. This distorts the interband absorption line shape for transitions to the upper Hubbard band and introduces additional transitions to the bound particle-hole states. With an increasing value of U_1, the intensity leaks from the former to the latter, while the total intensity is conserved. For the antiferromagnetic spin configuration, the local state is formed only when the depth of the potential well satisfies $U_1 \geq \frac{1}{2}$ and emerges below the bottom of the upper Hubbard band. In principle, one can take into account the effect of a general long-range interaction by modifying H_0

in (15) accordingly. It is found that a weak long-range interaction does not affect the total intensity of the interband absorption.

The present theory is intended as a first step toward understanding the interband absorption in some of the low-dimensional charge-transfer complex such as alkali-TCNQ[1,2] and chloranil-alkali salts, where strong electronic correlation seems to play a vital role. The effect of electronic coupling to intramolecular vibration or excitation is left out for a future study. Most of the low-dimensional systems undergo a dimerization at low temperatures. The effect of dimerization on interband absorption is under investigation by extending the present theory. A preliminary result for the antiferromagnetic ground state (with $U_1 = 0$) shows[9] that upon dimerization a main sharp (δ-function) absorption peak appears at the center of a gap (i.e., at $u = 0$) between two additional absorption bands extending from $u = \pm 2(|\tilde{t}| - |\tilde{t}'|)$ to $u = \pm 2(|\tilde{t}| + |\tilde{t}'|)$. Here $\tilde{t}$ ($\tilde{t}'$) is the intra-(inter-)dimer transfer integral. The former corresponds to transitions to intradimer bound excitonic state and the latter to extended states. The intensity of transitions to extended states is proportional to $(\tilde{t}'/\tilde{t})^2$. The total intensity changes upon dimerization by a factor $[(\tilde{t}\tilde{a})^2 + (\tilde{t}'\tilde{a}')^2]/2(ta)^2$ from the value given in (28). Here $\tilde{a}$ and $\tilde{a}'$ are intradimer and interdimer spacings, respectively. Finally, to make an order of magnitude estimate for σ_0 in (28), one finds a reasonable value[2]

$$\sigma_0 \simeq 4.86 \times 10^3 (t/U_0)(ar_0/b^2)\ (\Omega\,\mathrm{cm})^{-1}$$

for the antiferromagnetic ground state, where $r_0 = 5$ Å and ab^2 is the volume of the unit cell. a and b are measured in units of Å. In this paper we have ignored the effect of phonon broadening. The latter is expected to smear out the sharp resonances of interband transitions.

ACKNOWLEDGMENT

This work was supported in part by the U. S. Department of Energy under Contract No. AT(29-1)-789.

APPENDIX

In this appendix we evaluate I^a and I^b defined in (27) and derive the sum rule (28). Inserting (20) in (27) and changing the limits of the two-dimensional integration, we have

$$I^b = \sigma_0 \int_0^1 dx \int_{-x}^{x} du\, \frac{Q(x,p)(x^2-u^2)^{1/2}}{4U_1 u + x^2 + 4U_1^2}. \tag{A1}$$

Transforming $u = x\cos\theta$, and carrying out the θ integration, one finds

$$I^b = \sigma_0 \int_0^1 dx\, Q(x,p) x^2 f(x, U_1), \tag{A2}$$

where

$$f(x, U_1) = \begin{cases} \pi/8U_1^2, & x < 2U_1 \\ \pi/2x^2, & x > 2U_1. \end{cases} \tag{A3}$$

Hence, for $U_1 > \frac{1}{2}$,

$$I^b = \frac{\pi\sigma_0}{8U_1^2} \int_0^1 Q(x,p) x^2\, dx, \quad U_1 \geq \tfrac{1}{2}, \tag{A4}$$

which yields

$$I^b = \pi\sigma_0(1+p)/16U_1^2, \quad U_1 \geq \tfrac{1}{2}. \tag{A5}$$

On the other hand, inserting (26) in (27), one finds

$$I^a = \frac{\pi\sigma_0}{8U_1^2} \int_0^{\eta} Q(x,p)(4U_1^2 - x^2)\, dx, \tag{A6}$$

where η is the smaller of $2U_1$ and 1. Combining (A4) and (A6), and using

$$\int_0^1 Q(x,p)\, dx = 1, \tag{A7}$$

one obtains

$$I^a + I^b = \tfrac{1}{2}\pi\sigma_0, \quad U_1 \geq \tfrac{1}{2}. \tag{A8a}$$

For $U_1 \leq \frac{1}{2}$, (A2) and (A3) yield

$$I^b = \frac{\pi\sigma_0}{2} - \frac{\pi\sigma_0}{8U_1^2} \int_0^{2U_1} Q(x,p)(4U_1^2 - x^2)\, dx \tag{A9}$$

which leads, in view of (A6), to

$$I^a + I^b = \tfrac{1}{2}\pi\sigma_0, \quad U_1 \leq \tfrac{1}{2}. \tag{A8b}$$

The second part of (29) follows from a straightforward evaluation of (A6).

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