Theory of the optical conductivity of (TMTSF)$_2$PF$_6$ in the mid-infrared range

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We propose an explanation of the mid-infrared peak observed in the optical conductivity of the Bechgaard salt (TMTSF)$_2$PF$_6$ in terms of electronic excitations. It is based on a numerical calculation of the conductivity of the quarter-filled, dimerized Hubbard model. The main result is that, even for intermediate values of $U/t$ for which the charge gap is known to be very small, the first peak, and at the same time the main structure, of the optical conductivity is at an energy of the order of the dimerization gap, like in the infinite $U$ case. This surprising effect is a consequence of the optical selection rules.

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I. INTRODUCTION

It is by now well established experimentally that there is a well defined structure in the mid-infrared optical conductivity of the Bechgaard salt (TMTSF)$_2$PF$_6$. According to the most recent data of Dressel et al., this structure moves from about 1000 cm$^{-1}$ at room temperature to 200 cm$^{-1}$ at 20 K, while its intensity increases upon lowering the temperature. Given the width and the intensity of this structure, it seems difficult to explain it in terms of phonons, and the most natural thing to do it to look for an explanation in terms of electronic excitations.

It is not so easy however to understand why there should be an absorption due to electronic transitions in that energy range. To see that, let us consider the simplest description of the Bechgaard salt that contains the essential physics, namely the quarter-filled, dimerized Hubbard model described by the following Hamiltonian:

$$
H = -t_1 \sum_{i \text{ even}, \sigma} (c_{i+1\sigma}^\dagger c_{i\sigma} + \text{h.c.})
- t_2 \sum_{i \text{ odd}, \sigma} (c_{i+1\sigma}^\dagger c_{i\sigma} + \text{h.c.}) + U \sum_i n_{i\uparrow} n_{i\downarrow}
$$

(1)

where $c_{i\sigma}^\dagger, c_{i\sigma}$ create and annihilate holes in the HOMO of the TMTSF molecules. For (TMTSF)$_2$PF$_6$, reasonable parameters are $t_1=250$ meV, $t_2/t_1=9$ and $U/t_1=5$. Note that a Luttinger liquid description would not be of much use here given the energy range we are interested in.

Now, let us see which electronic transitions could be present in such a model. If the interactions are ignored, the only allowed transitions are the vertical transitions from the lower band to the upper band. They give rise to a continuum starting at $\Delta_D \equiv 2\sqrt{t_1^2 + t_2^2} \approx 670$ meV, which is roughly one order of magnitude too large. Including $U$ and assuming that $U/t_1=5$ will induce transitions at energy $U \approx 1.25$ eV, which is even larger. In fact there is only one characteristic energy scale that has the right order of magnitude, namely the dimerization gap $\Delta_D = 2(t_1 - t_2) = 50$ meV. This led Pedron et al. to assume that the double occupancy of a site must be excluded, or equivalently that $U$ is infinite. Then the charge carriers can be described as a half-filled system of spinless fermions, in which case the vertical transition has an energy of $\Delta_D$. There is a problem however with that explanation. If $U$ is infinite, then we know that the charge gap $\Delta_D$ is equal to the dimerization gap $\Delta_D$. But such a large charge gap is inconsistent with the experimental fact that the conductivity remains metallic down to very low temperatures. In fact, the metallic character of the conductivity puts an upper bound on the charge gap which is consistent with the above-mentioned parameters.

In this paper, we show that the structure observed in the optical conductivity is actually consistent with the model of Eq. (1) with $t_1=250$ meV, $t_2/t_1=9$ and $U/t_1=5$. The main point is that the charge excitations with energy around $\Delta_D$ responsible for the metallic conductivity cannot be seen in the optical conductivity because of the optical selection rules. The first allowed transition occurs at an energy of the order of the dimerization gap $\Delta_D$, which is much larger than $\Delta_D$ for these values of the parameters.

The paper is organized as follows. In section II, we first discuss the general properties of the optical conductivity in the model of Eq. (1). In section III, we describe the numerical method and we derive the form of the finite-size corrections we can expect for the position of the first peak of the optical conductivity. In sections IV and V, we present the results for large and small dimerization respectively. Finally, a discussion of the results in connection to (TMTSF)$_2$PF$_6$ is given in section VI.
II. GENERAL PROPERTIES OF THE CONDUCTIVITY

Let us start with a qualitative description of the optical conductivity in various cases of the Hamiltonian of Eq. (1) at quarter-filling. They are illustrated in Fig. 1.

a) Non-interacting electrons on a non-dimerized lattice ($U=0$, $t_2=t_1$): In that trivial limit, the only contribution is of course the zero frequency Drude peak.

b) Interacting electrons on a non-dimerized lattice ($U \neq 0$, $t_2=t_1$): There is still a Drude peak because the system remains metallic, but there is also some incoherent spectral weight around $\omega = U$.

c) Non-interacting electrons on a dimerized lattice ($U=0$, $t_2 \neq t_1$): The dimerization splits the dispersion into 2 bands with the equation:

$$E(k) = \pm \sqrt{t_1^2 + t_2^2 + 2t_1t_2 \cos(2ka)}$$

(2)

where $2a$ is the lattice parameter. The conductivity exhibits a Drude peak since the system is metallic, and a continuum between $\Delta$ and $2(t_1 + t_2)$ due to vertical interband transitions. See Fig. 2.

d) Interacting electrons on a dimerized lattice ($U \neq 0$, $t_2 \neq t_1$): In that case the repulsion opens a gap because the lower band is effectively half-filled. So the system becomes insulating and the Drude peak disappears. Now the incoherent and Drude weight are related by the sum-rule

$$\int_0^{\infty} \sigma(\omega) d\omega = \frac{\pi e^2}{2L} < T >$$

(3)

where $< T > /L$ is the expectation value of the kinetic energy per-site in the ground state. This quantity is not dramatically reduced by the interaction $U$, and the lost Drude weight must be redistributed as an incoherent, low energy background. Part of the weight can also migrate to the upper Hubbard band at an energy of order $U$.

If $U$ is very large, the low energy, incoherent weight must be located around $\Delta_D$ to become the zone-boundary interband transition of spinless fermions in the $U = +\infty$ limit described by Pedron et al [2]. In the following our main goal is to determine whether for realistic parameters, i.e. for intermediate values of $U/t_1$, there is still a dominant low energy structure in the conductivity, and where it is located.

III. THE NUMERICAL METHOD

Our aim is to calculate the optical conductivity of the model at zero temperature. Starting from its definition as the current-current correlation function, the real part of the conductivity can also be written:

$$\sigma(\omega) = D\delta(\omega) + \frac{\pi e^2}{L} \sum_{n \neq 0} \frac{|\langle \psi_0 | \hat{j} | \psi_n \rangle|^2}{E_n - E_0} \delta(\omega - E_n + E_0)$$

In this formula, $E_0$ is the ground state energy, $n$ labels the excited states and $j$ is the paramagnetic current operator. The weight of the Drude peak $D$ is calculated from the Kohn relation [3] [11]:

$$D = \frac{\pi}{L} \frac{\partial^2 E_0}{\partial \phi^2} |_{\phi=0}$$

(4)

where $E_0(\phi)$ is the ground state energy as a function of the twist in the boundary conditions, while the incoherent part can be obtained as a continued fraction using Lanczos algorithm [4]. Extensive calculations of that sort have been performed for 2D models in the context of high $T_c$ superconductors [3].

We have performed exact diagonalizations on finite size clusters with $L = 8, 12, 16, 20$ sites. To reach the thermodynamic limit ($L = +\infty$) we have tried to perform a finite-size scaling of the results. The finite size corrections turn out to be very large concerning the location $\Omega$ of the first peak in the conductivity for the following reasons: In the infinite $U$ limit, the charge and spin variables are decoupled (see Ogata and Shiba [2]). The charge part is that of spinless fermions with twisted boundary conditions and this twist is given by the momentum of the spin part. Now, for $U = +\infty$ there is no energy associated to spin excitations, and the spinless fermions are free to choose the boundary conditions that minimize this energy, namely antiperiodic boundary conditions. In that case, the allowed values of the momentum are given by $k = (2\nu + 1)\pi/La$ (see Fig. 2). The zone boundary $k = \pi/2a$ does not belong to the allowed momenta and the larger occupied $k$ is at $\pi/2a - \pi/La$. So the first peak in the conductivity is located at

$$\Omega = \Delta_D(L) = \sqrt{t_1^2 + t_2^2 + 2t_1t_2 \cos(\pi - 2\pi/L)}$$

(5)

In other words, there is a finite-size correction to the known result $\Omega = \Delta_D$ in the thermodynamic limit. In the case of large but finite $U$, the spin energy is still negligible compared to that of the charge degrees of freedom, and the charge part keeps the same boundary conditions. This suggests that the finite-size corrections to $\Omega$ will scale according to $\cos(\pi - 2\pi/L)$. We shall see that this scaling form is actually remarkably accurate down to rather small values of $U/t_1$.

IV. LARGE DIMERIZATION

For clarity, let us start with a case where all the important features of the conductivity can be best seen in spite of the limitations due to the finite size of the clusters. In units of $t_1$ we choose $t_2 = 0.5$ and study various repulsions. On Fig. 3 we show the influence of the cluster size on the incoherent spectrum for a given repulsion. This incoherent part exhibits a sharp peak which is shifted toward low frequencies when the size increases, while its relative weight is more or less constant. Figure 4 shows...
the effect of the repulsion ($U/t_1$ change from 0 to 10) for $L=16$. The main peak increases with size and approaches $\Delta_D(L)$ for large $U$ as expected.

Because of the dimerization, the lower band is half filled and the repulsion induces an insulating behavior in the thermodynamic limit. So the Drude weight given by Eq. (5), which does not vanish for finite systems, should scale to zero upon increasing the size of the cluster. Our numerical results are effectively consistent with a vanishing Drude weight in the thermodynamic limit, although the finite size scaling function is not very clear (see Fig 5).

We have also checked the sum-rule of Eq. (3). The finite range of integration could bring problems in practical computations, but in the case of quarter–filled systems, there is essentially no weight at high frequencies [13,14] and one can safely stop the integration at $\omega = 2U$. In all cases we found that the sum–rule was satisfied with an accuracy better than 1%.

In order to show that the incoherent conductivity exhibits a well defined structure at low energy, we have calculated the relative weight of the first peak with respect to the total incoherent part. The results are given in Table I. This proportion is insensitive to the size and increases with the repulsion. This suggests that the first peak will dominate the incoherent part in the thermodynamic limit, even for intermediate repulsions.

To find the location $\Omega$ of this peak, we have tried several finite–size scaling. The only way to obtain a good scaling is to plot $\Omega^2$ versus $\cos(\pi - 2\pi/L)$. Some results are presented in Fig. 3. The extrapolated values are given in Table II. In the present case, the location of the first peak roughly follows the charge gap $\Delta_\rho$, which is relatively large for this value of the dimerization.

V. SMALL DIMERIZATION

We now turn to a smaller dimerization, namely $t_2 = 0.9t_1$, having in mind intermediate repulsions $U \simeq 5t_1$. The incoherent conductivity $\sigma_{\text{inc}}$ calculated for $L=20$ is shown in Fig. 2. As in the previous case $\sigma_{\text{inc}}$ is still dominated by its first peak. The relative importance of this peak increases from 34.3% on 8 sites to 53.1% on 20 sites.

In the present case $\sigma_{\text{inc}}$ represents a rather small part of the oscillator strength (from 2% for 8 sites to 4.5% for 20 sites). Because of the weak dimerization, the charge gap is small ($\Delta_\rho = 0.02t_1$), and the corresponding length $v_F/\Delta_\rho$ is much larger than the sizes we can reach. So the Drude peak takes almost all the oscillator strength in our simulation. But this peak will certainly disappear in the thermodynamic limit since the system is insulating. So what really matters is whether the relative weight of the first peak be sizable, which it is.

Concerning the location of the first peak, we found that scaling $\Omega^2$ with $\cos(\pi - 2\pi/L)$ was still very accurate and for $U = 5t_1$ this scaling leads $\Omega/t_1 = 0.17$ in the thermodynamic limit. Now, for $t_2 = .9t_1$ and $U = 5t_1$, the charge gap $\Delta_\rho$ equals 0.02 and the dimerization gap $\Delta_D$ equals 0.2. So we found that the first peak appears at an energy which is of the order of the magnitude of the dimerization gap, and that there is no weight at energies corresponding to the charge gap. How can we understand this result? If the charge gap is identified to the lowest excitation of the system which leaves the total spin $S$ unchanged, the difference between $\Omega$ and $\Delta_\rho$ should be directly observable on the excitation spectrum. Such a spectrum is plotted in Fig. 3. The lowest charge excitation occurs at the border of the Brillouin zone, while $\Omega(L)$ corresponds to a vertical excitation keeping $S=0$. Besides, the first singlet state coupled to the groundstate by the current operator is not the lowest $S=0$ excited state but the third one [16]. This is presumably due to the fact that the current operator being odd under the inversion, only odd states can be coupled to the groundstate, which is even. $\Omega(L)$ and $\Delta_\rho$ are thus clearly different for $L$ finite. Besides, they have very different scalings: On one hand $\Delta_\rho$ goes to a very small value like $1/L$ as shown on Fig 3. The exact value 0.02 provided by a perturbative calculation can actually not be identified by such a scaling. On the other hand, $\Omega(L)^2$ scales as $\cos(\pi - 2\pi/L)$ toward 0.17.

So our results indicate that the first peak of the optical conductivity is located at an energy much larger than the charge gap. We cannot exclude that, upon increasing the size, other states will appear that have the right symmetry to be coupled to the groundstate by the current operator. Such states could for instance involve several excitations of momentum $\pi$ and of energy of order $\Delta_\rho$ leading to a small threshold at $2\Delta_\rho$ in the optical conductivity. But according to the increase with $L$ of the relative weight of the first peak (from 34.3% for 8 sites to 53.1% for 20 sites), the feature at $\Omega \simeq 0.17t_1$ should in any case remain the prominent structure of the conductivity in the thermodynamic limit. Finally, the difference with the case treated in the previous section presumably comes from the fact that the excitations have very little dispersion when the dimerization is large because the bands are flat.

So it seems that the explanation proposed by Pedron et al [2] is essentially valid: For intermediate values of $U/t_1$ and small dimerization, the conductivity has a large peak around the dimerization gap $\Delta_D$ although the charge gap is very small.

VI. DISCUSSION

In conclusion, we have shown that the model of Eq. (1) with reasonable parameters leads to a peak in the optical conductivity at an energy of about 0.17$t_1 \simeq 40$ meV. This energy has the right order of magnitude. So this provides a good candidate to explain the mid-infrared...
structure observed in the Bechgaard salt (TMTSF)$_2$PF$_6$. What about the fine details of this mid-infrared structure? As stated in the Introduction, this peak moves toward lower energies when the temperature is decreased, and its weight increases. Both features are actually quite natural consequences of the present explanation.

Let us first consider the fact that the peak moves to lower energies when the temperature is lowered. The Hamiltonian of Eq. (1), which is purely 1D, is not an accurate description of the electronic structure of the Bechgaard salts at low temperatures where 2D effects start to dominate. Looking at the actual 2D band structure calculated on the basis of the structure deduced from X-Ray measurements performed at 300 K and 4 K, one can see that there is a clear evolution leading to a much smaller dimerization gap at low temperatures. Whether this gap still yields a structure in the optical conductivity when the system must be considered as 2D cannot be concluded on the basis of the present calculation and should be checked independently, but it seems likely that the structure we have calculated will move smoothly to lower energies.

Concerning the intensity, the data of Dressel et al. [3] suggest that the increase of weight of that structure upon lowering the temperature is accompanied by a decrease of the weight of the background, which can be interpreted as a broadened Drude peak. Although the model we are looking at is insulating at zero temperature, we expect a lowering the temperature is accompanied by a decrease of ρ at low energies.

TABLE I. Relative weight of the first peak in the incoherent part, with boundary conditions ensuring a non-degenerate ground state.

TABLE II. Comparison between the charge gap and the dimerization gap. (1) Vertical transition in the non interacting case at ω = Δ0. (2) Finite size dimerization gap ΔD (L = 16). (3) Dimerization gap. The circles (resp. triangles) are the allowed wave vectors for L=16 and periodic (resp. antiperiodic) boundary conditions.

FIG. 1. Schematic picture showing the influence of the repulsion and of the dimerization on the structure of the conductivity. ΔD = 2(t1 - t2) and Δ0 = 2√t1 + t2. Fig. (d) is typical of large values of U. For clarity, the Δ0 peaks of the incoherent part of the conductivity have been broadened.

FIG. 2. Dispersion in the non-interacting case with dimerization. (1) Vertical transition in the non interacting case at ω = Δ0. (2) Finite size dimerization gap ΔD (L = 16). (3) Dimerization gap. The circles (resp. triangles) are the allowed wave vectors for L=16 and periodic (resp. antiperiodic) boundary conditions.

FIG. 3. Evolution of the optical conductivity with the size of the cluster, for t2 = 0.5t1, U = 5t1 and ϵ = 0.05t1 (width of the δ function).

FIG. 4. Evolution of the optical conductivity with the on site repulsion U for t2 = 0.5t1, L = 16 and ϵ = 0.05t1 (width of the δ function).

FIG. 5. Finite size scaling of the relative weight of the Drude peak (D(L)/(πe^2 < -T > /L)) for t2 = 0.5t1.
FIG. 6. Finite size scaling of the square of the frequency \( \Omega(L) \) (in units of \( t_1 \)) of the first peak of the incoherent conductivity.

FIG. 7. The optical conductivity for \( t_2 = 0.9t_1, U = 5t_1, L = 20 \) and \( \epsilon = 0.05t_1 \) (width of the \( \delta \) function).

FIG. 8. The first excitations versus the impulsion for \( t_2 = 0.9, U = 5, L = 20 \). The impulsion \( k \) is related to \( \nu \) by \( k = -\pi/L + 2\pi\nu/L \) because of antiperiodic boundary conditions. The circles (resp. triangles) represent states with a total spin \( S=0 \) (resp. \( S \neq 0 \)). (1) First excitation coupled to the ground state by the current operator. (2) First singlet excitation.

FIG. 9. Finite size scaling of the lowest charge excitation for \( t_2 = 0.9 \) and \( U = 5 \).

| \( U = 2.5 \) | \( U = 5 \) | \( U = 10 \) |
|---|---|---|
| \( L = 8 \) | 46.8% | 69.3% | 75.2% |
| \( L = 12 \) | 49.6% | 67.3% | 74.6% |
| \( L = 16 \) | 51.5% | 64.3% | 68.2% |

| \( U = 2.5 \) | \( U = 5 \) | \( U = 10 \) |
|---|---|---|
| \( \Omega \) | 0.22t_1 | 0.50t_1 | 0.74t_1 |
| \( \Delta_{\rho} \) | 0.2t_1 | 0.45t_1 | 0.7t_1 |
\[ \sigma(\omega) \]

(a) \[ U=0 \quad t_1=t_2 \]

(b) \[ U\neq0 \quad t_1=t_2 \]

(c) \[ U=0 \quad t_1\neq t_2 \]

(d) \[ U\neq0 \quad t_1\neq t_2 \]

\[ \Delta_0 \]

\[ \omega = 2(t_1 + t_2) \]

\[ \Delta_0 \]

\[ \omega \]

\[ \Delta_0 \]

\[ U \]

\[ \Delta_0 \]

\[ U \]

\[ t_1 + t_2 \]

\[ t_1 - t_2 \]

\[ E(k) = \frac{k}{a} \]

\[ k_f = \frac{\pi}{2a} \]

[Graph showing dispersion relation with points labeled (1), (2), and (3).]
