Anomalous temperature dependence of the single-particle spectrum in the organic conductor TTF-TCNQ

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The angle-resolved photoemission spectrum of the organic conductor TTF-TCNQ exhibits an unusual transfer of spectral weight over a wide energy range for temperatures 60K < T < 260K. In order to investigate the origin of this finding, here we report numerical results on the single-particle spectral weight \( A(k, \omega) \) for the one-dimensional (1D) Hubbard model and, in addition, for the 1D extended Hubbard and the 1D Hubbard-Holstein models. Comparisons with the photoemission data suggest that the 1D Hubbard model is not sufficient for explaining the unusual \( T \) dependence, and the long-range part of the Coulomb repulsion also needs to be included.

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The low-dimensional interacting systems receive attention because of their unusual electronic properties. In this respect, the high-resolution Angle-Resolved Photoemission Spectroscopy (ARPES) measurements on the quasi-one-dimensional organic conductor tetrathiofulvalene-tetracyanoquinodimethan (TTF-TCNQ) have provided evidence for non-Fermi liquid behavior in this compound. In particular, the ARPES experiments have found that the single-particle spectral weight at the Fermi wavevector \( k_F \) is transferred over an energy range of \( \approx 1.3eV \) of the Fermi level in the TCNQ-derived band, as the temperature \( T \) decreases from 260K to 60K. In a Fermi liquid the spectral-weight transfer would have occurred within \( \sim k_BT \) of the Fermi level. Here, we investigate the origin of this unusual ARPES data and its meaning for the electronic structure of TTF-TCNQ by using the Dynamical Density Matrix Renormalization Group (DDMRG), Quantum Monte Carlo (QMC) and the exact diagonalization methods.

There are various possibilities as to what might be the origin of the anomalous \( T \) dependence of the single-particle spectral weight at the Fermi level, \( A(k_F, \omega) \), in TTF-TCNQ: (i) It has been suggested that the \( T \)-dependence of the ARPES data can be explained within the one-dimensional (1D) Hubbard model. In this case, the anomalous \( T \)-dependence of \( A(k_F, \omega) \) over the conduction bandwidth has been attributed to the strong-correlation effects. Indeed, by using the Bethe-Ansatz solution, the photoemission spectrum has been fitted excellently to the dispersion of the spinon and holon bands of the 1D Hubbard model with the parameters \( t = 0.4eV \) for the hopping matrix element and \( U = 2eV \) for the Coulomb repulsion. The recent observation of the 3\( k_F \) structures in \( A(k, \omega) \) by the ARPES also supports this picture. (ii) An alternative point of view is that an extended Hubbard model with long-range Coulomb repulsion is necessary, particularly because the screening of the long-range Coulomb repulsion is expected to be weaker for the surface layer of TTF-TCNQ. (iii) Another possibility is that the electron-phonon interaction, in addition to the strong Coulomb repulsion, plays a role in producing the unusual \( T \) dependence. In this paper, our goal is to differentiate among these possibilities. For this purpose, we present DDMRG and finite-temperature QMC results on \( A(k_F, \omega) \) of the 1D Hubbard model. In addition, we present exact-diagonalization results for the 1D extended Hubbard model which includes a near-neighbor repulsion \( V \) and DDMRG results for the 1D Hubbard-Holstein model.

In the following, we show that, above a characteristic temperature determined by the effective magnetic exchange \( J_{eff} \), spectral-weight transfer takes place over a wide energy range in the 1D Hubbard model. This is similar to the \( T \) dependence observed in the ARPES experiments. However, below this temperature, the weight transfer is negligible. We find that the Hubbard parameters \( t = 0.4eV \) and \( U = 2eV \) give too large a value for \( J_{eff} \), and with these parameters it is not possible to explain the ARPES \( T \) dependence. On the other hand, the \( T = 0 \) exact-diagonalization results on the 1D extended Hubbard model show that the nearest-neighbor Coulomb repulsion increases the bandwidth of the spinon and the holon excitations. This can lead to a smaller value for \( t \) for fitting the ARPES dispersions, and a reduced value for \( J_{eff} \), hence, giving better agreement with the ARPES data. In addition, the DDMRG results on the Hubbard-Holstein model show that, at \( T = 0 \), the electron-phonon interaction influences \( A(k_F, \omega) \) only at \( |\omega| \ll 1.3eV \) for physical values of the phonon frequency \( \omega_Q \). However, it remains to be seen how the electron-phonon interaction influences \( A(k, \omega) \) at finite \( T \). The main finding of this paper is that the 1D Hubbard model is not sufficient for explaining simultaneously the \( T \) dependence and the dispersion of the photoemission spectrum of TTF-TCNQ. We suggest that it is necessary to include at least the
long-range part of the Coulomb repulsion. We will consider the case of electron-filling $\langle n \rangle = 0.60$, since the filling of the TCNQ band is 0.59. We note that $A(k, \omega)$ of the 1D Hubbard model was studied with the QMC [3, 4] and the DDMRG [6, 10] as well as with the Bethe ansatz [11].

Within the DDMRG method, the single-particle spectral weight is obtained at $T = 0$ from

$$A(k, \omega) = -\frac{1}{\pi} \text{Im} \left\langle 0 \left| c_{k,\uparrow}^{\dagger} \frac{1}{E_0 - \omega - i\gamma} c_{k,\uparrow} \right| 0 \right\rangle$$

where $c_{k,\uparrow}$ annihilates an electron with wavevector $k$ and spin $\uparrow$, $|0\rangle$ and $E_0$ are the ground state and the eigenenergy, respectively, and $\gamma$ is a small positive number. The DDMRG results were obtained with the open boundary conditions. At finite temperatures, we obtain $A(k, \omega)$ by using the determinantal QMC technique [12]. This method yields the single-particle Green’s function along the Matsubara time axis, from which $A(k, \omega)$ is obtained by the maximum-entropy analytic continuation [13]. We have checked the convergence of the maximum-entropy results as the statistics of the QMC data improved. In the following, $A(k, \omega)$ will be plotted in units of $t^{-1}$. In order to determine the characteristic temperature of the magnetic correlations, we present QMC data on the uniform magnetic susceptibility $\chi(q \to 0)$ where

$$\chi(q) = \int_0^\beta d\tau \sum_\ell e^{-i\alpha\ell} \langle m^z_{i+\ell}(\tau)m^z_i(0) \rangle$$

with $m^z_i = n_{i,\uparrow} - n_{i,\downarrow}$.

We also present exact-diagonalization results on $A(k, \omega)$ for the 1D extended Hubbard model,

$$H_{ext} = H_0 + V \sum_i n_i n_{i+1}$$

where $V$ is the nearest-neighbor Coulomb repulsion. The $A(k, \omega)$ of the 1D extended Hubbard model was previously studied with the exact diagonalization technique [14]. In addition, we present DDMRG results on $A(k_F, \omega)$ of the Hubbard-Holstein model defined by

$$H_{HH} = H_0 + \omega_0 \sum_i b_i^{\dagger} b_i + g \sum_i (b_i^{\dagger} + b_i) n_i$$

where $b_i^{\dagger}$ (b_i) is the creation (annihilation) operator for a dispersionless phonon at site $i$, $\omega_0$ is the phonon frequency, and $g$ is the electron-phonon coupling constant.

We first discuss DDMRG and QMC results on the 1D Hubbard model. Figures 1(a) and (b) show the $T$ dependence of $A(k_F, \omega)$ for $U = 5t$ and $8t$. The DDMRG results were obtained for a 60-site chain with 36 electrons, while the QMC results are for a 32-site ring with $\langle n \rangle = 0.60$. In the DDMRG calculations we have used a finite energy broadening $\gamma = 0.05t$. For $U = 5t$, we observe that the spectral-weight transfer occurs over an energy range $\approx 2t$ of the Fermi level, as $T$ decreases from $0.5t$ down to $0.125t$. However, the weight transfer is negligible between $T = 0.125t$ and $T = 0$. For $t \approx 400meV$, $T = 0.125t$ corresponds to $\approx 600K$. Hence, in this case, the amount of spectral-weight transfer between $T = 600K$ and $T = 0K$ is negligible, which disagrees with the ARPES results. In order to study the dependence on $U/t$, in Fig. 1(b) we show results for $U = 8t$. Comparison of Figs. 1(a) and (b) shows that the transfer of weight at low $T$ is enhanced for $U = 8t$ with respect to $U = 5t$.
with decreasing $T$. The transfer of intensity is also observable as $T$ decreases from the room temperature down to the CDW transition temperature $T_{CDW} = 53 K$ [16, 17].

The density-functional-theory calculations deduce that the hopping parameter $t = 0.175 eV$ for bulk TTF-TCNQ, while the analysis of the ARPES data yields the Hubbard parameters $t = 0.4 eV$ and $U = 5 t$ [4]. This enhancement of $t$ for the surface layer has been attributed to a possible tilting of the TCNQ and TTF molecules at the surface. In this paper, we have seen that the parameters $t = 0.4 eV$ and $U = 2 eV$ give $J_{eff} \approx 1600 K$, which is too high to explain the $T$ dependence of $A(k, \omega)$. At this point, we suggest that the long-range part of the Coulomb repulsion might play an important role. For demonstration, we present exact-diagonalization results on $A(k, \omega)$ for the 1D extended Hubbard model with $U = 2 eV$. Figure 3 compares $A(k, \omega)$ obtained for $t = 0.25 eV$ and $V = 0.5 eV$ with that for $t = 0.4 eV$ and $V = 0$ at wavevectors $k = 0$ and $k = \pi/4$. For the 16-site lattice, $k = \pi/4$ is the closest wavevector to $k_F$. We observe that, at $k = 0$ and for $t = 0.4 eV$ and $V = 0$, the holon and spinon branches are located at $\approx -0.68 eV$ and $\approx -0.27 eV$, respectively. For parameters $t = 0.25 eV$ and $V = 0.5 eV$, these structures are located at similar energies. Hence, it is possible to reproduce the locations of the spinon and holon branches by using a reduced value for $t$ within the 1D extended Hubbard model. This behavior is also observed at $k = \pi/4$. Figure 3 also shows that $V$ induces incoherent spectral weight at higher $|\omega|$. For the 1D extended Hubbard model, we expect $J_{eff} \propto 4t^2/(U - V)$. These results suggest that taking into account the long-range part of the Coulomb repulsion in fitting the ARPES dispersion can lead to a reduced $t$ and, hence, might reduce $J_{eff}$ and the characteristic temperature for the single-particle weight transfer. However, it is necessary to calculate $A(k, \omega)$ for the

FIG. 2: (color online) Temperature dependence of the uniform magnetic susceptibility $\chi(q \rightarrow 0)$, plotted in units of $t^{-1}$, for the 1D Hubbard model. We use these data to determine the effective magnetic exchange.

FIG. 3: (color online) Exact-diagonalization results on the single-particle spectral weight $A(k, \omega)$ at $k = 0$ and $k = \pi/4$ for the 1D extended Hubbard model which has onsite and nearest-neighbor Coulomb repulsions $U$ and $V$, respectively. These calculations were performed for $U = 2 eV$ on a 16-site ring with 10 electrons corresponding to $\langle n \rangle = 0.625$. Here, spectra obtained for $t = 0.25 eV$ and $V = 0.5 eV$ are compared with that for $t = 0.4 eV$ and $V = 0$. The density-functional-theory calculations deduce that the hopping parameter $t = 0.175 eV$ for bulk TTF-TCNQ, while the analysis of the ARPES data yields the Hubbard parameters $t = 0.4 eV$ and $U = 5 t$ [4]. This enhancement of $t$ for the surface layer has been attributed to a possible tilting of the TCNQ and TTF molecules at the surface. In this paper, we have seen that the parameters $t = 0.4 eV$ and $U = 2 eV$ give $J_{eff} \approx 1600 K$, which is too high to explain the $T$ dependence of $A(k, \omega)$. At this point, we suggest that the long-range part of the Coulomb repulsion might play an important role. For demonstration, we present exact-diagonalization results on $A(k, \omega)$ for the 1D extended Hubbard model with $U = 2 eV$. Figure 3 compares $A(k, \omega)$ obtained for $t = 0.25 eV$ and $V = 0.5 eV$ with that for $t = 0.4 eV$ and $V = 0$ at wavevectors $k = 0$ and $k = \pi/4$. For the 16-site lattice, $k = \pi/4$ is the closest wavevector to $k_F$. We observe that, at $k = 0$ and for $t = 0.4 eV$ and $V = 0$, the holon and spinon branches are located at $\approx -0.68 eV$ and $\approx -0.27 eV$, respectively. For parameters $t = 0.25 eV$ and $V = 0.5 eV$, these structures are located at similar energies. Hence, it is possible to reproduce the locations of the spinon and holon branches by using a reduced value for $t$ within the 1D extended Hubbard model. This behavior is also observed at $k = \pi/4$. Figure 3 also shows that $V$ induces incoherent spectral weight at higher $|\omega|$. For the 1D extended Hubbard model, we expect $J_{eff} \propto 4t^2/(U - V)$. These results suggest that taking into account the long-range part of the Coulomb repulsion in fitting the ARPES dispersion can lead to a reduced $t$ and, hence, might reduce $J_{eff}$ and the characteristic temperature for the single-particle weight transfer. However, it is necessary to calculate $A(k, \omega)$ for the
In summary, we have studied $A(k, \omega)$ of the 1D Hubbard model in order to investigate the unusual $T$ dependence of the photoemission intensity of TTF-TCNQ. We have also presented $T = 0$ results for the 1D extended Hubbard and the 1D Hubbard-Holstein models. We find that in the 1D Hubbard model the transfer of the single-particle spectral weight takes place over a wide energy range above a characteristic temperature, which is too high to explain the ARPES data. We have shown that the long-range part of the Coulomb repulsion can lead to a reduced value for $J_{\text{eff}}$ and, hence, to a better agreement with the ARPES data. Our results on the Hubbard-Holstein model show that, at $T = 0$, the electron-phonon interaction does not influence $A(k_F, \omega)$ over the wide energy range observed by the ARPES. In conclusion, these calculations give theoretical support to the notion that the anomalous $T$ dependence of the photoemission spectrum of TTF-TCNQ is due to the strong-correlation effects as suggested by Claessen et al. However, we also emphasize that the 1D Hubbard model is not sufficient for explaining the unusual $T$ dependence, and at least the long-range part of the Coulomb repulsion needs to be included.

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