

Charged excitons in doped extended Hubbard model systems

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Abstract. – We show that the charge transfer excitons in a Hubbard model system including nearest-neighbor Coulomb interactions effectively attain some charge in doped systems and become visible in photoelectron and inverse photoelectron spectroscopies. This shows that the description of a doped system by an extended Hubbard model differs substantially from that of a simple Hubbard model. Longer-range Coulomb interactions cause satellites in the one-electron removal and addition spectra and the appearance of spectral weight in the gap of doped systems at energies corresponding to the excitons of the undoped systems. The spectral weight of the satellites is proportional to the doping times the coordination number and therefore is strongly dependent on the dimension.

The possible importance of nearest-neighbor Coulomb interactions in the description of strongly correlated systems like the $3d$ transition metal oxides, low-dimensional organic charge transfer salts as well as solid C_{60} has been emphasized in a number of studies [1]-[6]. Although it is clear that a nearest-neighbor Coulomb interaction will not reduce the gap for charged excitations in a half-filled Hubbard system with an on-site interaction larger than the one-electron bandwidth, as we recently showed [7], it has also been emphasized by Varma [8] that such interactions may be very important in describing doped systems like the high- T_c superconductors. In undoped half-filled Hubbard models nearest-neighbor Coulomb interactions introduce local charge-conserving excitonic states at energies below the charged excitation conductivity gap which are visible in optical spectroscopies. These states are not visible in one-electron removal or addition spectroscopies since they do not carry a charge. The presence of such states is important, however, since they enhance the nearest-neighbor superexchange interactions which involve virtual excitations of which the lowest in energy will be these excitonic states [9]. The situation is quite different in doped systems. For example, in a hole-doped otherwise half-filled system there will be electron addition states corresponding to adding an electron to an already occupied site with a hole in the nearest-neighbor site. Such a state will be at an energy corresponding to that of the exciton in the undoped system. In fact for higher doping there is even the possibility of adding an electron to an atom which has more than one hole on neighboring sites providing even lower-energy electron addition states because of the

nearest-neighbor Coulomb interactions. The spectral weight for these states in the electron addition spectrum appearing inside the original Hubbard gap will be stolen from the upper Hubbard band. This effect will cause the upper Hubbard band to collapse in intensity while moving up in energy even more rapidly than in a doped Hubbard system. In other words the spectral weight transfer from the high to the lower energy scales in the electron addition spectrum will be even more dramatic than that discussed for a Hubbard system by Eskes *et al.* [10].

The physical picture of what happens in the zero bandwidth limit is shown in fig. 1, taking U as the on-site energy and V as the nearest-neighbor electron repulsion. This picture also clearly shows where the spectral weight in the gap is coming from. It is interesting to note that for V close to the spin density wave to charge density wave transition value ($V_c = U/2$ in $1d$) the electron addition states corresponding to $U - 2V$ will be close to energy zero and will contribute to the low-energy scale physics. This particular electron addition state corresponds to a state with one hole in an otherwise half-filled Hubbard system accompanied by a nearest-neighbor electron hole excitation and bound to it. This is an oversimplified picture of a possible 3-particle resonance if V is large enough as envisaged by Varma *et al.* [1] for the high T_c 's. In this paper we want to give this very simple picture some theoretical justification with model calculations including also a finite bandwidth. We will also look at the influence of finite temperature and will study the consequences for the photoelectron spectrum of a system like off-stoichiometric K_3C_{60} .

To study this we use the Hamiltonian for the, orbitally non degenerate, extended Hubbard model given by

$$H = -t \sum_{\langle ij \rangle, \sigma} (c_{i\sigma}^\dagger c_{j\sigma} + \text{h.c.}) + U \sum_i n_{i\uparrow} n_{i\downarrow} + V \sum_{\substack{\langle ij \rangle \\ \sigma, \sigma'}} n_{i\sigma} n_{j\sigma'}, \quad (1)$$

where $n_{i\sigma} \equiv c_{i\sigma}^\dagger c_{i\sigma}$ and $c_{i\sigma}^\dagger$ ($c_{i\sigma}$) creates (annihilates) an electron (or hole) on site i with spin $\sigma = \uparrow$ or \downarrow . The hybridization is denoted by t and a nearest-neighbor pair by $\langle ij \rangle$. At half-filling the system is in a spin density wave state for $V < V_c$ and in a charge density wave state for $V > V_c$, where $V_c \approx U/Z$ and Z is the coordination number of the atoms in the lattice [11].

We performed exact diagonalization calculations of this Hamiltonian for a one-dimensional 14-site system with periodic boundary conditions looking at both the undoped and the two-hole-doped system. We take U large compared to the bandwidth, *i.e.* $U = 10t$ and vary V from 0 to $8t$ going through the spin density wave-charge density wave transition for $V = 5t$ at half-filling. We looked at the electron removal, electron addition and the optical excitations in each case. The results are shown in fig. 2. The electron addition and removal spectra are displayed towards the positive vertical direction for the doped system and to the negative direction for the half-filled system. The spectrum for the half-filled system is shifted in energy so that the spectral weight below the chemical potential corresponds to the number of electrons in the system with two holes. The dashed line corresponds to the onset of the optical spectrum for the half-filled system, where the zero of energy is taken at the chemical potential. In this figure we see exactly what we have described above in the simple picture in the atomic limit aside from somewhat broadened structures shifted in energy and with a large spectral weight transfer, all due to the finite values of the bandwidth. The undoped system shows the large correlation gap in the charged excitations and the appearance of the excitonic states in the gap in the optical spectrum for non-zero values of V . The doped system exhibits a strong broadening of both the electron removal and addition spectra with V , and shows a large amount of spectral weight appearing in the correlation gap for finite V . In addition to this filling-in of the pseudo-gap in the doped system as V increases we also see the appearance of satellites in the electron removal

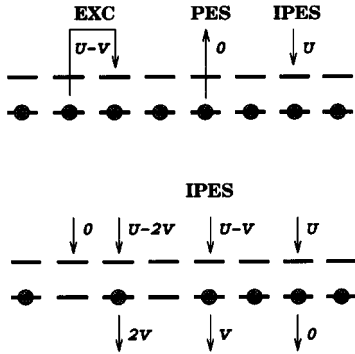


Fig. 1.

Fig. 1. – Schematical representation of an extended Hubbard model in the localized limit, the upper part for an undoped system, the lower part for a doped system. The energies for electron removal (pes), electron addition (ipes) and (optical) excitation are shown. A • represents an up or down electron.

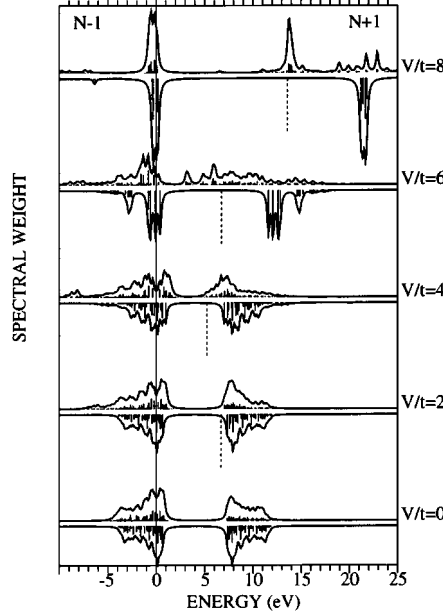


Fig. 2.

Fig. 2. – Electron addition and removal spectrum for a 14-site extended Hubbard model at half-filling (downward), and with a doping of 2 holes (upward). The spectrum for the half-filled system is shifted so that the chemical potential lies in the top of the valence band. The dashed line corresponds to the onset of the optical spectrum of the half-filled system, where the zero of energy is taken at the chemical potential $U/t = 10$.

part of the spectrum which correspond to the removal of an electron from a neighboring atom to that with a doped hole or from an atom with two such neighbors. These satellites will be centered at about V and $2V$ below the chemical potential, see fig. 1. The influence of t is to cause a mixing of these various groups of states causing them to repel each other and causing a spectral-weight transfer towards the lower-energy scale.

It is interesting to look at the spectral weights in more detail since they will be strongly influenced by the dimensionality of the system or rather the coordination number. We consider first doping with only one hole. In the atomic limit and for $V = 0$ there are 3 poles in the (inverse) photoemission spectrum, one below the chemical potential with a weight of $N(1 - x)$, one just at the chemical potential with a weight $2x$ and one at U above the chemical potential also with a weight of $N(1 - x)$, where N is the number of sites and x the hole doping (discussed in detail in [10]). The pseudogap in the electron addition spectrum as discussed above is U . A small bandwidth (finite t) broadens these states into bands and causes spectral weight to be transferred from the states at U to the chemical potential in the electron addition part of the spectrum. For finite V the situation changes markedly. Now there are in total 5 poles: one at $-V$ with a weight of Zx , one just below the chemical potential with a weight of $N(1 - x) - Zx$, one just above the chemical potential with a weight $2x$, one at $U - V$ with a weight Zx and one at U with a weight $N(1 + x) - Zx$. The spectrum for ten sites is shown in fig. 3. The spectral

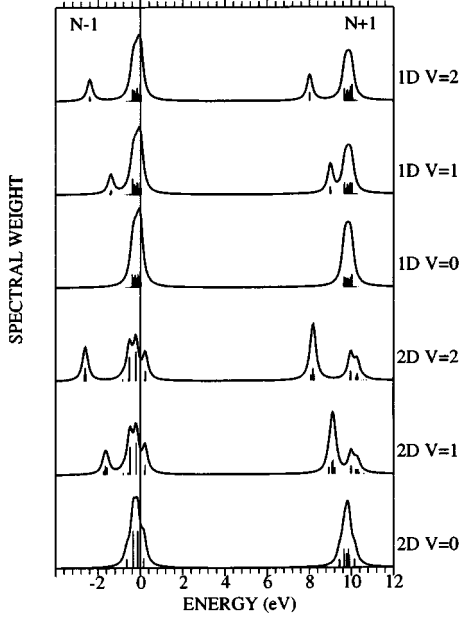


Fig. 3.

Fig. 3. – Electron addition and removal spectrum small bandwidth limit for ten sites in one and two dimensions. The doping is 0.1, $U = 10$ eV, and $t = 0.1$ eV

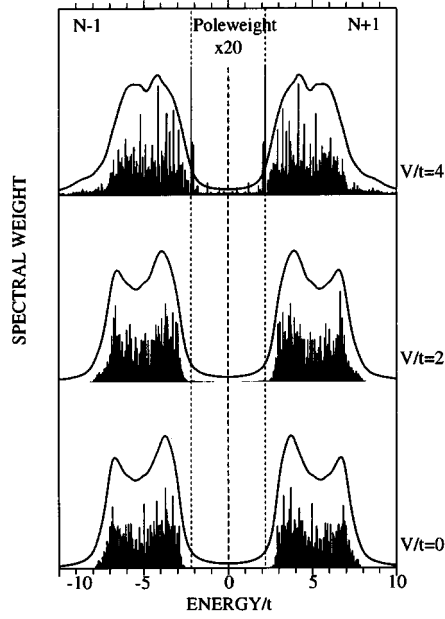


Fig. 4.

Fig. 4. – Electron addition and removal spectrum at a temperature $kT/t = 1$ with $U/t = 10$ for $V/t = 0, 2$ and 4 , for a half-filled 8-site extended Hubbard ring. The intensities of the poles between the dashed lines are amplified by a factor of 20.

weight of the satellites in this limit of small doping and small t scales with the coordination number so that their intensities will be two times as large in 2D than the 1D spectra shown in fig. 2. At higher doping concentrations also more poles can appear, in the atomic limit at energies of $-nV$, nV and $U - nV$, where n is an integer between 1 and Z in analogy with the discussion above for the two-hole-doped 1D system. Here n corresponds to the number of occupied and empty neighboring sites in the final state. We see therefore that the pseudogaps in the spectrum occurring for small V of magnitude U will quickly fill up with spectral weight and the total energy spread of the spectrum will increase rapidly as V and the doping are increased.

In this atomic limit the intensities of the various peaks will be determined solely by the statistical distribution of possible configurations. This will change as we switch on the bandwidth due to t . Increasing t will of course further increase the spread of the spectrum; however, as demonstrated in the $V = 0$ case [10], spectral weight will rapidly be transferred towards the lower-energy scale from the higher-energy scales until finally for large enough t all signs of the higher-energy features will disappear. The final result at large t will be a band of states concentrated around the chemical potential with a total width of about $2Zt$ as in one-electron theory. In this limit one-electron band theory will be valid.

At finite temperature the spectral function is given by

$$A(k, \omega) = \frac{1}{Z} \sum_{a,b,\sigma} \delta(\omega - E_b + E_a) \langle a | c_{k\sigma} | b \rangle \langle b | c_{k\sigma}^\dagger | a \rangle e^{-\beta E_a}, \quad (2)$$

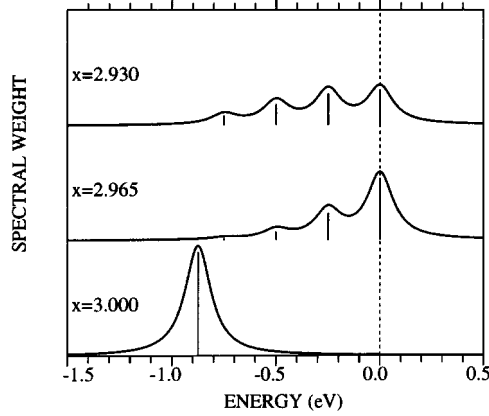


Fig. 5. – Electron removal spectrum for 3-fold degenerate EHM on a fcc lattice in the zero bandwidth limit for $x = 3 - \delta$ electrons per site. $U = 1.75$ eV and $V = 0.25$ eV. In the $x = 3$ spectrum we took the chemical potential to be in the middle of the gap.

where $|b\rangle$ represents the final states, and $\beta = 1/kT$. The temperature dependence is determined by the Boltzmann factor $e^{-\beta E_a}$ for the initial state $|a\rangle$ and the partition function is given by $Z = \text{Tr} e^{-\beta H}$. Note that the sum in (2) involves all final and all initial states, so that for an exact diagonalization of the Hamiltonian (1) we need all eigenvalues and eigenstates of both initial and final states, which limits our cluster sizes considerably. In fig. 4 the spectral function at half-filling as a function of temperature for $U/t = 10$, and with $V/t = 0, 2$ and 4 , for a one-dimensional eight-site cluster is shown. As the temperature increases, states inside the gap in the EHM gradually obtain more weight, as opposed to the simple Hubbard model, where there is no weight inside the gap observed. This is easy to understand if one realizes that the effect of the temperature is to occupy excited states of the N -particle system, which, in the case of the extended Hubbard model, include the states with a nearest-neighbor exciton. If an electron is removed from such an excited state, which is closer to the vacuum level, the energy of this electron is lowered with the exciton binding energy. So the situation at finite temperature is similar to that at finite doping, be it that at finite temperature the exciton is present in the initial state, and at finite doping, the exciton is present in the final state. The gradual filling-in of the gap in the EHM is directly due to the correlations present in this model. For instance, in a band semiconductor described by one-electron theory, the gap remains intact even at elevated temperature, but some weight occurs in photoemission corresponding to the thermally excited electrons in the conduction band.

Let us apply these observations to C_{60} and its potassium-doped derivatives, which are described by an orbital degenerate extended Hubbard model. Photoemission experiments on K_3C_{60} show that this compound is metallic but that the low-energy part in the spectrum is broadened over a range of about 1 eV [12]. This feature cannot be a band structure effect since the width of the t_{1u} band is expected to be at most about 0.6 eV [13] and that of the occupied part only 0.3 eV. One possible explanation involves the smearing-out of spectral weight due to vibrational excitations and plasmons which can accompany the removal of an electron, as argued by Gunnarsson *et al.* and Knupfer *et al.* [14], [15]. An alternative explanation is that the material is a slightly off-stoichiometric strongly correlated system and therefore a (bad) metal. In this case one would expect, as argued above, a spreading-out of spectral weight because of satellites associated with the Coulomb interactions U and V , as suggested by us [16]. The problem with this has been in the past that rather high non-stoichiometries are required to

get sufficient intensity out of high energies in the model where only U is considered. However, things may improve if we include the now known rather large values of V [3] in addition to U . As discussed, above the intensities of the satellites can be rather large as the coordination number Z is 12 for an fcc lattice. To check this, we show in fig. 5 the photoemission spectrum for a 3-fold degenerate Hubbard model with zero bandwidth with on average $3 - \delta$ electrons per site. Even a very small deviation from the $x = 3$ insulating regime shifts the chemical potential into the lower Hubbard band and gives low-energy satellites with high intensities. This may provide an explanation for the large spread in the photoemission spectra of K_3C_{60} in spite of the fact that in K_3C_{60} the deviation from perfect stoichiometry is only 0.09 [17]. In the case of a finite bandwidth, we expect, as observed in the 1D calculations above, that the satellites will shift somewhat towards the chemical potential and that weight will be transferred to the low-energy part of the spectrum.

We conclude that the features of a Hubbard model with inter-site Coulomb interactions upon doping or at finite temperature are both qualitatively and quantitatively different from the simple Hubbard model. In the excitation spectrum at finite doping, the nearest-neighbor Coulomb interaction introduces satellites both in the high- and low-energy part of the spectrum and renormalizes the pseudogap. It increases the low-energy spectral weight. At finite temperatures states inside the gap obtain spectral weight, and the gap seems to fill in gradually. We have demonstrated that excitonic states in the insulating undoped system visible only in optical spectroscopies attain an effective charge in the doped systems and become visible in the electron removal and addition spectra. These states quickly fill in the gap with spectral weight especially in higher dimensions. We have also argued that the inclusion of the nearest-neighbor Coulomb interactions in the case of C_{60} may provide an explanation for the large spread in the photoemission spectra.

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