The Hubbard model with orbital degeneracy and in polarizable media
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In this chapter it is shown that a nearest neighbor Coulomb interaction does not reduce the gap for charged excitations in a system with an on-site interaction larger than the one-electron bandwidth, but introduces 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 (super-)exchange interactions which involve virtual excitations of which the lowest in energy will be these excitonic states.

3.1 Introduction

Hubbard-like models [1] are extensively used in attempts to describe the electronic structure and related physical properties of strongly correlated systems. The Coulomb interactions usually considered is the on-site interaction $U$, and for the extended Hubbard model also the nearest neighbor interaction $V$, leading to a Hamiltonian for an $s$ band of the form $[2,3,5-8]$:

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

(3.1)

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 \( \langle ij \rangle \). 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 \( \text{Co}_6 \) has been emphasized in a number of studies [9-13]. An interesting aspect of this model is that there is a parameter regime displaying spin order, crossing over to a regime displaying charge order, as will be shown below.

In order to determine if and how the nearest neighbor Coulomb interaction reduces the effective Coulomb interaction, the influence of \( V \) on the correlation gap, the optical conductivity and the (super)exchange for a half filled system is studied in this chapter. In the exact diagonalization calculations for small clusters we restricted ourselves to the strong coupling regime, i.e. the regime where the bandwidth is smaller than the on-site Coulomb interaction, where it is expected that finite site effects are small. The results will be explained in a qualitative way by using arguments that become exact in the zero-bandwidth regime. The influence of doping the system will be discussed in the following chapter.

### 3.2 Conductivity gap

Let us start with a brief review of some aspects of the extended Hubbard model described by Eq. (3.1). For a half filled \( s \) band and for \( V < V_c \), the system has an antiferromagnetic spin density wave (SDW) ground state, which can be schematically represented as \( | \uparrow \downarrow \uparrow \downarrow \rangle \). For \( V > V_c \) the ground state is a diamagnetic charge density wave [4, 5], which can be represented as \( | \downarrow \uparrow \uparrow \rangle \). The critical value of \( V \) is approximately located at \( V_c \approx U/z \), where \( z \) is the coordination number. In a one-dimensional system the phase transition is found to be second order for small \( \frac{U}{t} \) and first order for large \( \frac{U}{t} \), with the crossover occurring at \( \frac{U}{t} \approx 3 \) [5, 17].

In Fig 3.2 the value for the gap is shown, calculated by exact diagonalization using...
3.2. **Conductivity gap**

![Figure 3.2](image)

**Figure 3.2:** Gap as a function of the inter-site Coulomb repulsion $V$ in a one-dimensional system of 14 sites and a two-dimensional system of 10 sites. $U=10$, $W=4$.

![Figure 3.3](image)

**Figure 3.3:** Schematic representation of the excitonic state and the lowest electron removal (PES) and addition (IPES) state in the localized limit.

A 14 site cluster in one dimension and a 10 site cluster in two dimensions with periodic boundary conditions. We see that the conduction gap defined as $E_{GS}^{N-1} + E_{GS}^{N+1} - 2E_{GS}^N$, which is the gap between the first ionized state and the first electron affinity state, is independent of $V$ up to a critical value of $V_c = U/2$. In the 1D system there is a slight drop of the gap near the phase transition, an effect that will be explained below. For $V > V_c$ the gap increases with $V$. At $V_c$ there is a phase transition from the SDW to the CDW groundstate. In the limit $t \to 0$ the gap is $U$ for $V < V_c$ and is $4V - U$ for $V > V_c$ (for general bi-partite lattices the gap is given by $2zV - U$ for $V > V_c$).

That the gap is almost constant up to $V_c$ can easily be understood by realizing that in separating the electron from a hole to large distances the nearest neighbor electron-hole attraction is not operative so that charged excitations are not screened and therefore the correlation gap is not reduced [14]. This is schematically shown in Figure 3.3.

In figure 3.4 the calculated value for the gap is shown for a small cluster of 10 atoms in one and two dimensions near the phase transition where $U = zV$, for
Figure 3.4: Correlation gap (thick lines) as a function of the inter-site Coulomb repulsion $V$ in a 1D (left) and 2D (right) system of 10 sites for different bandwidths $W$. The three upper thin lines are the $N$-particle groundstate energies differentiated in $V$. The three lower thin lines are the $N$-1-particle groundstate energies differentiated to $V$.

different values of the bandwidth $W$, which is proportional to the hybridization $t$. There is a remarkable difference between the 1D and 2D case. In 2D the gap stays constant up to the phase transition and if the hybridization is increased, it is lowered with a constant value independent of the ratio $U/V$. In the 1D system, the behavior is different. Near the phase transition, the gap is somewhat lowered depending on the hybridization.

This decrease of the gap, typical for the 1D system, can be explained by examining the $N+1$ and $N-1$ electron systems carefully. In the same figure the groundstate energy of the $N-1$, $N$ system differentiated with respect to $V$ is shown for the 1 and 2D system. The groundstate energy of the $N+1$ system can be found from $E^{N-1}$ by particle-hole symmetry. From the figure we can see that the groundstate energy of the $N$ particle system scales linearly with $V$, as expected in the localized picture, but that the groundstate energy for the 1D system with one extra electron or hole, near the phase transition strongly deviates from the linear behavior. This can be explained by realizing that the kinetic energy of one extra hole/electron near the phase transition in 1D is much larger than the kinetic energy of the hole/electron far away from the point of phase transition. In Fig. 3.5 a schematic picture is shown for the 1D system near the phase transition with one extra electron that creates a doubly occupied site. Suppose that $U = 2V$ for the system. The energy associated with moving one electron, far away from the doubly occupied site, to its neighbor, and so creating a doubly occupied site there is $U - V$, so the contributions of the processes to the lowering of the groundstate energy are of the order of $2Nt^2/(U - V)$, when $t \ll U - V$. As a starting point one can neglect these contributions to the kinetic energy, because they are of the order of the exchange $J$. Now there are two qualitatively different processes, which are first order in $t$, i.e. they do not involve
virtual excitations and are independent of the Coulomb interactions. First, the doubly occupied site can delocalize in the lattice, moving from one site to the neighboring site. But also the process where an electron that is next to a doubly occupied site moves to its neighbor, does not involve a Coulomb interaction, because the Coulomb energy before the hop of the electron is $3V$, and after the hop it is $U + V = 3V$, see Fig 3.5. So it is as if there are effectively moving two particles, two 'kinks', in the lattice, decreasing the total kinetic energy of the system. In the 2D case the latter excitation involves a Coulomb interaction: the energies are resp. $5V$ and $U + 3V$, where at the phase transition $U = zV = 4V$, so these excitations will be of the order of $t^2/2V$, so of the order of $J$. This explains the qualitatively different behavior in a 1D and 2D system and shows that the decrease of the gap around the SDW-CDW phase transition is an effect that is typical for a 1D system and doesn't occur in higher dimensions.

### 3.3 Exciton

In Fig. 3.6 the combined one electron removal and addition spectrum of the extended Hubbard model in one dimension calculated by exact diagonalization using a 14 site cluster with periodic boundary conditions is shown. Also shown in Fig 3.6 are excitations related to optical spectra, calculated using the correlation function:

$$Im\langle \psi_{GS} | O^\dagger \frac{1}{z-H} O | \psi_{GS} \rangle$$

with $O = \sum_{i,\sigma} (c_{i,\sigma}^\dagger c_{i+a,\sigma} - c_{i+a,\sigma}^\dagger c_{i,\sigma})$, which is proportional to the kinetic energy. These are drawn with the zero of energy at the $E_{GS}^{N-1}$ (i.e. the top of the valence band). We see states at energies below the gap which are excitonic in origin. These excitonic states soften as $V$ increases approaching the center of the gap for $V \rightarrow V_c$. 

*Figure 3.5:* Schematic representation of the propagation of an added electron in a one-dimensional system precisely at the SDW-CDW phase transition.
Chapter 3. Extended Hubbard model at half filling

Figure 3.6: Electron removal, electron addition and optical spectra for a 14 site extended Hubbard ring. For each value of $V$ the upper curves are the electron removal/addition spectra and the lower curve is the optical spectrum. The zero for the optical spectrum is at the first ionization states, indicated by the arrow. The parameters $U = 10$ eV and $t = 1$ eV are taken.

For the CDW phase, excitonic states are again present in the gap at an energy of $3V - U$ for $t \to 0$ above the groundstate energy of the $N - 1$ particle system. The influence of $V$ is to introduce new charge transfer excitonic (charge neutral) states inside the gap.

3.4 Exchange

The effective exchange interaction in the SDW state is determined by the energies of virtual nearest neighbor electron-hole excitations. In the strong coupling limit, these are at an energy $U$ for $V = 0$, leading to an exchange $J \approx -4t^2/U$. $V$ has the influence of lowering the energy of the excited state since it is an attractive nearest neighbor electron-hole interaction. So the exchange is, in perturbation theory, given by $J \approx -4t^2/(U-V)$. This is of importance when, for example, considering the magnitudes of parameters in a $t$-$J$ model, i.e. $t/J$ can be considerably smaller than
one may have estimated from only $t$ and $U$. The relationship for $J$ gives the impression that $V$ acts to screen $U$ [18]. The exchange, however, involves locally charge neutral excitations. Charged excitations are not screened and therefore the correlation gap, as shown above, remains unaltered.

### 3.4.1 Single band system

A frequently used approach to discuss the strong-coupling limit of Hubbard-type models is the perturbation expansion in $t/U$ [19, 20], which leads to an effective Hamiltonian operating in the subspace of states without double occupancies, the well-known $t-J$ model. By virtue of its perturbational derivation, the relation $J = 4t^2/U$ holds, so that it seems that a necessary condition for the validity of $t-J$-like models is the relation $J/t = 4(t/U) \ll 1$. In this section it is shown that this is not necessarily the case; rather, Hubbard models with an additional inter-site repulsion which is sufficiently strong to bring the system close to a charge-density-wave instability may provide 'physical' realizations of $t-J$ models with $J/t \approx 1$. We also show that the situation is reversed in a charge-transfer insulator, where inter-site Coulomb repulsion on the contrary suppresses the super-exchange.

To begin with, it is advantageous to develop a simple picture of a correlated insulator. We restrict ourselves to $1D$ systems in what follows, the main reason being that exact diagonalization for reasonably large $2D$ clusters of the single or even two-band Hubbard model is not feasible. One expects, however, that the physical considerations outlined below retain their validity in any dimension. We consider the single band Hubbard model given by Eq. (3.1). At half-filling and in the limit $V = 0$, $U \to \infty$ we have precisely one electron per lattice site for the Hubbard model (see the states labeled '0' in Figure 3.7).

Switching on the inter-site kinetic energy then will lead to charge fluctuations: in the Hubbard model, an electron can jump to a nearest neighbor, thus creating a 'hole' and a 'double occupancy' on nearest neighbors (an electron-hole pair). The energy thereby is increased by the large amount $U$. In subsequent steps the hole and the double occupancy can separate even further, but all states generated in this way have the same large Coulomb energy $U$ (see Figure 3.7). By analogy with the problem of a particle moving in a $1D$ attractive $\delta$-potential one may therefore expect that the probability to find a hole and a double occupancy at a distance of $n$ lattice spacings decreases rapidly with $n$. The canonical transformation to a Heisenberg or $t-J$ Hamiltonian with only nearest neighbor exchange then obviously is equivalent to assuming that states where a hole and an electron are more distant than nearest neighbors (nearest neighbor $d$-sites for the case of the charge transfer system) can be completely neglected.

Let us now consider the case $V > 0$. For the single-band Hubbard model the energy necessary to create a charge fluctuation on nearest neighbors is lowered to $U - V$ (see Figure 3.7). The energy to drag apart hole and double occupancy, however, remains unchanged, so that the separation between the two Hubbard bands (which are associated with 'free' propagation of hole or double occupancy) stays unaffected [14, 15]. Invoking again the analogy with a particle moving in a $1D$ attractive potential...
one might instead expect the formation of a ‘bound state’ between a hole and a double occupancy on nearest neighbors, which manifests itself as an excitonic excitation at an energy well below the Hubbard gap in the optical conductivity, as shown in the previous section. The $V$-term therefore does not reduce the Hubbard gap, and in particular does not ‘screen’ $U$ to turn the correlated insulator into a weakly correlated metal. The question remains, however, whether a transformation to a $t-J$ model with only nearest neighbor exchange still makes sense in the presence of the $V$-term. Obviously, if there is an appreciable probability to have the electron-hole pair on more distant than nearest neighbor sites, longer range spin correlations will become important in the effective low energy Hamiltonian. To address this question exact diagonalization of small clusters is used; note that for the short-range/high energy processes which mediate the Heisenberg exchange finite size effects probably play only a minor role. The dynamical spin correlation function $S(q,\omega)$, is calculated for different values of $V$ and shown in Figure 3.8. With increasing $V$, all peaks move to higher energy, the overall shape of the spectra being unaffected. Rescaling the frequencies the different $S(q,\omega)$ can be made practically identical, as demonstrated in Figure 3.8b. Assuming the relation $J = 4t^2/U$ to hold for $V=0$, we can use the rescaling factors to extract the effective Heisenberg exchange $J_{\text{eff}}(V)$, shown in Figure 3.8c. Obviously values of $J_{\text{eff}}/t$, as large as 0.8, i.e. far outside the ‘perturbational’ range are possible. Figure 3.8c also shows the simple estimate $J_{\text{eff}}(V) = 4t^2/(U-V)$, which provides a reasonable approximation for the numerical values. It should be stressed that for small values of $V$ this functional form of $J_{\text{eff}}(V)$ is rather trivial;
what is not, however, is the validity of this relation up to the value $V=U/2$.

### 3.4.2 Charge transfer system

Now consider the charge transfer system

$$H = -t \sum_{i,j \in N(i), \sigma} (d_{i,\sigma}^\dagger c_{j,\sigma} + H.c) + U \sum_i n_i^\dagger n_i - \Delta \sum_i n_i + V \sum_{i,j \in N(i)} n_i n_j,$$

which consists of strongly correlated ‘$d$’-orbitals separated by uncorrelated ligands ($N(i)$ denotes the two ligand sites neighboring the $d$-site $i$). The on-site energy $-\Delta$ of the $d$-orbitals is taken to be negative, and in addition to the $d$-site Coulomb repulsion $U$ an additional Coulomb repulsion $V$ between nearest neighbor $d$ and ligand orbitals, also referred to as $U_{pd}$ in literature, is included. At ‘half-filling’ and in the limit $V=0$, $U \rightarrow \infty$ we have precisely one electron (or hole) per $d$-site in the charge transfer system.

From Figure 3.7 one may expect that the $V$-term effectively increases the charge transfer energy $\Delta$ to $\Delta + V$ (it should be stressed, that this refers to ‘bare’ or ‘model’ parameters; in the case of the charge transfer insulator, the energy required to drag apart hole and double occupancy becomes $\min(\Delta + 2V; U)$ in the presence of the nearest neighbor repulsion, so that the experimentally measured charge transfer gap would be increased to $\Delta + 2V$). Contrary to the case of direct exchange, this suggests a suppression of the exchange constant $J$. This is demonstrated in Figure 3.9, which shows the dynamical spin correlation function for the charge transfer system with different values of $V$. From the rescaling of the SCF (see Figure 3.9b) again the effective exchange constant can be extracted, which is shown in Figure 3.9c. The figure also shows a simple estimate based on $4^{th}$ order perturbation theory, where $J = (2t_{pd}/(\Delta + V))^2 \cdot (1/\Delta + 1/U)$, which however provides only a rough estimate.

### 3.4.3 CuO$_2$ system

We start from a two band Hubbard model [2,3] for the copper-oxygen planes in the high $T_c$ superconductors, taking into account the Cu $d_{x^2-y^2}$, O $p_x$ and O $p_y$ orbitals:

$$H = \epsilon_d \sum_{i,\sigma} d_{i,\sigma}^\dagger d_{i,\sigma} + \epsilon_p \sum_{j,\alpha} p_{j,\alpha}^\dagger p_{j,\alpha}$$

$$+ \sum_{<i,j>, \sigma, \alpha} t_{pd}^\alpha (d_{i,\sigma}^\dagger p_{j,\alpha} + h.c.) \delta_{\sigma,\alpha'}$$

$$+ \sum_{<j',> \sigma, \alpha'} t_{pp}^\alpha (p_{j,\alpha}^\dagger p_{j',\alpha'} + h.c.) \delta_{\sigma,\alpha'}$$

$$+ U_{dd} \sum_i n_i^\dagger n_i + U_{pp} \sum_{j,\alpha, \alpha'} n_{j,\alpha} n_{j,\alpha'} + U_{pd} \sum_{<ij>, \sigma, \alpha} n_{i,\sigma} n_{j,\alpha}, \quad (3.3)$$

where the summation over $i$ is over the sub-lattice of Cu atoms, $j$ over the O sub-lattice and $<ij>$ denotes neighboring sites. The index $\alpha$ for the oxygen sites is
Figure 3.8: (a) Spin correlation functions of a 10-site 1D Hubbard ring for different $V$ ($U=10$, $t=1$).

(b) Same as (a) but with the frequencies rescaled so as to make the energies of the dominant peak at $2\pi/5$ identical for all spectra.

(c) Effective Heisenberg exchange, $J_{\text{eff}}(V)$, calculated from the rescaling factors used in (b), the dashed line shows $J_{\text{eff}}(V) = 4t^2/(U - V)$. 
Figure 3.9: (a) Spin correlation functions of a 6-unit cell 1D Charge transfer ring for different $V$ ($\Delta=3$, $U=8$, $t=1$).

(b) Same as (a) but with the frequencies rescaled so as to make the energies of the dominant peak at $2\pi/3$ identical for all spectra.

(c) Effective Heisenberg exchange, $J_{eff}(V)$, calculated from the rescaling factors used in (b). The dashed line has been calculated from 4th order perturbation theory.
an index over the spin degrees of freedom $\sigma$ and the orbital degrees of freedom $p_{x,y}$ and $\epsilon_d$, $\epsilon_p$ are the on-site energy for the $d$ and $p$ electrons, respectively, $t_{pd}$ describes the hopping between $d$ and $p$ orbitals, $t_{pp}$ the oxygen-oxygen hopping and $U_{dd}$, $U_{pp}$ the Coulomb repulsion for two electrons on the same Cu and O site, respectively. The Cu-O inter-site Coulomb repulsion is $U_{pd}$. The hopping integrals between $p_x$, $p_y$ and $d_{x^2+y^2}$ can be found with the Slater-Koster method [24] and tight binding fits to band-structure calculations [25]. The parameter set (for holes) used is given in the table below.

<table>
<thead>
<tr>
<th>Parameter set (eV)</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p_d\sigma$</td>
<td>1.5</td>
</tr>
<tr>
<td>$p_p\sigma$</td>
<td>-1.0</td>
</tr>
<tr>
<td>$p_p\pi$</td>
<td>0.25</td>
</tr>
<tr>
<td>$U_{dd}$</td>
<td>7.0</td>
</tr>
<tr>
<td>$U_{pp}$</td>
<td>5.0</td>
</tr>
</tbody>
</table>

In the undoped, insulating compound there are as many holes as copper atoms in the system and these hole mainly reside in the $d_{x^2+y^2}$ orbitals. The charge transfer energy is defined as $\Delta_0 = \epsilon_p - \epsilon_d + U_{dd}$. In the localized limit the charge transfer energy is exactly equal to the conductivity gap. The more subtle point now is that this is only true if $U_{pd} = 0$, in the localized limit the gap, generalized for non-zero $U_{pd}$, is $\Delta_{eff} = \Delta_0 + 2U_{pd}$. This effect arises because each Cu atom is surrounded by 4 oxygen atoms without any holes, but each oxygen atom is only surrounded by 2 Cu sites, each with one hole. In the high T$_c$ systems $U_{pd}$ is estimated to be between 0.5-1.5 eV.

Now our task is to calculate the effective exchange $J$ as a function of $\Delta$ and $U_{pd}$. We learned from the previous section that for this purpose it is sufficient to consider
two copper sites (2 holes) in a full oxygen lattice (compare ref [26]). The topology of the Cu$_2$O$_{65}$ cluster used in the exact diagonalization is shown in figure 3.10. The exchange constant for different values of $U_{pd}$ is shown in figure 3.11. As in the previous section it is found that increasing $U_{pd}$ suppresses the exchange, mainly due to the increase of the effective charge transfer gap. However, if we calculate $J$ as a function of the effective gap, we find that $U_{pd}$ enhances the exchange, see figure 3.11. The reason is that the inter-site Coulomb repulsion creates excitons with an energy lower than the gap and these excitonic states enhance the (super-)exchange, as in the single band system.

3.5 Conclusions

In summary, the influence of inter-site Coulomb repulsion $V$ in the Hubbard model at half filling was investigated. It was shown that $V$ does not screen the correlation gap but introduces charge neutral excitations inside the gap.

For single band Hubbard models, the results suggest an enhancement of the exchange constant, roughly as $J(V) = 4t^2/(U - V)$, whereas the spin dynamics still remains consistent with that of an ideal Heisenberg antiferromagnet. The remarkable feature of the results is that this rescaling seems to hold up to the CDW instability, which opens the way to unexpectedly large values of the ratio $J/t$. In particular, for the strong correlation case close to a CDW instability in 1D, our results suggest values of $J$ comparable to the original hopping integral. Therefore, real materials which may be described by a strong correlation single band Hubbard model close to a CDW instability may provide realizations of $t-J$-like models with ‘unphysically’ large values of $J/t \approx 1$. For higher spatial dimensions, the critical value of $U/V$ for the formation of the CDW state is smaller than in 1D, which seems to preclude
large $J$ values due to inter-site repulsion. However, an alternative possibility here could be the suppression of the CDW due to a non-bipartite lattice structure, which can rule out the CDW even for large values of $V$; an interesting example here could be solid $C_{60}$, which crystallizes in the FCC structure. Auger spectroscopy [21] gives values of $U \approx 1.5eV$, whereas analysis of the exciton dispersion [22] in un-doped $C_{60}$ suggests values of $U - V$ as small as $0.35eV$, which is also consistent with other experimental estimates [11]. This is to be compared to the average bandwidth of the LUMO-derived bands of $\approx 0.3eV$ [23]. While the inter-site Coulomb repulsion may be more efficiently screened in the doped material than the on-site $U$, leading to an increase of $U - V$, one still may expect relatively large values of $J$.

For charge transfer systems the super-exchange via ligand orbitals on the contrary is suppressed by the inter-site Coulomb repulsion because the nearest neighbor repulsion $V$ increases the ‘bare’ charge transfer energy $\Delta_0$. However, if the charge transfer gap is kept constant while introducing $V$, the super-exchange increases because $V$ introduces low energy excitonic states. This might be relevant for theoretical models of cuprate superconductors which rely on large values of $V$ [3].

References