New phases in an extended Hubbard model explicitly including atomic polarizabilities

We consider the influence of a nearest neighbor Coulomb interaction in an extended Hubbard model and introduce a new interaction term which simulates atomic polarizabilities. This has the effect of screening the on-site Coulomb interaction for charged excitations, unlike a nearest neighbor Coulomb interaction which reduces energies of locally neutral excitations. The spin density - charge density wave phase transition, however, is determined by the unscreened on-site Coulomb repulsion. The order of this phase transition is affected by polarization. New phases appear, one of which is ferroelectric, when atomic polarizabilities are explicitly included.

5.1 Introduction

Hubbard like models [1] are extensively used in attempts to describe the electronic structure and related physical properties of strongly correlated systems. The basic assumption made in arriving at such models is that the long range Coulomb interactions are effectively screened and the short range on-site and nearest neighbor Coulomb interactions can be treated as effective parameters screened from their free ion values [1, 2]. The Coulomb interactions usually considered are 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 [3–9]:

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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 $\langle ij \rangle$.

Only the open shell valence orbitals are considered explicitly. It is assumed that all of the other interactions and closed shell orbitals merely lead to renormalized parameters $U, V$ and $t$, but do not change the low energy scale physics. To our knowledge we present the first study of the validity of such an approach. We introduce a new term which treats the dominant contribution to the screening of the atomic $U$ value in insulators, by including the atomic polarizabilities explicitly. Such a term is known to reduce the Cu d-d Coulomb interactions in high $T_c$'s from the atomic value of 16 eV to the solid state value of about 5 eV [10], and in $C_{60}$, $U$ is reduced from its gas phase value of 3.6 eV to about 1.6 eV because of the molecular polarizabilities [11]. Such polarization screening effects are very large and of the same magnitude as $U$ itself. The importance of such an atomic polarizability in describing properties of insulators is well known, determining the optical dielectric constants via the Clausius-Mossotti relation and Mott-Littleton-like [12] approaches, and also are the driving force in the formation of layered structures such as NiI$_2$, TaS$_2$ etc. [13].

The new term $H_{\text{pol}}$ directly screens the bare on-site Coulomb interaction $U$ from its atomic value and reduces the correlation gap. As is well known, a nearest neighbor interaction $V$ yields a charge density wave (CDW) ground state for $V > V_c$. Quite unexpectedly $V_c$, which in one dimension is close to $U/2$, is determined by the unscreened value of $U$ and not the screened value, as is implicitly assumed if one uses simply an extended Hubbard model. The nature of the phase transition, however, can be affected and polarization screening can drive it from 1st to 2nd order. Furthermore $H_{\text{pol}}$ introduces a new type of charge density wave as well as a ferroelectric phase into the phase diagram in one dimension. Contrary to recent claims [14], we find that $V$, unlike $H_{\text{pol}}$, does not act to reduce the correlation gap determined by $U$, but introduces charge transfer excitonic states in the correlation gap of a Mott-Hubbard insulator. It does however act to increase the nearest neighbor exchange $J$ and therefore affects strongly the magnetic susceptibility [15] and also influences the cohesion energy [16]. We hereby demonstrate that the explicit inclusion of screening mechanisms in model Hamiltonians can lead to interesting new physics and that they do not merely renormalize the parameters.
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 $U$ [14]. The exchange, however, involves locally charge neutral excitations. In the insulating state charged excitations are not screened and therefore the correlation gap is not reduced [18]. This can be easily understood by realizing that in separating the electron from a hole to large distances the nearest neighbor electron-hole attraction is not operative. The influence of $V$ is to introduce new charge transfer excitonic (charge neutral) states inside the gap.

We will derive a Hamiltonian which describes a particular form of screening by considering a band of (strongly correlated) electrons that interact with local electronic excitations. Consider a system of atoms which have deep lying, occupied $s$ or $p$-orbitals and empty $p$ or $s$-orbitals that lie well above the conduction band. For example the $2p$ electrons and the $3s$ empty states of an O$^{2-}$ in an oxide. In an oxide, however, these orbitals and the strongly correlated orbitals are on different atoms. For simplicity we take the deep lying orbitals to be $s$ orbitals and the high lying ones to be $p$ orbitals, neglect the spin of the electrons in the $s$ and $p$ levels, and assume that there is no hybridization with the correlated band. The energy splitting between these orbitals is $\Delta_{sp}$. In the presence of an external potential $V(r)$ these states will mix. If the external potential is generated by an electric field that is constant over the dimension of the atom, we get: $X_{sp} = \int \phi_s(r)r\phi_p(r)d^3r$. This results in a dipole moment at a site $i$ of: $P_i = -eX_{sp}(p^+_is_i + s^+_ip_i)$. When we take the zero of energy at
the s-level, we end up with a polarization Hamiltonian of the form

$$H_{\text{pol}}^0 = \sum_i -\mathbf{P}_i \cdot \mathbf{F}_i + \Delta_{\text{sp}} p_i^\dagger p_i.$$  \hfill (5.2)

The main contribution to the electric field on a site $i$ will originate from the charges on neighboring sites. If we neglect higher order multipole terms, the electric field on site $i$ is given by

$$\mathbf{F}_i = \frac{e}{a^2} \sum_{j \in \{\text{n.n.}(i)\}} \hat{n}_j \delta_{ij},$$  \hfill (5.3)

where $a$ is the interatomic spacing and $\delta_{ij}$ is the unit position vector connecting neighboring sites $i$ and $j$. If we combine Eq. (5.2) and Eq. (5.3) we arrive at an explicit form for the polarization Hamiltonian in one dimension of

$$H_{\text{pol}}^{1\text{D}} = \frac{e^2}{a^2} X_{\text{sp}} \left| \sum_i (\hat{n}_{i+1} - \hat{n}_{i-1}) (p_i^\dagger s_i + s_i^\dagger p_i) \right| + \Delta_{\text{sp}} p_i^\dagger p_i.$$  \hfill (5.4)

The Hamiltonian Eq. (5.2) includes three bands. In the next section we will present some exact diagonalization results on the extended Hubbard model with inclusion of this Hamiltonian. Before doing this, we derive a single band model equivalent to Eq. (5.2), which of course cannot describe the full polarization processes, but which is valid at low energies. The induction of a dipole moment by the electric field will lower the energy of the system.

Consider the Hamiltonian $H = H_{\text{EMH}} + H_{\text{pol}}^0$ in the limit that $\Delta_{\text{sp}} \gg t$. We treat $H_{\text{pol}}$ as a perturbation; the zero order wave function is $|\phi_0\rangle$, with energy $E_0$, and the zero order excited state is $|\phi_i\rangle = p_i^\dagger s_i |\phi_0\rangle$, with energy $E_0 + \Delta_{\text{sp}}$. Second order perturbation theory gives:

$$E = E_0 - \sum_i \frac{|\langle \phi_i | H_{\text{pol}}^{1\text{D}} | \phi_0 \rangle|^2}{\Delta_{\text{sp}}}$$

$$= E_0 - \sum_i \frac{(eX_{\text{sp}})^2}{\Delta_{\text{sp}}} F_i^2.$$  \hfill (5.5)

Combined with Eq. (5.3) this results in a polarization Hamiltonian:

$$H_{\text{pol}} = -P \sum_i \left( \sum_{j \in \{\text{n.n.}(i)\}} \hat{n}_j \delta_{ij} \right)^2,$$  \hfill (5.6)

with $P = \frac{e^2}{a^2} X_{\text{sp}}^2$. The interaction in Eq. (5.6) is the instantaneous, non-retarded part of the interaction in Eq. (5.2). In Fig. 5.1 we show how the surrounding atoms polarize
due to such higher order Coulomb interactions. This formula for the polarization is equivalent to the expression for the polarization energy used by de Boer et al. [19]:

\[ E_{\text{pol}} = \frac{1}{2} \sum_i \alpha_i F_i^2, \tag{5.7} \]

where \( \alpha_i = 2P_{\text{sp}}^2 \) is the polarizability at site \( i \) and dipole-dipole corrections are neglected.

### 5.3 Screening of the Gap

Using exact diagonalization of finite clusters we studied the influence of adding \( H_{\text{pol}} \) to the extended Hubbard model. In figure 5.2 the gap values screened due to the full polarization Hamiltonian 5.2 and its perturbational equivalent Hamiltonian 5.6 are compared. This shows that the perturbingal expressing used in 5.6 gives results which are very close to those of the full Hamiltonian. Therefore we use Hamiltonian 5.6 to describe screening in the rest of this chapter. In Fig. 5.3 we show the conduction gap as a function of \( V \), for various values of \( P \) for a two dimensional 10 site cluster and a 1D 14 site cluster at half filling. We see that for \( P = 0 \), \( V \) hardly influences the gap for \( V < V_c \), as discussed above. We have also studied the cluster size dependence up to ten sites and found that finite size effects do not alter this conclusion. We also see, as expected, that \( P \) does reduce the gap and has the influence of screening \( U \). Strangely enough though, the SDW-CDW transition occurs at the unscreened
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**Figure 5.3:** Size of the conduction gap $E_{\text{gap}}$ as a function of the inter-site Coulomb repulsion $V$ for a one dimensional 14 site cluster (lower curves) and a two dimensional 10 site extended Mott-Hubbard cluster (upper curves), with inclusion of polarizable atoms. The on-site Coulomb repulsion $U$ is kept constant at 10 eV, while $E_{\text{pol}}$ was varied. ($E_{\text{pol}} = 0$ for the top curve, further: $E_{\text{pol}} = 0.5, 1.0$ eV). The hybridization $t$ is 1 eV.

value of $V_c = U/4$ in two dimensions. This is easy to understand by simply realizing that in the CDW state each site has inversion symmetry so no net fields are present and therefore $H_{\text{pol}} = 0$ for the ground state. So to produce the doubly occupied sites in the CDW phase costs the unscreened energy $U$. For $t = 0$, the total energy $E_{\text{SDW}} = zNV/2$ and $E_{\text{CDW}} = NU/2$.

### 5.4 New Phases

For an hyper-cubic lattice it is possible to exactly map the total Hamiltonian onto a new Hamiltonian which has a more transparent form. The interaction part of this Hamiltonian reads:

$$H_{\text{int}} = (U - 2zP) \sum_{l'} n_{l'} n_{\bar{l}} + V \sum_{l_i} n_{l_i} n_{l_{i+\bar{l}}},$$

$$+ zP \sum_{l_i} n_{l_{i}} n_{l_{i+2\bar{l}}},$$

(5.8)

where the sum over $i$ is the sum over the unit lattice vectors $\bar{a}_i$. Now the "screening" of $U$ by $P$ is directly evident, but a new repulsive next nearest neighbor interaction is also present. This new repulsive term adds new phases into the phase diagram.

In Fig. 5.4 we show the new phase diagram for $t = 0$ for a one dimensional infinite system. We see the usual SDW-CDW transition for $V = U/2$ at small $P$. For small
Figure 5.4: Phase-diagram in an infinite one dimensional extended Hubbard system including polarization screening in the atomic limit. $P$ is the polarization energy and $V$ the nearest neighbor Coulomb repulsion. A Spin Density Wave phase, two types of Charge Density Wave phases and an Intermediate ferroelectric phase are indicated. For each phase, translation invariant electron configurations are schematically shown.

We see another SDW-CDW transition but now to a sort of charge density wave of bipolarons. Note that for $P = U/4$ we expect bipolarons to form but because of the long range repulsive term introduced by $H_{\text{pol}}$ these bipolarons already appear at $P = U/8$. In this phase each atom tries to be in an as large as possible electric field. Also of interest is the intermediate phase of Fig. 5.4. This is a ferroelectric phase which is obtained as a result of competition between $V$ and $P$ and consists of a combined charge density wave and spin density wave. Note that $P$ need not be small with respect to $U$ and $V$, since the reduction of $U$ can be of the order of $U$, as discussed above. This is especially true if one would also include lattice polarization effects which can lead to bipolaron ($U - 2zP < 0$) effects.

Polarization screening is also of influence on the nature of the SDW-CDW phase transition. We studied this by calculating the CDW order parameter distribution functions for a one dimensional small cluster. The CDW order parameter

$$m_0 = \sum_i \langle \Psi_{\text{GS}} \mid (-1)^i n_i \mid \Psi_{\text{GS}} \rangle$$

of the groundstate wave function has a unique value. However, within the real-space basis that we do our calculations, one can think of it as being a sum over a distribution of possible values of $m$, with probabilities $P(m): m_0 = \sum_m mP(m)$ [17]. In the thermodynamic limit the order parameter will take a value that minimizes the total energy, i.e. the maximum of the calculated distribution. We obtain the nature
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Figure 5.5: Distribution function of the CDW order parameter for an eight site extended Hubbard ring, with $U = 10$ eV and $t = 1$ eV. Left: $P = 0$ eV and $V = 2.08$ eV (upper curve), 2.10, 2.12, 2.14 and 2.16 eV. Right: $P = 0.25$ eV and $V = 2.04$ eV (upper curve), 2.08, 2.12, 2.16 and 2.20 eV. Each curve is plotted with an offset of 0.01.

of the phase transition by noting whether the maximum of the distribution changes continuously (2nd order), or discontinuously (1st order).

We calculated the order parameter distribution function for $\frac{U}{t} = 4$ and for $P = 0$ and $P = 0.25$, respectively, see Fig. 5.5. For $P = 0$, three local maxima in the distribution are present at the phase transition. This indicates that the global maximum of the order parameter changes discontinuously and the transition is 1st order. For $P = 0.25$, however, the maximum changes continuously, indicating a 2nd order phase transition. This can be understood as follows. Close to the transition, but still in the CDW state, the low-lying energy excitations are ’droplets” of the SDW state [6]. Polarization screening tends to soften the excitonic states below the conductivity gap. In our model the energy of a droplet of size $n$ is $\epsilon(n) = V - ct - 4P - n(U - 2V)$, with $c$ a constant. $V - ct - 4P$ is the surface energy, which is the dominant term for small $n$ and acts as a energy barrier for the phase transition. So the surface energy is lowered by $P$, implying that $P$ can drive the SDW-CDW phase transition from 1st to 2nd order.

5.5 Conclusions

From these considerations we may conclude that a description by means of Hubbard-like Hamiltonians, using renormalized parameters, may yield misleading results. When we take screening effects into account explicitly, we showed that the conductivity gap in the spin density wave regime is determined by the screened on-site Coulomb repul-
sion and independent of nearest neighbor Coulomb repulsion. The point, however, at which the transition from the spin density wave to the charge density wave regime takes place, is determined by the bare values of on-site and nearest neighbor Coulomb interactions. We gave a full phase diagram for the interaction part of the extended Hubbard model including polarization screening. Two new phases, one of which is ferroelectric, and a $U = 0$ phase transition appear. The $U = 0$ phase transition between two different types of charge density waves shows that the effect of a nearest neighbor Coulomb interaction and a polarizability are quite different. Furthermore polarization screening tends to drive the SDW-CDW phase transition from 1st to 2nd order. This may serve as an example of the fact that in predicting phase transitions in the various Hubbard models, screening cannot be taken into account by using effective parameter sets, but that screening mechanisms should be explicitly incorporated in the model Hamiltonian. We believe that more studies of this type of Hamiltonian, including also the effect of $t$ on the phase diagram, different dimensions and frustrated lattices, could lead to new insight into correlated systems. Of special interest also is a study of a system in which the polarizable atoms are different from the ones with the open shell as for example in CuO or the high $T_c$ superconductors.

References


