# New Phases in an Extended Hubbard Model Explicitly Including Atomic Polarizabilities

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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 neighbor Coulomb interaction which reduces energies of locally neutral excitations. We find that the spin density to 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. We show that new phases appear, one of which is ferroelectric, when atomic polarizabilities are explicitly included.

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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]

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

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 $\langle ij\rangle$.

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 that 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 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 $H_{\text{pol}}$ has the direct influence of screening 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 first to second 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.

We start with a brief review of some aspects of the extended Hubbard model described by Eq. (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 $|\underline{\uparrow}\,\underline{\downarrow}\,\underline{\uparrow}\,\underline{\downarrow}\rangle$. For $V > V_c$ the ground state is a diamagnetic charge density wave [6], which can be represented as $|\,\underline{\uparrow\downarrow}\;\underline{\uparrow\downarrow}\rangle$. 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 $U/t$ and first order for large $U/t$, with the crossover occurring at $U/t \approx 3$ [6,17].

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 charged neutral excitations. Charged excitations are not screened and therefore the correlation gap is not reduced [18]. This 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. The influence of $V$ is to introduce new charge transfer excitonic (charge neutral) states inside the gap.

To demonstrate this we show in Fig. 1 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. We see that the conduction gap defined as $E_{\rm GS}^{N-1} + E_{\rm GS}^{N+1} - 2E_{\rm GS}^{N}$, 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 $V_c = U/2$. For $V > V_c$ the gap increases with $V$. At $V_c$ there is a phase transition from the SDW to the CDW ground state. In the limit $t \rightarrow 0$ the gap is $U$ for $V < V_c$ and is $4V - U$ for $V > V_c$ (for general bipartite lattices the gap is given by $2zV - U$ for $V > V_c$).

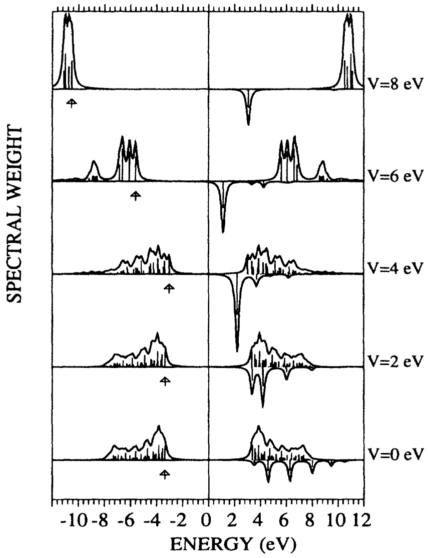

FIG. 1. Electron removal, electron addition, and optical spectra for a 14 site extended Hubbard ring. For each value of $V$ the upper curves are the electron removal or addition spectra and the lower curve is the optical spectrum. The zero for the optical spectrum is at the first ionization states, indicated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

Also shown in Fig. 1 is the optical conductivity, calculated using the current-current correlation function. These spectra are drawn with the zero of energy at $E_{\rm GS}^{N-1}$. We see states at energies below the conduction gap which are excitonic in origin. These excitonic states soften as $V$ increases and approach the center of the gap for $V \rightarrow V_c$. This behavior is not new and certainly not unexpected. For the CDW phase, excitonic states are again present in the gap at an energy of $3V - U$ for $t \rightarrow 0$ above the ground-state energy of the $N - 1$ particle system.

We now consider the atoms to be polarizable. In Fig. 2 we show how the surrounding atoms polarize due to higher order Coulomb interactions (for a discussion see de Boer, Haas, and Sawatzky [19]). Moving an electron from one atom to another, far away, will polarize the surrounding atoms of the created hole and of the created double occupied site. The polarization or relaxation energy that reduces the ionization potential $E^I$ and enhances the electron affinity $E^A$, is given by

$$E_{\rm pol} = \frac{1}{2} \sum_j \alpha_j \vec{F}_j^2 , \qquad (2)$$

where $\alpha_j$ is the polarizability at site $j$ and $\vec{F}$ is the electric field at site $j$. We have neglected dipole-dipole corrections [19]. So $E_{\rm pol}$ has the effect of reducing the gap from $U$ to $U - 2E_{\rm pol}$ in the limit $t \rightarrow 0$.

We want to study the consequences of explicitly including such an interaction in the Hamiltonian. Consider an interaction term such as

$$H_{\rm pol} = -P \sum_i \left( \sum_{j \in \{{\rm nn}(i)\}} n_j \vec{\delta}_{ij} \right)^2 , \qquad (3)$$

where $\vec{\delta}_{ij}$ is the unit position vector connecting neighboring sites $i$ and $j$ and $n_j \equiv \sum_\sigma n_{j\sigma}$ . The sum over the nearest neighbors is proportional to the electric field $\vec{F}_i$ on site $i$. With $E_{\rm pol} = zP$, $H_{\rm pol}$ describes the relaxation energy due to placing a charge in a polarizable medium.

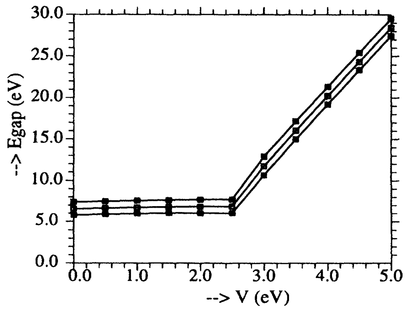

FIG. 2. Schematical representation of the excited SDW state. The charge excitation defining the effective Coulomb repulsion $U$ and induced polarizations are indicated.

It is assumed that polarization processes are much faster than the time scale related to the electron hopping.

Using exact diagonalization of finite clusters we studied the influence of adding $H_{\text{pol}}$ to the extended Hubbard model. In Fig. 3 we show the conduction gap as a function of $V$, for various values of $P$ for a 2D 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 in one and two dimensions and found that finite size effects do not alter this conclusion, although the 2D cluster is still rather small for studying the polarization effect. 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 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 double occupied sites in the CDW phase costs the unscreened value of $U$. For $t = 0$, the total energy $E_{\text{SDW}} = zNV/2$ and $E_{\text{CDW}} = NU/2$.

For a hypercubic lattice it is possible to exactly map the total Hamiltonian onto a new Hamiltonian that has a more transparent form. The interaction part of this Hamiltonian reads

$$H_{\text{int}} = (U - 2zP)\sum_{\vec{l}} n_{\vec{l}\uparrow}n_{\vec{l}\downarrow} + V\sum_{\vec{l},i} n_{\vec{l}}n_{\vec{l}+\vec{a}_i} + zP\sum_{\vec{l},i} n_{\vec{l}}n_{\vec{l}+2\vec{a}_i}, \qquad (4)$$

where the sum over $i$ is the sum over the unit lattice vectors $\vec{a}_i$. 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. 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 $V$ 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 $P = U/8$ provided they crystallize into a lattice as shown in Fig. 4. 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. 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 various one dimensional small clusters [20]. These indicate that the global maximum of the order parameter changes discontinuously and the transition is first order for small polarization. For large polarization the maximum changes continuously, indicating a second 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 sceening 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 $n$

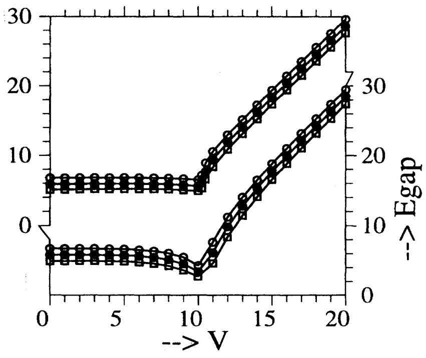

FIG. 3. Size of the conduction gap $E_{\text{gap}}$ as a function of the intersite Coulomb repulsion $V$ for a 1D 14 site cluster (lower curves) and a 2D 10 site extended Mott-Hubbard cluster (upper curves), with inclusion of polarizable atoms. The on-site Coulomb repulsion $U$ is kept constant at 10 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.

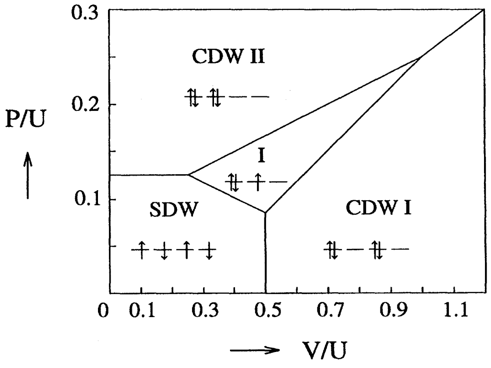

FIG. 4. Phase diagram in an infinite one dimensional extended Hubbard system including polarization screening in the atomic limit. $P$ is the polarization energy and $V$ the nearest-neighbor Coulomb repulsion. A spin density wave phase, two types of charge density wave phases, and an intermediate ferroelectric phase are indicated. For each phase, translation invariant electron configurations are schematically shown.

and acts as an 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 first to second order.

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 repulsion 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 first to second 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 $T_c$'s.

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[1] J. Hubbard, Proc. R. Soc. London A **276**, 238 (1963).
[2] J. Hubbard, Phys. Rev. B **17**, 494 (1978).
[3] V. J. Emery, Phys. Rev. Lett. **58**, 2794 (1987).
[4] F. C. Zhang and T. M. Rice, Phys. Rev. B **37**, 3759 (1988).
[5] V. J. Emery, in *Highly Conducting One-Dimensional Solids,* edited by J. T. Devreese, R. P. Evrard, and V. E. van Doren (Plenum, New York, 1979).
[6] J. E. Hirsch, Phys. Rev. Lett. **53**, 2327 (1984).
[7] Y. Zhang and J. Callaway, Phys. Rev. B **39**, 9397 (1989).
[8] X.-Z. Yan, Phys. Rev. B **48**, 7140 (1993).
[9] L. Milans del Bosch and L. M. Falicov, Phys. Rev. B **37**, 6073 (1988).
[10] J. Zaanen and G. A. Sawatzky, J. Solid State Chem. **88**, 8–27 (1990).
[11] R. W. Lof *et al.*, Phys. Rev. Lett. **68**, 3924 (1991).
[12] N. F. Mott and M. J. Littleton, Trans. Faraday Soc. **34**, 485 (1938).
[13] C. Haas, in *Physics of Intercalation Compounds,* edited by L. Pietronero and E. Tosatti (Springer, Berlin, 1981).
[14] V. P. Antropov, O. Gunnarson, and O. Jepsen, Phys. Rev. B **46**, 13 647 (1992).
[15] S. Mazumdar and A. N. Bloch, Phys. Rev. Lett. **50**, 207 (1983).
[16] P. Fulde and G. Stollhoff, J. Phys. (Paris) **50**, 2659 (1989).
[17] J. W. Cannon, R. T. Scalettar, and E. Fradkin, Phys. Rev. B **44**, 5995 (1991).
[18] M. B. J Meinders, L. H. Tjeng, and G. A. Sawatzky, Phys. Rev. Lett. **73**, 2937 (1994).
[19] D. K. G. de Boer, C. Haas, and G. A. Sawatzky, Phys. Rev. B **29**, 4401 (1984).
[20] J. van den Brink *et al.* (to be published).