Atomic screening and intersite Coulomb repulsion in strongly correlated systems

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(Received 8 December 1994)

We consider the influence of a nearest-neighbor Coulomb interaction in an extended Hubbard model and introduce an interaction term which simulates atomic polarizabilities. The inclusion of atomic polarizabilities in the model has the effect of screening the on-site Coulomb interaction for charged excitations, unlike a neighbor Coulomb interaction which reduces energies of neutral local excitations, leaving the conductivity gap unchanged. This is supported by an exact diagonalization study on small, mainly one dimensional, extended Mott-Hubbard systems. For large $V$, the system undergoes a phase transition from a spin-density wave (SDW) to a charge-density wave (CDW). It is shown that the SDW/CDW phase transition cannot be described correctly when using effective parameters, but that screening effects have to be included explicitly. Also other phases, one of which is ferroelectric, appear when atomic polarizabilities are included in the model Hamiltonian. We study $C_{60}$ in terms of the degenerate extended Hubbard model with screening effects.

I. INTRODUCTION

The discovery of high-temperature superconductivity has enhanced the interest in a set of Hubbard-like models that are used to describe the electronic structure of strongly correlated transition metal oxides. As already pointed out by Hubbard,\textsuperscript{1} for a realistic description of materials one should use the screened (effective) Coulomb repulsion $U$ in the Hubbard-like Hamiltonians, rather than the unscreened (bare) atomic values $U_0$. The screening energies are mostly comparable or even (much) larger than the effective Coulomb repulsions. For the 3$d$ transition metal Cu, for instance, $U_0 \approx 16$ eV is screened to $U \approx 5$ eV.\textsuperscript{2} In Sec. II, we show that a nearest-neighbor Coulomb repulsion cannot cause such a screening. In Sec. III, we introduce a model that illustrates how in these insulators the on-site Coulomb repulsion is screened by virtual high energy local charge excitations. These excitons are coupled to the correlated electrons by the intrinsic electric fields that the correlated electrons generate. We show that these indeed screen the on-site Coulomb repulsion. This, however, cannot be accounted for by using renormalized parameters in a simple Hubbard model. This because, for instance, the spin-density-wave/charge-density-wave (SDW/CDW) transition in the extended Hubbard model is governed by the bare values of the on-site and nearest-neighbor Coulomb repulsion. Furthermore, the screening introduces new phases, one of which is ferroelectric, in the model.\textsuperscript{3}

We first study the extended Hubbard model, which includes a nearest-neighbor Coulomb repulsion, and investigate whether the atomic on-site Coulomb repulsion is reduced (screened) by $V$. A motivation to do this, is that recently Brühwiler et al.\textsuperscript{4} reported a comparative carbon $1s$ autoionization study of solid $C_{60}$ and Xe-matrix isolated $C_{60}$. From differences in the spectra, they deduce that nearest-neighbor hopping of valence-band electrons in the presence of the C $1s$ core hole in solid $C_{60}$ is facilitated by a nearest-neighbor Coulomb repulsion $V$ of the order of $0.7$ eV. This implies that in stoichiometric $K_3C_{60}$, the energy cost for an electron to hop to its nearest neighbor is of the order of $U - V$. From this they assert, with reference to the extended Mott-Hubbard model calculations (which take both $U$ and $V$ into account) by Antropov et al.,\textsuperscript{5} that the on-site Coulomb repulsion $U$ is effectively reduced by $V$, with the result that the conductivity gap is not opened, in spite of the relatively small one-electron bandwidth $W$. They, therefore, claim that stoichiometric $K_3C_{60}$ is not a Mott-Hubbard insulator, because $(U - V)$ is comparable or less than $W$. We study the size of the conductivity gap for nondegenerate (single band), as well as degenerate Mott-Hubbard insulators as a function of the intersite Coulomb repulsion $V$ and it is shown in Sec. II that the assertions made by Brühwiler et al. and Antropov et al. are invalid. It is, however, noted that the energy to create a charge-neutral exciton is indeed reduced by the nearest-neighbor Coulomb repulsion. Therefore, $V$ does enter in the calculation of the exchange interaction, which for the extended Mott-Hubbard system yields in second order $J_{EMH} = 2t^2/(U-V)$, rather than $J_{MH} = 2t^2/U$. In Sec. IV, we study some nonbipartite lattices and the influence of orbital degeneracy, in order to come closer to the real world of transition metal and $C_{60}$ compounds.

II. SINGLE-BAND EXTENDED HUBBARD MODEL

The nondegenerate (single-band) extended Mott-Hubbard system has been studied by several people,\textsuperscript{6-11} although, to the best of our knowledge, the conductivity gap has never been studied explicitly. We consider the extended Mott-Hubbard (EMH) system at half filling.
The Hamiltonian is defined as

\[ H_{EMH} = -t \sum_{\langle ij \rangle} (\hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + \text{H.c.}) + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} \]

\[ + V \sum_{\langle ij \rangle} \hat{n}_{i\sigma} \hat{n}_{j\sigma'}, \]  

(1)

where \( \hat{n}_{i\sigma} = \hat{c}_{i\sigma}^\dagger \hat{c}_{i\sigma} \) and \( \hat{c}_{i\sigma} \) (\( \hat{c}_{i\sigma}^\dagger \)) creates (annihilates) an electron (or hole) on site \( i \) with spin \( \sigma = \uparrow \) or \( \downarrow \). A nearest-neighbor pair is denoted by \( \langle ij \rangle \). \( U \) is the on-site Coulomb repulsion between two electrons (holes) on the same site and \( V \) is the inter-site Coulomb repulsion between two electrons (holes) on neighboring sites. The hybridization between nearest-neighbor orbitals is denoted by \( t \), allowing electrons hopping to adjacent sites. The on-site energies are taken to be zero.

We first consider the EMH model in the localized limit \( \langle t \rightarrow 0 \rangle \). Furthermore, we assume a \( N \)-site bipartite lattice with two-interpenetrating sublattices \( A \) and \( B \) of identical structure, each consisting of \( N/2 \) sites. At half filling \( (N = \mathcal{N}, \text{with } N \text{ the number of electrons}) \) and for small \( V \), the ground state will contain exactly one electron on each site as schematically drawn for a one-dimensional lattice in the upper part of Fig. 1. Also, two types of excitations are shown. The ground-state energy of this SDW state is given by

\[ E_{GS,SDW} = \frac{1}{2} zVN, \]

(2)

where \( z \) is the number of nearest neighbors or coordination number. The conductivity gap of the \( N \)-particle system \( E_{GS}^N \) is defined as the difference between the ionization potential and electron affinity, yielding

\[ E_{gap}^N = E_I^N - E_A^N = E_{GS}^{N+1} + E_{GS}^{N-1} - 2E_{GS}^N. \]

(3)

It is now easy to show that the ground-state energies of the \( N+1 \) and \( N-1 \) particle system is given by

\[ E_{GS,SDW} = E_{GS,SDW}^N + zV + U, \]

(4)

\[ E_{GS,SDW} = E_{GS,SDW}^N - zV, \]

(5)

respectively. So for the SDW ground state, we find \( E_{gap,SDW} = U \), independent of the inter-site Coulomb interaction \( V \). Using open- instead of periodic-boundary conditions yields a surface state of the \( N+1 \) particle system pushed out into the conductivity gap. This will lead to a lowering of the gap with \( V \). However, this state has a bound electron on the surface and will not contribute to the conductivity.

For large \( V \), the ground state at half filling will form a CDW to avoid electrons on neighboring sites as much as possible. This situation is schematically sketched for a one-dimensional chain in the lower part of Fig. 1, as well as two possible types of excitations. The CDW-ground-state energy is given by

\[ E_{GS,CDW}^N = \frac{1}{2} U \mathcal{N} = \frac{1}{2} U N. \]

(6)

Comparing this energy with the SDW–ground-state energy \([\text{Eq. (2)}]\), it is seen that the EMH system will form a SDW when \( zV < U \), while it forms a CDW when \( zV > U \). In the CDW regime, the ground-state energies of the \( N+1 \) and \( N-1 \) particle system are given by

\[ E_{GS,CDW}^{N+1} = E_{GS,CDW}^N + 2zV, \]

(7)

\[ E_{GS,CDW}^{N-1} = E_{GS,CDW}^N - U, \]

(8)

respectively. This yields for the conductivity gap \( E_{gap,CDW} = 2zV - U \), which is larger than \( U \). Also at quarter filling and three-quarter filling, a CDW ground state is formed. For these doping concentrations the conductivity gap is equal to \( E_{gap} = zV \).

The fact that the gap is not reduced by \( V \), is not necessarily inconsistent with the experimental observations of Brühwiler et al.\(^4\) for \( C_{60} \). The energy involved for a nearest-neighbor inter-site hopping is indeed reduced by \( V \), as indicated in the upper part of Fig. 1. It is, however, important to realize that the corresponding state at about \( U - V \) is excitonic in nature, because it can only propagate if both hole and electron move together. It is, therefore, a charge-neutral exciton and does not contribute to the conductivity. Excitonic states may be observed in optical experiments, that probe the \( N \)-particle states of the system, but the excitation energies are, in general, not a measure for the charge-excitation gap.

If we include other longer-range diagonal Coulomb interactions (for instance, next-nearest-neighbor Coulomb repulsion) in the model, the above arguments remain unaltered. So the conclusions reached regarding the effect of a nearest-neighbor Coulomb interaction hold for any longer-range diagonal Coulomb interaction.

**A. Influence of intersite hybridizations**

It is expected that the above considerations do not change fundamentally when inter-site hybridization is included. To verify this, we performed an exact diagonal-
ization study for finite EMH clusters. We used periodic-boundary conditions and the Lanczos method, as, for instance, described in Refs. 12, 13, to calculate the ground-state energies, one-electron removal and addition spectra, as well as spin-spin and charge-charge correlation functions.

In the left part of Fig. 2, the imaginary part of the one-electron removal Green's function, corresponding to the photoemission (PES) spectrum and addition Green's function, corresponding to the inverse photoemission (IPES) spectrum is shown for a one-dimensional $N = 10$ site EMH cluster, at half filling $(N = N)$, for $U = 10$ eV, $t = 1.5$ eV, and for different values of $V$. In the right part of the figure, the corresponding values of the conductivity gap are shown, as well as $E_{\text{gap}}$ calculated for a two-dimensional ten-site EMH cluster. The conductivity gap hardly changes with $V$ when the half-filled system forms a SDW ground state ($zV < U$, $z = 2$ for the one-dimensional system, $z = 4$ for the two-dimensional system) and is of the order of $U - W$, where $W = 2zt$. This implies that the importance of correlation effects is dependent on the parameter $U/W$ and not on $(U - V)/W$. For $zV > U$, the conductivity gap increases with $V$, with a slope approximately equal to $2z$.

The calculation shows that for small values of $V$, the conductivity gap is somewhat increasing, while near the SDW/CDW phase transition it is somewhat decreasing. This is observed for one-dimensional four-, eight-, and ten-site clusters, but not for a six-site cluster. For two-dimensional systems, the decrease was almost absent. The maximal decrease was found to be about one quarter of the gap value at $V = 0$. However, no consistent relation between the ratio of $E_{\text{gap}}$ at $V = U/z$ and at $V = 0$, and $U/t$ and/or cluster size could be obtained. The decrease in $E_{\text{gap}}$ is due to the fact that the one-hole and one-electron-doped ground states gain more energy, due to the mixing of the SDW and CDW near the phase transition than the half-filled correlated insulator. This can nicely be seen in Fig. 3, where all eigenenergies of a half-filled (right), as well as one-hole-doped (left) four-site cluster, are shown for $U = 10$, $t = 1$ and different values of $V$. Also some corresponding eigenstate configurations are indicated. At half filling, there is a sharp change in slope of the ground-state energy, as a function of $V$ at the phase transition, while the ground-state energy of the hole-doped system varies more smoothly. The fact that the half-filled ground states for the one-dimensional four-, eight-, and ten-site clusters do not gain that much energy

![FIG. 2. Left: PES/IPES spectra, calculated for a $N = 10$ site extended Mott-Hubbard ring at half filling $(N = N)$, with $U = 10$ eV and $t = 1.5$ eV, for different values of the nearest-neighbor repulsion $V$. Right: The corresponding calculated conduction gap $E_{\text{gap}}$, as a function of the nearest-neighbor repulsion $V$ (•). Also plotted is $E_{\text{gap}}$ for a two-dimensional ten-site EMH system, with $U = 10$ and $t = 0.75$ (○).]

![FIG. 3. All eigenvalues of a one-hole-doped (left, $N = 3$) and half-filled (right, $N = 4$) four-site EMH cluster for $U = 10$ and $t = 1$ eV. The labels in the figures correspond to the eigenstate configurations in the localized limit: $a \sim \{\uparrow \downarrow \ldots \}$; $b \sim \{\uparrow \downarrow \ldots \}$; $c \sim \{\uparrow \downarrow \ldots \}$; $A \sim \{\uparrow \ldots \}$; $B \sim \{\uparrow \downarrow \ldots \}$; $C \sim \{\uparrow \downarrow \ldots \}$; $D \sim \{\downarrow \uparrow \ldots \}$; $E \sim \{\uparrow \downarrow \ldots \}$.]


due to the mixing of the SDW and CDW states, as the one-electron- and hole-doped ground state, is probably due to the fact that, near the phase transition, states become important which have a three-site unit cell, like, for instance, the state $|\uparrow \uparrow \downarrow \rangle$. These states will be frustrated in the one-dimensional four-, eight-, and ten-site clusters and will, therefore, be higher in energy, so the mixing with the low lying SDW and CDW states will be reduced. In the one-dimensional six-site cluster, where no decrease in the value of the conductivity gap near the phase transition was observed, these three-unit-cell states are not frustrated and may push the ground state to lower energy. Therefore, it is expected that the decrease in the conductivity gap near the phase transition is a finite size effect.

The appearance of excitonic states, as well as the phase transition from a SDW to a CDW when increasing the intersite Coulomb repulsion $V$ is shown in Fig. 4. In Fig. 4 the combined one-electron removal and addition spectrum of the extended Hubbard model in one dimension, calculated by exact diagonalization, using an eight-site cluster with periodic boundary conditions is shown. Also shown is the optical conductivity, calculated using the current-current correlation function. The optical spectra are drawn with the zero of energy at $E_{GS}$. Here, optical excitations at energies below the conduction gap, which are excitonic in origin are present. These excitonic states soften as $V$ increases and approach the center of the gap for $V \rightarrow V_c$.

The SDW/CDW phase transition can also clearly be seen in Fig. 5, where the charge structure factor

$$C(q) = \frac{1}{N} \sum_{i,j} e^{i\mathbf{q} \cdot (\mathbf{R}_i - \mathbf{R}_j)} \langle \hat{n}_i \hat{n}_j \rangle,$$

(9)

where $n_i = \sum_{\sigma} c_{i\sigma}^\dagger c_{i\sigma}$, is shown for a one-dimensional eight-site EMH cluster at half filling with $U = 10$ eV, and $t = 1$ eV, for $q = \pi$ and for different values of $V$. Also shown is the spin structure factor, defined as

$$S(q) = \frac{1}{N} \sum_{i,j} e^{i\mathbf{q} \cdot (\mathbf{R}_i - \mathbf{R}_j)} \langle S_i^z S_j^z \rangle,$$

(10)

where $\langle \cdot \rangle$ denotes the expectation value in the ground state and $S_i^z$ is the total spin in the $z$ direction at site $i$.

In a one-dimensional system the phase transition is found to be second order for small $V/U$ and first order for large $V/U$, with the crossover occurring at $V/U \approx 3$. According to Fig. 5, the phase transition occurs for a value of $V$, which is slightly larger than $U/\pi$. As pointed out by Hirsch,\textsuperscript{7} this is due to the fact that, for zero intersite hybridization, the degeneracy of the SDW [of the order of $N/2$] is much larger than the degeneracy of the CDW (equal to 2). When the hybridization is turned on, the SDW state lifts its large degeneracy with the result that its energy gain is larger than that of the CDW state. Therefore, at $U = zV$, the SDW ground state still will have a lower energy than the CDW ground state. For a one-dimensional system and to second order in $t$, the energy difference at $U = 2V$ is given by $E_{SDW} - E_{CDW} = -2t^2 N/2 \ln 2 - 1)/V$.

FIG. 4. Electron removal, electron addition, and optical spectra for an eight-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.

FIG. 5. The calculated spin-structure factor (left) and charge-structure factor (right) at $q = \pi$, divided by the number of sites, as a function of the nearest-neighbor repulsion $V$ for eight-site extended Mott-Hubbard ring with $U = 10$ eV and $t = 1$ eV. The structure factors are defined in the text.
III. ATOMIC SCREENING EFFECTS

Hubbard-like models 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. 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. For a realistic description of materials one should use the screened (effective) Coulomb repulsion \( U \) in the Hubbard-like Hamiltonians, rather than the unscreened bare atomic values \( U_0 \).

Consider an atom or molecule \( X \) with an incompletely filled shell, for instance, the 3d shell in the case of the transition metals or the \( t_2g \) orbital in the case of the fulerides. The bare atomic on-site Coulomb interaction \( U_0 \) of “atom” \( X \) is then defined as the difference between the atomic ionization potential \( E_{10} = E_{X^+} - E_X \) and electron affinities \( E_{A0} = E_X - E_{X^-} \). For a hydrogen atom \( (X = H) \) this yields \( U_0 = E_{10} - E_{A0} \approx 13.6 - 0.75 \approx 12.9 \) eV, and for \( X = C_{60} \), \( U_0 \) is approximately 3.0 to 3.5 eV. If a solid is constructed with these atoms, thereby creating a polarizable surrounding for one particular atom, the effective Coulomb repulsion \( U \) would be the energy required to move an electron from one atom to another atom far away. In that case, \( U \) is equal to the difference of ionization potential \( E_I = E_{GS}^{N-1} - E_{GS}^N \) and electron affinity \( E_A = E_{GS}^N - E_{GS}^{N+1} \) of the solid, where \( E_{GS}^{N(\pm 1)} \) are the ground-state energies of the \( N(\pm 1) \) electron system.

The effective Coulomb repulsion \( U \) is (mostly) much smaller than the bare Coulomb repulsion \( U_0 \). For \( C_{60} \) for instance, the bare Coulomb repulsion \( U_0 \) is screened to a value of \( U \approx 1.5 \) eV (Ref. 15) and for the 3d transition metal \( Cu \), \( U_0 \approx 18 \) eV is screened to \( U \approx 5 \) eV. This screening involves longer-range off-diagonal Coulomb interactions, which apparently have, in the end, a large effect. We now investigate if it is justified to neglect these in the low energy scale Hamiltonian.

A. A model Hamiltonian describing screening

We will derive a Hamiltonian that 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 \( P_i = -eX_{sp}(p_i s_i + s_i p_i) \). When we take the zero of energy at the \( s \) level, we end up with a polarization Hamiltonian of the form

\[
H_{\text{pol}}^0 = \sum_i -P_i \cdot F_i + \Delta_{sp} P_i^\dagger P_i. \tag{11}
\]

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

\[
F_i = -\frac{e}{a^2} \sum_{j \in \{ \text{n.n.}(i) \}} \hat{n}_j \delta_{ij}, \tag{12}
\]

where \( a \) is the interatomic spacing and \( \delta_{ij} \) is the unit position vector connecting neighboring sites \( i \) and \( j \). If we combine Eqs. (11) and (12), we arrive at an explicit form for the polarization Hamiltonian in one dimension of

\[
H_{\text{pol}}^{1D} = \frac{e^2}{a^2} |X_{sp}| \sum_i (\hat{n}_{i+1} - \hat{n}_{i-1})(p_i^\dagger s_i + s_i^\dagger p_i)
+ \Delta_{sp} P_i^\dagger P_i. \tag{13}
\]

The total Hamiltonian \( H = H_{\text{EMH}} + H_{\text{pol}}^0 \) includes three single-electron levels per site (excluding spin); being the \( s \) and \( p \) level describing the polarization [Eq. (11)] and the correlated Hubbard level [Eq. (1)]. In the next section, we will present some exact diagonalization results on the extended Hubbard model, with the inclusion of the polarization Hamiltonian [Eq. (11)]. Before doing this, we derive a single-band equivalent of this Hamiltonian, 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 \( \Delta_{sp} \gg t \). 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 \( E_0 + \Delta_{sp} \). The second order perturbation theory gives

\[
E = E_0 - \sum_i \frac{|\langle \phi_i | H_{\text{pol}} | \phi_0 \rangle|^2}{\Delta_{sp}^2}.
\]

Combined with Eq. (12), this results in a polarization Hamiltonian:

\[
H_{\text{pol}} = -P \sum_i \left( \sum_{j \in \{ \text{n.n.}(i) \}} \hat{n}_j \delta_{ij} \right)^2, \tag{15}
\]
with $P = \frac{x_0^2}{\Delta_{sp}}$. The interaction in Eq. (15) is the instantaneous, non-retarded part of the interaction in Eq. (11). In Fig. 6, 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.:\(^{17}\)

$$E_{\text{pol}} = -\frac{1}{2} \sum_i \alpha_i P_i^2$$  \hspace{1cm} (16)

where $\alpha_i = 2P x_0^2$ is the polarizability at site $i$ and dipole-dipole corrections are neglected.

For a hypercubic lattice, it is possible to map the total Hamiltonian $H = H_{\text{EMH}} + H_{\text{pol}}$ exactly onto a new Hamiltonian, which has a more transparent form. The interaction part of this Hamiltonian reads

$$H_{\text{pol}}^{\text{int}} = (U_0 - 2zP) \sum \hat{n}_R + V \sum_{\delta} \hat{n}_R \hat{n}_{R+\delta} + zP \sum_{\delta} \hat{n}_R \hat{n}_{R+2\delta},$$  \hspace{1cm} (17)

where the sum over $i$ is the sum over all lattice points, the sum over $\delta$ is over all unit lattice vectors and $z$ is the coordination number. The polarization renormalizes the on-site interaction and introduces a new repulsive next-nearest-neighbor interaction term.

\section*{B. Correlation gap and exchange}

We consider the extended Hubbard model at half filling and include instantaneous screening effects: $H = H_{\text{EMH}} + H_{\text{pol}}$. First consider the model in the localized limit ($t \to 0$). Removing an electron from a particular site will polarize its surrounding, thereby lowering the ground-state energy of the $N - 1$ electron system with an amount equal to the polarization energy $E_{\text{pol}} = zP$, as schematically shown in Fig. 6. Therefore, we find that the atomic ionization potential is diminished with the polarization energy, yielding $E_I = E_{10} - E_{\text{pol}}$. In the same way, it is found that adding an electron on a particular site results in a lowering of the $N + 1$ electron ground state (see Fig. 6) and yields, therefore, an increase of the electron affinity $E_A = E_{A0} + E_{\text{pol}}$. The effective Coulomb repulsion $U$ is now given by

$$U = U_0 - 2zP.$$ \hspace{1cm} (18)

This could be expected, since the interaction part of our Hamiltonian is given by Eq. (17), and we proved in Sec. II that the correlation gap only depends on $U$ and $t$, and is independent of (next) nearest-neighbor interactions.

In Fig. 7, an exact diagonalization result for the value of the correlation gap for a one-dimensional six-site cluster as a function of $P$ is shown. The validity of expression Eq. (18) is confirmed. Also shown is the gap value in the EMH with the retarded interaction Eq. (11). For small values of $X_{\text{sp}}^x / \Delta_{sp}$, this indeed yields the same results as for the non-retarded interaction Eq. (13). In Sec. II, the expression for the exchange in an EMH was given: $J = -2t^2/(U - V)$. When we include screening, this expression is still correct, with the understanding that $U$ in this expression is the effective on-site Coulomb repulsion, $V$ is not affected by this type of screening, and the next-nearest-neighbor interaction does not come into play in the second order strong coupling perturbation theory expression for $J$.

\section*{C. SDW-CDW phase transition}

Is the SDW-CDW phase transition in the EMH affected by screening? At first glance, one could expect that as the on-site Coulomb repulsion is screened and the nearest-neighbor Coulomb repulsion is not, that the phase transition occurs at $V_c = U/z$. It will be shown below, however, that the transition is governed by the bare values for the Coulomb repulsions: $V_c = U_0/z$. Using exact diagonalization of finite clusters, we first study the influence of adding $H_{\text{pol}}$ to the extended Hubbard model.
In Fig. 8, we show the conduction gap as a function of $V$, for various values of $P$ for a two-dimensional eight-site cluster at half filling. We see that for $P = 0$, $V$ does not influence the gap for $V < V_c$, as discussed above. We also see, as expected, that $P$ does reduce the gap and has the effect of screening $U$. Strangely enough though, the SDW-CDW transition occurs at the unscreened value of $V_c = U_0/4$ in two dimensions. This can be understood by realizing that in the CDW state, each site has inversion symmetry so no net fields are present and, therefore, $H_{pol} = 0$ for the ground state. So to produce the double occupied sites in the CDW phase costs the unscreened value of $U_0$. For $t = 0$, the total energy $E_{SDW} = zNV/2$ and $E_{CDW} = NU_0/2$.

So polarization screening does not affect $V_c$, but it is, however, 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 $m_0 = \sum_i \langle \Psi_{GS} \mid (-1)^i \hat{n}_i \Psi_{GS} \rangle$ of the ground-state wave function has a unique value. However, within the real space basis, one can think of it as being a sum over a distribution of possible values of $m$, with probabilities $P(m)$: $m_0 = \sum_m mP(m)$. 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 of the phase transition by noting whether the maximum of the distribution changes continuously (second order), or discontinuously (first order). We calculated the order parameter distribution function for $U/t = 4$ and for $P = 0$ and $P = 0.25$, respectively, see Fig. 9. 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 first order. For $P = 0.25$, however, 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. 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 of order 1. $V - ct - 4P$ is the surface energy, which is the dominant term for small $n$ 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.

**D. Other phases**

Apart from the SDW and CDW phases, the new repulsive term in $H_{pol}$ adds new phases into the phase diagram. In Fig. 10, we show the new phase diagram for a one-dimensional system in the localized limit, at half filling. 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. We expect that this phase appears when $P$ is large, so that the number of next-nearest-neighbor electrons is mini-
mized for the ground-state energy. The ground-state energy for the system with a charge-density wave of the type \[^{\cdw II}\text{type}^{\cdw II}\text{type}\], is

\[
E_{\text{GS,CDWII}}^N = \mathcal{N} \left( \frac{U}{2} + V - 4P \right). \tag{19}
\]

Combined with Eq. (2), this implies that a SDW-CDW II phase transition occurs at \(P = \frac{U}{8}\). This phase forms before the negative \(U\) regime, where \(U_0 - 2zP < 0\), i.e., \(P > \frac{U}{8}\) in one dimension, begins.

In the phase diagram Fig. 10 also an intermediate phase (INT) appears, a phase that consists of a combined charge-density and spin-density wave. The ground-state energy for the system in the intermediate phase, crystalized into a lattice with unit cell \(\ldots \uparrow \uparrow \downarrow \ldots \uparrow \downarrow \downarrow \ldots\) is

\[
E_{\text{GS,INT}}^N = \mathcal{N} \left( \frac{U}{3} + 2V - 6P \right). \tag{20}
\]

This results, for instance, in a triple point when \(E_{\text{GS,SDW}}^N = E_{\text{GS,CDW}}^N = E_{\text{GS,INT}}^N\), i.e., for \(V/U = 1/2\) and \(P/U = 1/12\).

The intermediate phase does not have a point of inversion symmetry. The inversed configuration \(\ldots \uparrow \downarrow \uparrow \ldots \uparrow \downarrow \downarrow \ldots\) is \(2P\) higher in energy than the configuration \(\ldots \uparrow \uparrow \uparrow \ldots \uparrow \uparrow \downarrow \ldots\). The lack of inversion symmetry implies that the intermediate phase is ferroelectric.

IV. FRUSTRATION AND ORBITAL DEGENERACY

When dealing with real systems like the transition metal, rare earth, or \(\text{C}_{60}\) compounds, the correlated electrons often move in orbitally degenerate bands and the crystal structure may be such that a simple CDW state is frustrated. For example, in \(\text{K}_{2}\text{C}_{60}\), the valence \(t_{1u}\) band is threefold orbitally degenerate and the fcc crystal structure is not bipartite. According to combined PES/IPES and Auger measurements \(U \approx 1.3 - 1.6\) eV in \(\text{C}_{60}\), which would suggest that stoichiometric \(\text{K}_{2}\text{C}_{60}\) is a Mott-Hubbard insulator, since \(U/W \approx 2 - 3\). However, \(V\) is believed to be about 0.7 eV. The influence of the polarizability of \(\text{C}_{60}\) on \(U\) has also been recognized, resulting in a screening of the bare \(U_0 = 3.4\) eV (Ref. 20) to about \(1.3 - 1.6\) eV.

In the next sections, we will address some of these questions. Section IVA concerns frustration effects. In Secs. IVB and IVC, we take the degenerate extended Hubbard model as a starting point and study the consequences of introducing screening mechanisms in the model. The degenerate extended Hubbard model (DEHM) description for alkali-metal doped \(\text{C}_{60}\) (Refs. 19–35) is studied extensively in Ref. 34.

A. Frustration

For alkali-metal doped \(\text{C}_{60}\) the formation of CDW may be important because it is believed that \(U\) is only two to three times larger than \(V\). For a bipartite lattice the SDW/CDW phase transition occurs at about \(U = zV\). The coordination number for the fcc structure of, e.g., \(\text{M}_{2}\text{C}_{60}\), is equal to \(z = 12\). However, the lattice structures of the alkali doped compounds are nonbipartite lattices and little is known about the ground state of these frustrated systems. It is, however, expected that also for nonbipartite lattices the conductivity gap at half filling cannot be reduced by \(V\). This can be seen using the same arguments as used in Sec. II in the localized limit. For small \(V \ll U\), the half-filled ground state of the frustrated system will also contain exactly one electron per site. Moving one electron to its nearest neighbor may cost an energy \(U - V\), but again this state will be a charge-neutral exciton, because the hole and the doubly occupied site have to move together. Moving the doubly occupied site away from the hole will again cost an extra energy \(V\). It may also be expected that for large \(V\), certain kinds of charge-density waves may be formed.

Although the value of \(V\) for which a phase transition as well as the form of the CDW may not be known yet, it is expected that the conductivity gap will be proportional to \(V\), but larger than \(U\). To check this, we performed exact diagonalizations on a one-dimensional eight-site nondegenerate frustrated EMH cluster. The cluster can be seen in the right part of Fig. 11. We adopted periodic-boundary conditions.

In Fig. 11, the value of the conductivity gap is shown at half filling (\(N = \mathcal{N}\)) for three different values of the intersite hybridization, \(t = 0, 0.5, 1\) eV, as a function of the nearest-neighbor Coulomb repulsion \(V\). We put \(P = 0\). In all cases the effective Coulomb repulsion \(U = 10\) eV. It can be seen that a phase transition occurs at about \(2V = U\), and not at \(zV = U\) (\(z = 4\)). For small \(V\), the ground state contains one electron per site while for large \(V\), a charge-density wave is formed. The two different phases are indicated in the right part of the figure.

As far as the value of the conductivity gap as a func-
tation of the intersite Coulomb repulsion $V$ is concerned, similar behavior is found as for the half-filled one- and two-dimensional bipartite lattices, although the value of $V$ for which a phase transition occurs may be different from $U/\pi$. Therefore, also for nonbipartite lattices, the conductivity gap cannot be reduced by $V$.

**B. Degeneracy**

In the previous sections, all considerations were made for a single-band nondegenerate extended Hubbard model. Because the transition metal compounds and doped $C_{60}$ should be described by a degenerate Hubbard model, it is worthwhile to investigate to what extent our considerations change for a degenerate system.

Consider the $f$-fold orbital degenerate extended Mott-Hubbard (DEMH) model, defined by the Hamiltonian

$$H_{\text{DEMH}} = \sum_{\langle ij \rangle, \sigma \atop m, m'} t_{mm'} (c_{im\sigma}^\dagger c_{jm'\sigma} + \text{H.c.}) + U \sum_{i, \sigma, \sigma' \atop m, m'} f t_{im\sigma} c_{im\sigma}^\dagger c_{im'\sigma'}^\dagger c_{im'\sigma'}$$

$$+ V \sum_{\sigma, \sigma' \atop m, m'} f c_{im\sigma} c_{im\sigma}^\dagger c_{jm'\sigma'} c_{jm'\sigma'}$$

where $i$ labels the site index, $\langle ij \rangle$ runs over all nearest-neighbor pairs, and $m$ and $m'$ denote the orbital index. The operator $c_{im\sigma}^\dagger$ ($c_{im\sigma}$) creates (annihilates) an electron with spin $\sigma = \uparrow$ or $\downarrow$ in orbital $m$ on site $i$ and $t_{mm'}$ is the hybridization between nearest-neighbor orbitals. Again, we neglect Hund’s rule exchange and assume that the on-site Coulomb repulsion $U$ and the nearest-neighbor Coulomb repulsion $V$ are independent of the orbital quantum numbers. The on-site orbital energies are taken to be zero.

Consider first the DEMH model in the localized limit, where the intersite hopping integrals $t_{mm'}$ are neglected. Furthermore, we again assume a bipartite lattice, with two interpenetrating sublattices $A$ and $B$ of identical structure, each consisting of $N/2$ sites. The energy of an $N$-particle state with an integer number of electrons per site, $n_A$ and $n_B$ on sublattices $A$ and $B$, respectively, is given by

$$E^N = \frac{NN_A n_B}{2} \left( \frac{n_A - 1}{n_A} U + \frac{n_B - 1}{n_B} U + zV \right) + \frac{n_A + n_B = 2n = N/2}{n_B}$$

Making use of the fact that $n_A + n_B = 2n = 2N/N$, we find

$$E^N = \frac{1}{2} n_A n_B (zV - U) + \left( n^2 - \frac{1}{2} \right) U$$

The second term is always positive. The first term is negative for $zV < U$ and will reach its minimum for the maximum value of $n_A n_B$. Therefore, the ground state will be that state with $n_A = n_B = n$, which corresponds to the SDW ground state. When $zV > U$, the first term is positive and will be minimal when $n_A n_B$ is minimal. Therefore, the ground state will form a CDW with a maximal electron (hole) density on one of the sublattices and a minimal density on the other. The occupation numbers are then given by $n_A = \min(2n, 2f)$ and $n_B = \max[0, 2(n - f)]$.

In Fig. 12 (upper part), we show the DMH ground-state configuration for $zV < U$ and two types of excitations. The bars represent the spatial degrees of freedom.

**FIG. 11.** Left: conduction gap $E^N_{\text{gap}}$ for the one-dimensional eight-site nondegenerate frustrated EHM ring at half filling ($N = N$), as a function of $V$. The on-site Coulomb repulsion $U = 10$ eV and hybridization $t = 0$ ($\ast$), $t = 0.5$ eV ($\circ$), and $t = 1.0$ eV. Right: the charge distribution at $t = 0$ for $2V < U$ (top) and $2V > U$ (bottom).

**FIG. 12.** Top: A schematic drawing of the ground-state configuration of a one-dimensional threefold DEMH system in the localized limit at half filling for $2V < U$, representing $K_3C_{60}$. Two types of excitations are indicated. Bottom: The charge-density wave ground-state configuration at half filling (left) and at an integer filling $n > 3$ (right). Possible types of excitations are indicated.
of the orbitals considered and the dots the electrons (spin in the localized limit and for zero exchange is not important). The ground-state energy of this \( N \) electron, \( \mathcal{N} \) site system with an integer number of electrons per site \( n = N/\mathcal{N} \) is, according to Eq. (22), given by

\[
E_{GS}^N = \left( \frac{1}{2}n(n - 1)U + \frac{1}{2}n^2zV \right)\mathcal{N}.
\]

(24)

It is easy to show that the \( N + 1 \) and \( N - 1 \) ground-state energies are given by

\[
E_{GS}^{N+1} = E_{GS}^N + nU + nzV,
\]

(25)

\[
E_{GS}^{N-1} = E_{GS}^N - (n - 1)U - nzV.
\]

(26)

Therefore, we find that also for the degenerate model the conduction gap \( E_{\text{gap}}^N = U \), independent of the nearest-neighbor repulsion \( V \). Furthermore, it is also independent of the range of \( V \).

In the lower part of Fig. 12, the CDW-ground-state configuration and possible excitations are illustrated for the half-filled system and for the case with \( n > f \). It is now easy to show that the conduction gap at half filling (\( n = f \) is equal to \( E_{\text{gap}}^N = U + 2f(zV - U) > U \) and for integer doping with \( n \neq f \), the conduction gap is given by \( E_{\text{gap}}^N = U \). It is also noted that CDW ground states are formed for noninteger occupations as being \( n + 1/2 \), with \( n = 0, 1, \ldots f \). For these occupation numbers, the conduction gap is equal to \( E_{\text{gap}} = zV \). The same considerations concerning the value of the conduction gap also apply for nonbipartite lattices, although the conditions for forming CDW's may be different.

C. Intersite hybridization and polarizabilities

To verify that the considerations will not change fundamentally when including intersite hybridization, we diagonalized the DEMH Hamiltonian [Eq. (21)] exactly. Considering the size of the many-body Hilbert space, we performed the exact diagonalization study on one-dimensional twofold degenerate \( \mathcal{N} = 4 \) site clusters. Furthermore, we used the same parameters as used by Antropov et al.,\(^5\) being an effective Coulomb repulsion \( U = 1.5 \) eV and hopping matrix elements \( t = 2t' = -0.08 \) eV, where \( t \) is the hybridization between orbitals with the same quantum number, while it is \( t' \) between orbitals.

FIG. 13. PES/IPES spectra, calculated for a twofold degenerate, quarter-filled (\( n = 1 \), left) and half-filled (\( n = 2 \), right), four-site Mott-Hubbard ring with \( U = 1.5 \) eV and \( W = 0.48 \) eV for different values of the intersite repulsion \( V \).

FIG. 14. Calculated \( E_{\text{gap}} \) as a function of \( V \) at half filling (\( \ast, n = 2 \)) and quarter and three-quarter filling (\( \circ, n = 1, 3 \)) of the twofold degenerate four-site Mott-Hubbard ring, with \( U = 1.5 \) eV and \( W = 0.48 \) eV.
with different quantum numbers. This yields a total bandwidth $W = 4(|t| + |t'|) = 0.48$ eV. Figure 13 shows the one-electron removal spectra (PES) and one-electron addition spectra (IPES) at quarter filling ($n = f/2$, where $n = N/N$ is the average number of electrons per site, left) and at half filling ($n = f$, right) for different values of $V$. It can be seen that the conduction gap, shown in Fig. 14, hardly changes with $V$, for small $V$. Furthermore, the conductivity gap is of the order of $U - W \approx 1$ eV, implying that the importance of many-body effects is dependent on the parameter $U/W$ and not on $(U-V)/W$. For $2V > U$, the conductivity gap increases with $V$ for the half-filled ($n = 2$) system and is quite independent of $V$ for the quarter ($n = 1$) and three-quarter ($n = 3$) filled system. The same decrease of the conduction gap near the SDW/CDW phase transition is observed as for the nondegenerate system.

In Fig. 15, we show the charge-structure factor [Eq. (9)] with $\tilde{n}_j = \sum_{\sigma} c^\dagger_{jm\sigma} c_{jm\sigma}$, as well as the spin-structure factor Eq. (10), at half and quarter filling for $\alpha = \pi$ and for different values of $V$. Because of electron/hole symmetry, the structure factors for electrons at quarter filling is equal to the structure factors for holes at three-quarter filling. It is clearly seen that a SDW/CDW phase transition occurs near the $2V = U$ line. Looking in more detail we find that, as for the nondegenerate system, the phase transition occurs for $V$ slightly higher than $U/2$, due to the higher entropy of the SDW phase.

It is straightforward to show that the same considerations concerning the influence of screening effects on the formation of CDW's, as discussed for the nondegenerate model Hamiltonian, also apply for the degenerate system. Therefore, we expect that for a bipartite lattice the SDW/CDW phase transition occurs at $xV \approx U_0$, where $U_0$ is the unscreened atomic (molecular) Coulomb repulsion. This is nicely seen in Fig. 16, where the calculated value of the conduction gap $E_{\text{gap}}$ is shown for the twofold degenerate extended Mott-Hubbard model, including the possibility that the atoms can polarize. The polarization term added to the DEMH Hamiltonian is given by Eq. (13), with the change that $\tilde{n}_j = \sum_{m\sigma} c^\dagger_{jm\sigma} c_{jm\sigma}$. The calculations are performed on a four-site cluster at half filling with $t = 2t' = -0.08$ eV at a constant value of the unscreened atomic Coulomb repulsion $U_0 = 3$ eV, for different values of the intersite Coulomb repulsion $V$, and polarization energy parameter $P$. In the left part of Fig. 16, the value of the conduction gap is shown for the quarter-filled system ($n = N/N = 1$), while in the right part it is shown for the half-filled system $n = 2 = f$. It is observed that Fig. 16 is qualitatively the same as Fig. 8 and that the SDW/CDW phase transition is determined by the unscreened atomic Coulomb repulsion $U_0$ and occurs for the one-dimensional bipartite lattice at a value of $2V$ slightly larger than $U_0$. 

![Image](image_url)
V. CONCLUSIONS

Within the nondegenerate as well as degenerate extended Mott-Hubbard (EMH) model, including an on-site Coulomb repulsion $U$, nearest-neighbor repulsion $V$, and intersite hybridization, it is shown that the conduction gap of a correlated insulator cannot be reduced by $V$, contrary to what was suggested in literature. The energy required to move an electron to its nearest neighbor, thereby creating a doubly occupied site and an empty site, is indeed reduced by $V$. Therefore, $V$ does enter in the calculation of the exchange interaction, which for the extended Mott-Hubbard system yields in second order $J_{\text{EMH}} = 2t^2/(U - V)$, rather than $J_{\text{MH}} = 2t^2/U$. However, these excitations correspond to charge-neutral excitons formed at an energy about $U - V$. They may be seen in optical experiments, but will not contribute to the conductivity, because an additional $V$ will be required to break up this exciton into a free double occupied site and hole, thereby canceling the influence of $V$ for the conduction gap.

Hubbard-like Hamiltonians, where screening effects are incorporated by 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.

For a bipartite lattice, the extended Mott-Hubbard insulator undergoes a phase transition from a SDW to a CDW when $zV$ exceeds $U$, where $z$ is the number of nearest neighbors. For the CDW ground state at half filling, the conduction gap increases with $V$. The conduction gap for integer-doped degenerate EMH insulators, other than half filled, stays approximately constant as a function of $V$. For frustrated, nonbipartite lattices, as, e.g., a fcc lattice, the same considerations concerning the value of the conduction gap apply, with the understanding that the conditions for forming CDW’s may be different.

ACKNOWLEDGMENTS

We wish to thank D. I. Khomskii for useful discussions. This work was financially supported by the Nederlandse Stichting voor Fundamenteel Onderzoek der Materie (FOM) and the Stichting Schelkundig Onderzoek Nederland (SON), both financially supported by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO). J.L. is supported by the E.C.