Optical phonons in a quarter-filled 1D Hubbard model

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The influence of dispersion-less quantum optical phonons on the phase diagram of a quarter-filled Hubbard chain is studied using the Density-matrix renormalization group technique. The ground state phase diagram is obtained for frequencies corresponding to the intramolecular vibrations in organic conductors. For high vibrational modes the system is only slightly affected by the electron-phonons coupling. It remains in a Lüttinger liquid phase as long as the electronic repulsion is larger than the polaronic binding energy. For low vibrational modes the phase diagram is very rich. A noticeable point is the existence of a $4k_F$ CDW phase for small values of the correlation strength. For realistic values of the electron repulsion and of the electron-phonons coupling constant a large phonons-mediated reduction of the Lüttinger liquid parameter $K_\rho$ was found compared to the pure electronic model.

I. INTRODUCTION

Electron-phonons interactions have always attracted a lot of attention. Indeed, they are responsible for a large number of phase transitions, such as BCS superconductivity or Peierls transitions. Among the materials for which electron-phonons coupling are important, molecular materials constitute a special class. A trivial statement is that molecular crystals differ from simple crystals by the fact that their basic units are molecules. These basic units are therefore structured systems with a large number of internal degrees of freedom that may interact with the valence or conduction electrons. In particular, molecular crystals have two kinds of electron-phonons interactions. The first one is inter-molecular and the phonons essentially couple to the electronic structure through a modulation of the hopping parameter between two molecular sites. This electron-phonons coupling is responsible for the Peierls transitions and has been extensively studied. The second type of interaction is intra-molecular. The totally-symmetric molecular vibrational modes couple to the electronic structure, essentially through a modification of the on-site parameters such as molecular orbital energies and on-site repulsions. In the 60’s, Little suggested that intra-molecular vibrations could be responsible for superconductivity in organic conductors, more recently they were proposed as mediators for supra-conductivity properties in materials such as fullerides.

Indeed in systems such as the organic conductors, there is a broad spectrum of intra-molecular vibrations ranging from $200 cm^{-1}$ to $2000 cm^{-1}$ that is between $\sim t/5$ and $\sim t$, where $t$ is the hopping inter-molecular integral responsible for the conduction. Moreover it was shown that these vibrations couple quite well with the electronic degrees of freedom both in the high and low vibrational range of the Raman spectrum. This fact can easily be understood from simple chemical considerations. Indeed, the molecules acting as basic units in these systems share number of characteristics such as being large, strongly conjugated, and built from pentagonal cycles. These characteristics allow them to adjust their geometry to
their electronic charge at a low energetic cost, essentially by a modification of the angles in the pentagonal cycles. This mechanism leads to an important electron intra-molecular vibration coupling.

Previous studies on correlated electronic systems coupled to intra-molecular vibrations have essentially explored the two asymptotic regimes, (i) the weak coupling regime that can be treated by perturbative expansion from the electronic model and (ii) the strong coupling or polaronic regime. It is clear that the study of the intermediate coupling regime cannot be done by analytic treatments and requires up to date numerical techniques. The purpose of this work is to fill this gap and systematically explore the phase diagram of a one dimensional, correlated, electronic system coupled to intra-molecular vibrations, both as a function of the coupling constant and the correlation strength. The present paper systematically studies the Hubbard-Holstein model for a one dimensional quarter-filled chain for two values of the vibration frequency, $\omega = 0.2t$ and $\omega = t$, respectively corresponding to the top and the bottom part of the organic conductors Raman spectra. For each phase, properties such as spin and charge gaps, distance dependence of the spin, charge and singlet correlation functions, etc, are reported.

The next section analyses the Hubbard-Holstein model and develops the computational details. The third section reports and discusses the results and the last section is devoted to the conclusion.

II. MODEL ANALYSIS AND COMPUTATIONAL DETAILS

A. The Hubbard-Holstein model

The Hubbard-Holstein Hamiltonian associates a Hubbard Hamiltonian, which includes short range electron correlations, with dynamical phonons. The latter are linearly coupled with the electronic degrees of freedom as in the Holstein model.

$$H = H_e + H_{ph} + H_{e-ph}$$

with

$$H_e = \epsilon \sum_{i,\sigma} n_{i,\sigma} + t \sum_{i,\sigma} (c_{i+1,\sigma}^\dagger c_{i,\sigma} + c_{i,\sigma}^\dagger c_{i+1,\sigma}) + U \sum_i n_{i,\uparrow} n_{i,\downarrow}$$

$$H_{ph} = \omega \sum_i (b_i^\dagger b_i + 1/2)$$

$$H_{e-ph} = g \sum_i n_i (b_i^\dagger + b_i)$$

where $c_{i,\sigma}^\dagger$, $c_{i,\sigma}$ and $n_{i,\sigma}$ are the usual creation, annihilation and number operators of electrons of spin $\sigma$ on site $i$ ($n_i = n_{i,\uparrow} + n_{i,\downarrow}$). $b_i^\dagger$ and $b_i$ are the intra-molecular phonons creation and annihilation operators.

From the point of view of the isolated molecule the Hubbard-Holstein (HH) model tries to mimic the relaxation of the molecular geometry as a function of the ionicity. Indeed the on-site part of the HH model can be rewritten as

$$H_i = \epsilon n_{i,\sigma} + U n_{i,\uparrow} n_{i,\downarrow} + \omega \left( b_i^\dagger b_i + 1/2 \right) + g n_i \left( b_i^\dagger + b_i \right)$$

$$= \omega \left[ \left( b_i^\dagger + n_i \frac{g}{\omega} \right) \left( b_i + n_i \frac{g}{\omega} \right) + \frac{1}{2} \right] + \left( U - 2 \frac{g^2}{\omega} \right) n_{i,\uparrow} n_{i,\downarrow} + n_i \left( \epsilon - \frac{g^2}{\omega} \right)$$

The above formulation points out the three effects treated in the HH model.
1. The modification of the molecular orbital energy: $\varepsilon \longrightarrow \varepsilon - g^2/\omega$. This effect is very important (i) in multi-band systems since it strongly affects the relative filling in the different bands and (ii) in opened systems where electrons can jump in and out from an external bath. In our case it just changes the energy reference.

2. The decrease of the effective on-site bi-electronic repulsion: $U \longrightarrow U - 2g^2/\omega$. In the strong coupling regime the effective electron-electron interaction can become attractive due to the electron-phonons interaction, and two electrons held together via molecular vibrations.

3. The displacement of the harmonic oscillator describing the intra-molecular vibrations as a function of the molecular charge $n_i$: $\omega \left[b_i^\dagger b_i + 1/2\right] \longrightarrow \omega \left[(b_i^\dagger + n_i g/\omega)(b_i + n_i g/\omega) + 1/2\right]$. This term mimics the relaxation of the molecular geometry as a function of the molecule ionicity. The $\lambda = n_i g^2/\omega$ term acts as an effective molecular coordinate for which the equilibrium geometry is linearly shifted from $\lambda = 0$, when the molecular site does not carry any electron, up to $\lambda = 2g^2/\omega$, when it carries 2 electrons.

One sees from equation 3 that the vibronic molecular states are coherent phonons states, eigenstates of the shifted harmonic oscillators. They can be referred as $|n_i, S_{zi}, \nu_{i_j}^{n_i}\rangle$, where $\nu_{i_j}^{n_i}$ is the vibrational quantum number of the molecule $i$ when it supports $n_i$ electrons,

$$H_i|n_i, S_{zi}, \nu_{i_j}^{n_i}\rangle = \left[n_i \left(\varepsilon - \frac{g^2}{\omega}\right) + \delta(n_i - 2) \left(U - 2\frac{g^2}{\omega}\right) + \omega \left(\nu_{i_j}^{n_i} + \frac{1}{2}\right)\right]|n_i, S_{zi}, \nu_{i_j}^{n_i}\rangle$$ (3)

where $\delta$ is the Dirac function.

B. Computational details

The calculations on the infinite chain are performed using the infinite system Density Matrix Renormalization Group method. The main problem risen by the HH model is the infinite number of vibronic states on each sites. In order to render the calculations feasible, the basis set have been truncated to the lowest vibronic states of each molecular site, that is $|n_i, S_{zi}, \nu_{i_j}\rangle$ such that $\nu_j = 0, 1$. This choice is physically reasonable since (i) we work at $T = 0$ and therefore only the lowest vibronic states are expected to be involved, (ii) the molecules form well defined entities that are only perturbatively modified by the presence of their neighbors. The drawback of this choice is that we directly work in the vibronic basis set and the truncation of the basis set destroys any further possibility to separate the electronic degrees of freedom from the vibrational ones. We will see later, from a wave function analysis of the different phases, that the truncation does not affect the results of our calculations as long as we are not too close to a phase transition.

In the phase diagram explorations we kept 100 states per renormalized block, while in the properties calculations 256 states were kept. The charge and spin gaps where computed using a double extrapolation (i) on the system size and (ii) on the number of states kept $m$. Typically the extrapolations over $m$ were done from three DMRG calculations with respectively 100, 150 and 256 states kept. The maximum number of sites is 84 and the correlation functions presented below are done for this chain length. In some cases, exact diagonalizations on small clusters have also been performed in order to better analyze either the wave function or the energy spectrum.
III. RESULTS

The present work explores in a systematic and unbiased way the whole range of electron-phonons coupling regime (from $g/t = 0$ to $g/t = 1.25$) as well as the whole range of correlation strength (from $U/t = 0$ to $U/t = 16$), for two values of the phonons frequency: $\omega = 0.2t$ and $\omega = t$. These frequencies have been chosen in order to approximatively correspond to the low and high part of the Raman spectrum of the TTF$_5$, TMTSF$_3$ or M(dmit)$_2$ molecules. The adiabatic regime corresponds to the parameter domains $\omega/t \ll 1$ and $g/\omega \ll 1$, and the strong coupling regime corresponds to $g/\omega \gg 1$ and $\omega/t \gg 1$.

A. $\omega = 0.2t$

Figure 1 reports the phase diagram for $\omega = 0.2t$ as a function of $g/\omega$ and $U/t$ which are, with $\omega$, the three relevant parameters in the HH model (see eq. 2).

![Phase diagram](image)

**FIG. 1.** Phase diagram of the Hubbard-Holstein model for $\omega = 0.2t$. The solid line corresponds to $U - 2g^2/\omega = 0$, the long-dashed line corresponds to $U_{\text{eff}}/t_{\text{eff}} = (U - 2g^2/\omega)/t \exp(-g^2/\omega^2) = \pm 4$, the dashed line corresponds to $U_{\text{eff}}/t_{\text{eff}} = 600$. The dotted-dashed line correspond to equal phonons polarization and electronic energies (as defined in reference 12). The inset blows up the small $g/\omega$ and small $U/t$ part of the graph.

Five different phases have been characterized: two insulating phases where the electrons are strongly localized, a polaronic phase (diamonds) and a bi-polaronic phase (circles) and three metallic phases (crosses, stars and plus). These phases were characterized using the following set of tools

(i) the variation of the energy with the number of sites,
(ii) the spin and charge gaps,
(iii) the spin, charge and singlet-singlet correlation functions,
(iv) density matrices at the central sites.
1. The bi-polaronic phase

In the strong coupling regime, $U_{\text{eff}} = U - 2\omega (g/\omega)^2$ becomes negative and a bi-polaronic phase was found. As expected, the attractive character of $U_{\text{eff}}$ strongly couples the electrons in pairs. For instance, for $U/t = 4$, $g/t = 1$ and 84 sites ($U_{\text{eff}} = -6t$, $g/\omega = 5$), the probability of having a lonely electron on the central site is smaller than $10^{-12}$. The electron pairing induced by the intra-molecular vibrations is very strong, however, due to the Franck-Condon factors, this phase does not correspond to the singlet super-conducting phase but rather to a localized bi-polaronic phase. Let us suppose that an electron on a site $i$ would like to hop on a neighboring $j$, omitting the spin degree of freedom the hopping term can be written as

$$a_j^\dagger a_i |n_i, \nu_{\alpha}^{n_i}; n_j, \nu_{\beta}^{n_j}) = t |n_i - 1, \nu_{\alpha}^{n_i}; n_j + 1, \nu_{\beta}^{n_j})$$

that is the hopping integral between the molecular vibronic ground states is rescaled by the product of the Franck-Condon factors on the two sites $i$ and $j$, $\langle \nu_{\alpha}^{n_i} | \nu_{\alpha}^{n_i+1} \rangle$. The relaxation energy or self-trapping energy (due to the vibrations) of the electron pair on a site can be evaluated as the difference between the vertical ionization potential (or electron affinity) and the adiabatic one,

$$E_{\text{relax}}(i) = \sum \nu_{\alpha}^{n_i \pm 1} \omega (\nu_{\alpha}^{n_i \pm 1})^2$$

For $U/t = 4$ and $g/t = 1$ this relaxation energy is as large as $5.00t$. Figure 2 shows the overlap between the vibrational ground state corresponding to $n_i$ electrons on site $i$ ($\nu_{0i}^{n_i}$) and the different vibrational states corresponding to $n_i \pm 1$ electrons ($\nu_{\alpha}^{n_i \pm 1}$). One sees immediately that for large or even intermediate values of $g/\omega$ the overlap between the low energy vibrational states is very small. The consequence is that the electron hopping between two neighboring sites is strongly hindered; either the transfer takes place towards small quantum-number vibrational states and the transfer integral is strongly renormalized by the small Franck-condon factors, or the transfer takes place towards large quantum-number vibrational states and it is hindered by the vibrational energetic cost. It is clear that the same phenomenon hinders even more the pair hopping since the displacement is twice as large and the Franck-Condon factor is squared ($\langle \nu_{0i}^{n_i} | \nu_{0i}^{n_i \pm 2} \rangle = \exp(-2g^2/\omega^2)$).
FIG. 2. Overlap between the ground-state of the undisplaced harmonic oscillator and the eigenstates of the displaced oscillator for different values of the displacement $g/\omega$.

If one looks at the energy per site as a function of the system size (or DMRG iteration number), one sees that it is nearly constant. The amplitude of variation between the 4 sites system and the 84 sites system is smaller than $5 \times 10^{-12}$ for $U/t = 4$ and $g/\omega = 5$, the typical example we have chosen for this phase. This fact could have been surprising but it is easily understood in the context of a strongly hindered hopping. Taking into account the electron pairing and the strong localization one can reasonably approximate the system wave-function by $\Psi_{BP}$

\[
\begin{array}{ccccccc}
\uparrow & \downarrow & \uparrow & \downarrow & \cdots & \cdots & \cdots \\
\end{array}
\]

of energy

\[
E(\Psi_{BP}) = N_{\text{sites}} \left( \frac{1}{4} U_{\text{eff}} - \frac{1}{2} \frac{g^2}{\omega} + \frac{1}{2} \frac{1}{\omega} \right)
\]

The quality of this approximation can be checked on the energy. The computed DMRG energy per site differs from $E(\Psi_{BP}) = -3.9$ by at the most $7 \times 10^{-12}$ in $t$ units. Exact diagonalization on a 4-sites system, where the wave function can be explicitly analyzed, confirms this result. The projection of the exact ground state on $\Psi_{BP}$ being larger than $1 - 10^{-7}$. In fact the ground state of the 4-sites system is 4 times quasi-degenerated and the infinite system ground state infinitely degenerated. Indeed, in the absence of inter-site Coulomb repulsion, any choice for the localization of the electron pairs is equivalent. Even with a $1/r$ Coulomb repulsion one sees that the infinite system should remain 4 times quasi-degenerated, the degeneracy lifting being of the order of magnitude of the rescaled hopping integral between the low energy vibrational states, that is of the order of $t \exp(-g^2/\omega^2)$ $(1.4 \times 10^{-11}$ for $U/t = 4$ and $g/\omega = 5$). The charge gap is therefore exponentially small, the exact diagonalization of the 4-sites system shows that the first exited state with a "real" gap is a one-boson vibrational excited state at $\omega$. The spin gap is of the order of magnitude of $U_{\text{eff}}$ $(6.0$ in our example) since it necessitates the breaking of an electron pair.

2. The Luttinger liquid phase

In the weak coupling regime — for small values of $g/\omega$ — up to the intermediate coupling regime for intermediate values of the correlation strength, one finds a phase which is essentially a Tomanaga-Luttinger liquid [15] with parameters slightly rescaled by the presence of the vibrations compare to the purely electronic system. This result was expected, from continuity from the pure Hubbard model, and from previous works from Voit and Schulz [8] (within a renormalization group (Rg) scheme in an incommensurate system). We will further refer to this phase as the Tomanaga-Luttinger (TL) phase. While restricted to a very small range of $g/\omega$, for large values of the correlation strength, it is worth to notice that this phase extends up to values of $g/\omega$ larger than 1 for intermediate values of $U$ (see figure [1]). For very small values of $U$, the competition between the TL phase and a bi-polaronic phase limits the extension of the former to a parameter range for which the effective repulsion remains positive, that is $g/\omega < \sqrt{U/2\omega}$. The study of the charge-charge and spin-spin correlation functions yield that the main effect of the vibrational degrees of freedom is to rescale the TL liquid parameters — in
particularly the value of $K_\rho$ — compared to the purely electronic system. This result is in total agreement with the conclusions derived by Voit et al.

A simple approach would bring us to think that the value of $K_\rho$ is increased by the vibrational degrees of freedom since the effective electron-electron repulsion is strongly reduced by the electron-phonons interactions. Let us see what really comes out of the calculations. The correlation functions have been computed on a 84 sites system with 256 states kept in the DMRG procedure. They exhibit the expected behavior as a function of the inter-site distance with a power law decay, in agreement with the ungaped nature of both the spin and charge channel. Figure 3 shows the charge structure factor for the pure Hubbard model as well as the Hubbard-Holstein one for the $U/t = 1$ and $g/\omega = 1.25$ set of parameters.

\[ K_\rho = \frac{d}{dq} \left( \pi \int_0^{+\infty} \langle (n_e(0) - \langle n_e(0) \rangle) (n_e(r) - \langle n_e(r) \rangle) \rangle e^{iqr} \, dr \right) \bigg|_{q=0} \]  

And is clearly smaller for the $U/t = 1$ and $g/\omega = 1.25$ set of parameters than for the $U/t = 1$ Hubbard model. The $K_\rho$ values computed from the structure factors are 0.79 for $g/\omega = 1.25$ and 0.89 for the Hubbard Hamiltonian — in total agreement with the values found in the literature from numerical resolution of the Bethe ansatz solution\[^{18}\]. This unexpected reduction of $K_\rho$ was already noticed by Voit et al.\[^{8}\] from Rg considerations. One should notice that it cannot be attributed to the rescaling of the hopping integral since

\[ \frac{U_{\text{eff}}}{t_{\text{eff}}} = \frac{U - 2g^2/\omega}{t \exp(-g^2/\omega^2)} = 1.31 \]  

and the corresponding value of $K_\rho$ is much larger than 0.85\[^{18}\].

\[ 3. \text{ The } 4k_F \text{ CDW phase} \]

In a regime of intermediate coupling and intermediate to large correlation strength, we found a phase for which the charge correlation functions are domi-
nated by $4k_F$ charge density wave (CDW) fluctuations. The multiplication of the correlation functions by $r^2$ ($r$ being the inter-sites distance) allows the elimination, when the Fourier transform is performed, of the $1/r^2$ term that contribute at all frequencies. The frequency analysis of $r^2$ times the correlation function is therefore much clearer, and the relative importance of the $2k_F$ and $4k_F$ terms enhanced. Figure 4 reports this Fourier analysis for $U/t = 4$ and $g/\omega = 1.25$. One can see that while the spin-spin correlation function is change very little compared to the Hubbard model, the $2k_F$ contribution to the charge-charge correlation function has disappeared and a strong $4k_F$ contribution has set place. Figure 5 reports the same correlation functions as a function of the inter-sites distance. Both charge and spin correlation functions decrease as a power law as a function of the inter-sites distance speaking in favor of a gap-less system in both the spin and charge channels. The charge and spin gaps have been computed independently from double extrapolations (i) on the chain length and on the number of states kept in the DMRG calculations, i.e. 100, 150 and 256. While the charge channel clearly extrapolates toward a null gap, in the spin channel the question is not as clear. Indeed, the gap is found to be $\Delta_\sigma(100) = 8.1 \times 10^{-3}$ for a DMRG calculation where 100 states are kept, $\Delta_\sigma(150) = 8.3 \times 10^{-3}$ for 150 states kept and $\Delta_\sigma(256) = 8.6 \times 10^{-3}$ for 256. These gap values are very small however they do not extrapolate toward a null value when the quality of the calculation increases. This behavior pleads for a non null but very small gap in the spin channel. One should note that this result is not incoherent with the spin-spin correlation function behavior since such a small gap means a very large coherence length, of the order of magnitude of $\Delta_\sigma^{-1}$, i.e. the exponential behavior of the correlation function should take place at inter-sites distances larger than the chain length.

In the Luttinger liquid theory the $4k_F$ phase is supposed to occur for values of the $K_\rho$ parameter smaller than $1/3$, that is (i) in very strongly correlated systems and (ii) for values of $K_\rho$ unreachable in the Hubbard model — for which $0.5 \leq K_\rho \leq 1$. The presence of intra-molecular vibrations not only allows the existence of a $4k_F$ CDW phase, but this phase can be reached for values of the bi-electronic repulsion as small as $U/t = 2.5$ (and most probably even lower). We computed the $K_\rho$ values
from the structure factors and found that similarly to what happened in the TL phase, the $K_ρ$ value is strongly diminished in comparison to the purely electronic case. For $U/t = 4$ and $g/t = 0.25$ the value of $K_ρ$ is 0.56 while it is 0.71 for the $U/t = 4$ Hubbard model. One should however note that the 0.56 value is in good agreement with the $K_ρ$ expected for the effective parameters, $U_{eff}/t_{eff} = 16.1$.

4. The small polarons phase

For positive $U_{eff}$ but relatively large values of $g/ω$, the system is in a small polarons phase (diamonds on fig. 4). Indeed the electrons are no longer paired but are still strongly localized. The probability of having two electrons on the central site is smaller than $10^{-9}$ for $U = 8$, $g/t = 0.75$ and 82 sites ($g/ω = 3.75$ and $U_{eff} = 2.375$). These lonely electrons remain strongly coupled to the intra-molecular vibrations. The on-site vibrational relaxation energy is as large as $2.8t$ and the rescaled hopping integral between the ground vibrational states as low as $7.8 \times 10^{-7}$. The ground-state wave-function can be approximated by the totally localized wave-function $Ψ_p$

\[ \uparrow \downarrow \uparrow \downarrow \uparrow \]

and the residual hopping term treated perturbatively. The overlap of the exact ground-state wave-function of an 4-sites system with $Ψ_p$ is as large as 0.99 for $U/t = 8$ and $g/t = 0.75$ and even as large as 0.98 for $U = 4$ and $g/t = 0.5$ which is very close to the phase transition. Coherently, the DMRG energies per site remains nearly constant as the system size increases, with a maximal variation of $3 \times 10^{-7}$ from $E(Ψ_p)/N_{sites} = -1/2g^2/ω + 1/2ω$, for $U = 8$ and $g/t = 0.75$. As for the bi-polaronic phase the absence of Coulombic inter-site repulsion in our model induces a strong quasi-degeneracy of the ground-state: 12 times for the 4-sites system but infinitely for the infinite system. Even in the presence of a $1/r$ repulsion, the system would remain at least twice quasi-degenerated due to the even sites versus odd sites equivalence with an additional factor of 4 due to the spin quasi-degeneracy. Capone et al.[12] have studied the conditions of existence of this phase by exact diagonalization on small clusters (4 and 6 sites). They found that the localized polarons phase is stable as long as the polarization energy defined as $ε_{pol} = -N_{sites}ρ(1-ρ)g^2/ω$ is larger than the electronic energy $ε_{elec}$, $ρ$ is the filling of the system. The curve $ε_{pol}/ε_{elec} = 1$ is reported on fig. 4 with a dashed-dotted line and fits relatively well with the phase boundary in the infinite system. In the same spirit curves of constant $U_{eff}/t_{eff}$ have been plotted. This small polarons phase corresponds to very large values of the $U_{eff}/t_{eff}$ ratio.

5. The Luther-Emery phase

Finally for negative values of $U_{eff}$, but large values of $t_{eff}$ a delocalized phase takes place for which all spin, charge and on-site singlet correlation functions seem to decrease with the inter-site distance as a power law. Figure 5 reports the absolute values of the correlation functions for $U/t = 0.05$ and $g/t = 0.1$, that is $g/ω = 0.5$, $U_{eff} = -0.05$ and $t_{eff} = 0.78$. In all computed cases ($U/t = 0.2$, $g/ω = 1$ and 1.3 ; $U/t = 0.05$, $g/ω = 0.5$) the charge density fluctuations dominate, however as $U_{eff}/t_{eff}$ decreases the on-site singlet fluctuations increases compared to the charge ones. A direct calculation of the charge and spin gaps yield a clearly ungapped charge channel and a slightly gaped spin channel. The computed spin gaps are
\[ \Delta_\sigma = 0.05 \text{ for } U/t = 0.05 \text{ and } g/t = 0.1, \text{ and } \Delta_\sigma = 0.06 \text{ for } U/t = 0.2 \text{ and } g/t = 0.2. \] These very small values are compatible with the power law decrease of the spin correlation functions since with such small gaps, the correlation length is very large — of the order of magnitude of \( \Delta_\sigma^{-1} \) — and therefore the exponential decay of the correlation function cannot take place at distances smaller than the order of magnitude of the chain length. One can therefore identify this phase with a Luther-Emery model. The values of \( K_\rho \) extracted from the structure factors are again smaller than the values of the purely electronic model, with \( K_\rho = 0.99 \) for \( U/t = 0.05 \) and \( g/t = 0.1 \), and \( K_\rho = 0.89 \) for \( U/t = 0.2 \) and \( g/t = 0.2 \). Of course, they are as well smaller than the \( K_\rho \) values corresponding to the negative \( U_{\text{eff}} \).

**FIG. 6.** Absolute value of the charge (stars), spin (crosses) and singlet (plus) correlation functions for \( U/t = 0.05 \), \( g/t = 0.14 \) and \( \omega/t = 0.2 \).

**B. \( \omega = t \)**

Figure 7 reports the phase diagram for \( \omega = t \) as a function of \( g/\omega \) and \( U/t \).

**FIG. 7.** Phase diagram of the Hubbard-Holstein model for \( \omega = t \). The solid line corresponds to \( U - 2g^2/\omega = 0 \).

For this intermediate value of the phonons frequency, one finds only three phases,
a slightly perturbed Lüttinger liquid phase for $U_{\text{eff}} > 0$, a Luther-Emery phase for $U_{\text{eff}} < 0$ and small $g/\omega$, a localized bi-polaronic phase for $U_{\text{eff}} < 0$ and larger $g/\omega$.

For $U_{\text{eff}} > 0$, the phase is delocalized, dominated by $2k_F$ SDW fluctuations. Both charge and spin correlation functions decrease as power laws as a function of the inter-sites distance and both spin and charge channels are ungaped to numerical accuracy. The structure factors for the $U/t = 4$ Hubbard model and for the Hubbard-Holstein model with $U/t = 4 g/\omega = 0.5$ and $U/t = 4 g/\omega = 1$ are reported in figure 8. As can be seen the HH model is in this case indistinguishable from the pure Hubbard model and, as a consequence, the $K_\rho$ values as not sensitive (to numerical accuracy) to the electron-phonons coupling. In fact everything goes as if we were in the adiabatic regime while the model parameters can be as far from it as $\omega/t = 1$ and $g/\omega = 1.25$. This is typically a case where the Born-Oppenheimer approximation is fully valid and the electronic and vibrational degrees of freedom are nearly independent.

![Figure 8: Structure factors for $U/t = 4$. The solid line corresponds to the pure Hubbard model, the crosses and the circles to the Hubbard-Holstein model with respectively $g/t = 0.5$ and $1$.](image)

For $U_{\text{eff}} < 0$ one has a Luther-Emery phase for small values of $g/\omega$. This phase is very similar to the one found for $\omega/t = 0.2$, with an effective attractive on-site interaction and large effective hopping integrals. The CDW and the on-site singlet fluctuations dominate, and become of the same order of magnitude for $g/\omega = 0.5$ and $U/t = 0.2$. For larger values of the electron-phonons coupling, the CDW are larger than the singlet fluctuations ($g/\omega = 1$ and $U/t = 1$). As for the $\omega = 0.2$ case, all three correlation functions — spin-spin, charge-charge and singlet-singlet — present a power law behavior as a function of the inter-sites distance for the 84 sites system. The direct calculation of the charge and spin gaps yield and ungaped charge channel and a slightly gaped spin channel with $\Delta_\sigma = 0.04t$ for $U/t = 1$ and $g/t = 1$, as well as for $U/t = 0.2$ and $g/\omega = 0.5$. Again, the smallness of the spin gap explains the power law behavior of the spin-spin correlation functions at the computed distances. This time however the values of $K_\rho$ are larger than in the Hubbard model, in agreement with the attractive effective on-site interaction. $K_\rho \approx 1.1$ for both $U/t = 1 g/t = 1$ and $U/t = 0.2 g/t = 0.5$.

When $g/\omega$ increases — but still for negative $U_{\text{eff}}$ — one goes from the Luther-Emery phase toward a localized bi-polaronic phase through a cross-over. Indeed, for $U/t = 1$ and $g/\omega = 1.5$ the system is clearly localized in a bi-polaronic phase
with the usual characteristics: nearly constant energy per site, large projection of the wave function on $\Psi_{BP}$ (0.94 for the 4 sites system), etc... For $U/t = 1$ and $g/\omega = 1.25$ however, the system is in an intermediate regime. The delocalization is still reasonably large with an effective hopping of $0.21t$ and a projection of the 4 sites system wave function on $\Psi_{BP}$ of only 0.72. In this crossover regime, the system is gaped both in the spin and charge channels, with a spin gap of $\Delta_{s} = 0.43$ and a charge gap of $\Delta_{\rho} = 0.84$. Figure 9 reports the charge, spin, and singlet fluctuations. As expected all of them decrease exponentially with the inter-site distance. When the electron-phonons coupling increases, the system localization increases and the wave function tends toward the totally localized wave function $\Psi_{BP}$. Coherently, the spin gap increases and is expected to follow the same variations as $|U_{\text{eff}}| = 2g^2/\omega - U$, since one needs $|U_{\text{eff}}|$ in order to break the singlet pairing on the sites. In totally localized systems ($g = +\infty$), the charge channel is ungaped since in the absence of any delocalization integral, the different possible choices for the localization of the pairs have the same energy. The charge gap can therefore be expected to be scaling as the rescaled hopping integral $t_{\text{eff}} = t\exp(-g^2/\omega^2)$. That is exponentially decreasing when the electron-phonons coupling increases.

![Correlation functions](Fig9.png)

**FIG. 9.** Absolute values of the charge (stars), spin (cross) and singlet (plus) correlation functions in a semi-log scale. $U/t = 1$, $g/t = 1.25$ and $\omega = t$.

**IV. CONCLUSION**

We have investigated the phase diagram of the Hubbard-Holstein Hamiltonian in a quarter-filled chain for two values of the phonons frequency. These frequencies have be chosen in order to correspond to the low ($\omega = 0.2t$) and high ($\omega = t$) frequencies of the intra-molecular totally-symmetric vibrations of $TTF$, $TMTSF$ and related molecules from which the organic conductors are built.

For the $\omega = t$ frequency, the phase diagram is very simple. For a positive effective on-site interactions ($U_{\text{eff}} = U - 2g^2/\omega > 0$), the system is in a Luttinger-Liquid phase with slightly rescaled parameters compared to the purely electronic system. For negative effective on-site interactions ($U_{\text{eff}} < 0$) and small electron-phonons coupling, the system is in a Luther-Emery phase, however the spin gap remains very small and the coherence length large. The $K_{\rho}$ parameter is again rescaled compared to the purely electronic system, in agreement with the effective model $U_{\text{eff}} = U - 2g^2/\omega$, $t_{\text{eff}} = t\exp(-g^2/\omega^2)$. When the electron-phonons coupling...
increases, the system goes toward a localized bi-polaronic phase through a soft
cross-over.

At low frequency ($\omega = 0.2t$) however, a rich phase diagram have been found with 5
different phases, some delocalized and some strongly localized. For positive effective
interactions one has three different phases. For small electron-phonons coupling and
intermediate coupling for small correlation strength, the system is in a Lüttinger
Liquid phase. For intermediate electron-phonons coupling, the system is in a phase
for which the $2k_F$ charge fluctuations disappear and the charge correlation functions
have only $4k_F$ CDW fluctuations. For large electron-phonons coupling, the system
is strongly localized in a polaronic phase. When the effective interaction become
negative, one finds a Luther-Emery phase for small electron-phonons coupling, and
a strongly localized bi-polaronic phase for intermediate to large couplings. The
Luther-Emery phase has a very small spin gap (of the order of 0.05$t$ and the spin-
spin correlation functions exhibit a power law decrease up to at least 60 to 80 sites).
Unlike for $\omega/t = 1$, for $\omega/t = 0.2$ the delocalized phases do not behave as would the
$U_{\text{eff}} = U - 2g^2/\omega$, $t_{\text{eff}} = t\exp(-g^2/\omega^2)$ effective Hubbard model. Indeed the $K_\rho$
parameter is strongly decreased due to the electron-phonons interactions while the
decrease of the effective repulsion (compared to the pure Hubbard model) would
have led us to expect an opposite behavior.

This surprising decrease of the $K_\rho$ parameters should be put in context with val-
ues of the $K_\rho$ parameters found in photo-emission experiments on $\text{TM}_{\text{MTS}}\text{F}$ and
$\text{TM}_{\text{MTT}}\text{F}$ quasi-one-dimensional organic compounds. Indeed Zwick et al found a density of states exponent $\alpha = 1/4(K_\rho + 1/K_\rho - 2)$ slightly larger than
1 ($K_\rho \leq 0.25$) in the metallic phase. According to the Lüttinger Liquid theory the
system should be insulating for such large values of $\alpha$. Tentative explanations have
been made by Schwartz et al, involving an effective doping of a Mott insulator
due to the inter-chain hopping. On another hand, the electron intra-molecular vi-
bractions interactions are never considered in these systems. For the low frequency
modes of these systems, the typical energy scale of the electron-phonons interac-
tion : $2g^2/\omega$ is of the order of magnitude of one-half to one-fourth the intra-chain
hopping amplitude, that is in the intermediate regime of our phase diagram. For
such values of the electron-phonons coupling constants and values of the electronic
repulsion between one to four $t$, the system is in a Lüttinger liquid phase for which the
intra-molecular vibrations strongly decrease the $K_\rho$ parameter compared to its
electronic value. It is clear that the Hubbard model lacks at least nearest-neighbor
bi-electronic repulsion in order to well represent these systems. It can however be
expected that the trend toward a strong reduction of the $K_\rho$ parameters, observed
in the Hubbard-Holstein model, would be similar with longer range interactions,
and that the coupling of the electronic degrees of freedom with the intra-molecular
vibrations would lead to values of the $\alpha$ parameter unreachable in a purely elec-
tronic model. Considering these trends, it is reasonable to think the the electron
intra-molecular vibrations coupling will have to be considered in order to obtain a
realistic description of the observed photo-emission experimental data.
1 W.A. Little, Phys. Rev. 134, A1415-1424 (1964).
2 A.S. Alexandrov, V.V. Kabanov, Phys. Rev. B 54, 3655, (1996).
3 M. Meneghetti, R. Bozio, I. ZAnon, C. Pelice, C. Ricotta, M. Zanetti, J. Chem. Phys. 80, 6210 (1984).
4 H. L. Liu, D. B. Tanner, A. E. Pullen, K. A. Abboud, J. R. Reynolds, Phys. Rev. B 53, 10557 (1996).
5 A. Girlando, F. Marzola, C. Pelice, J.B. Torrance, J. Chem. Phys. 79, 1075 (1983).
6 D. Pedron, R. Bozio, M. Meneghetti, C. Pelice, Phys. Rev. B 49, 10893 (1994).
7 R. Ramakumar, Y. Tanaka, K. Yamaji, Phys. Rev. B 56, 795 (1997).
8 J. Voit and H.J. Schulz, Phys. Rev. B 37, 10068 (1988).
9 J. Voit, Phys. Rev. Letters 64, 323 (1990).
10 G. Wellein, H. Roder, H. Fehske, Phys. Rev. B 53, 9666, (1996).
11 A.S. Alexandrov, V. V. Kabanov, D.K. Ray, Phys. Rev. B 49, 9915 (1994).
12 M. Capone, M. Grilli, W. Stephan, J. Supercond., 12, 75 (1999).
13 T. Holstein, Ann. Phys. 8, 325 (1959).
14 S.R. White, Phys. Rev. lett. 69, 2863 (1992); S.R. White, Phys. Rev. B 48, 10345 (1993).
15 F.D.M. Haldane, J. Phys. C 14, 2585 (1981).
16 M. Dzierzawa, in The Hubbard model, Ed. by D. Baeriswyl et al., New York (1995)
17 J. Voit, Rep. Prog. Phys. 58, 977 (1995).
18 H.J. Schulz, Int. J. Mod. Phys. B 5, 57 (1991).
19 A. Luther and V.J. Emery, Phys. Rev. Lett. 33, 589 (1974).
20 M. Dzierzawa, in The Hubbard model, Ed. by D. Baeriswyl et al., New York (1995)
21 F. Zwick, S. Brown, G. Margaritondo, C. Merlic, M. Onellion, J. Voit and M. Grioni, Phys. Rev. Lett. 79, 3982 (1997).
22 B. Dardel, D. Malterre, M. Grioni, P. Weibel, Y. Baer, J. Voit, D. Jerome, Europhys. lett. 24, 687 (1993).
23 A. Schwartz, M. Dressel, G. Gruner, V. Vescoli, L. Degiorgi, and T. Giarmarchi, Phys. Rev. B 58, 1261 (1998).