Interplay of Orbital Degeneracy and Superconductivity in a Molecular Conductor

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We study electron propagation in a molecular lattice model. Each molecular site involves doubly degenerate electronic states coupled to doubly degenerate molecular vibration, leading to a so-called E-e type of Jahn-Teller Hamiltonian. For weak electron-phonon coupling and in the anti-adiabatic limit we find that the orbital degeneracy induces an intersite pairing mechanism which is absent in the standard non-degenerate polaronic model. In this limit we analyse the model in the presence of an additional on-site repulsion and we determine, within BCS mean field theory, the region of stability of superconductivity. In one dimension, where powerful analytical techniques are available, we are able to calculate the phase diagram of the model both for weak and for strong electron-phonon coupling.

I. INTRODUCTION

When atoms or molecules with orbitally degenerate valence levels are arranged to form a solid, the degeneracy of the isolated constituents is often broken, once the solid is formed. In many cases, in fact, the crystal field, produced by the surrounding atoms/molecules, is able to remove the original degeneracy. Yet, if the crystal symmetry is sufficiently high the orbital degeneracy may not be completely lifted. In this situation the Jahn-Teller (JT) effect, arising from coupling electrons to vibronic modes, may play an important role. In particular it can induce a global symmetry-lowering lattice deformation lifting the residual degeneracy (“static” Jahn-Teller effect). However if the phonon frequencies are high in comparison with the electron hopping, the static distortion may become disadvantageous and the original symmetry may be recovered dynamically (“dynamic” Jahn-Teller effect). A primary and well known consequence of the dynamic mixing between electronic and vibronic degrees of freedom, is the renormalization of several electronic matrix elements by the so-called Ham factors. Apart from this suppression factor, other interesting properties may arise when dynamical JT effect is important.

For instance, in the context of superconductivity in fullerenes, it has been recently proposed that the dynamical JT effect may be associated with an increase of the electronic pairing interaction. In the specific case of charged fullerene molecules, the JT effect arises mainly from coupling the partially occupied $t_{2u}$ orbitals with the $H_g$ vibronic modes, even though for a realistic description one has to take into account other modes such as $A_g$ and other orbitals, such as $h_u$ and $t_{1g}$. Since the physical model is very complicated, in Ref. 4 a simplified version was introduced, aimed at capturing the essential physics of the problem. The model consists of a lattice of molecules, each with two degenerate orbitals coupled to a doubly-degenerate vibronic mode. The Hamiltonian of each molecule is described by a so-called E-e JT Hamiltonian, which is the simpler case of dynamic JT effect. In spite of its simplicity, the lattice of E-e molecules was shown to exhibit in the strong coupling limit rather striking and unexpected features. In particular it was found that, even if the polaronic attraction is disregarded, two electrons in the vacuum still bind with a binding energy proportional to the effective hopping (the bare hopping reduced by the Ham factor). At higher density however the model could only be analyzed numerically and in one dimension.

Besides the application to $C_{60}$, the doubly degenerate Jahn-Teller model might provide useful information for other systems where the Jahn-Teller effect is expected to be important, such as compounds containing magnetic ions with unfilled $d$ or $f$ shells. In this case it is well known that the interplay between the Jahn-Teller effect and the strong electronic correlations plays a very important role in determining both the structural and the magnetic properties (for a review mainly on transition metal compounds see e.g. Ref. 5 and Ref. 6 and for rare earth compounds see Ref. 7). A typical example where the doubly degenerate JT model could be relevant is a transition metal ion, whose valence state is five-fold orbitally degenerate. In cubic symmetry, the crystal field splits the $d$-levels into a three-fold degenerate $t_{2g}$ level and a two-fold degenerate $e_g$. Exactly for a tetrahedral distortion, the two-fold degenerate $e_g$ is the ground state.

In this paper we study the lattice of E-e molecules in the weak electron-phonon coupling regime and for phonon frequencies higher or comparable to the electron bandwidth. Since any perturbation, however small, has always important consequences for degenerate levels, most of the interesting features originally recognized in Ref. 3 for strong electron-phonon coupling, are already present in the weak coupling regime. This limit has in addition the big advantage of allowing an analytical approach which will provide new useful results valid in any dimension. Moreover
in one-dimension, where powerful analytical techniques are available, we are able to characterize the whole phase diagram of the model, both in the weak and in the strong coupling regimes.

The paper is organized as follows. In Section II we introduce the model and discuss the properties of a single molecule both in the weak and strong coupling regimes. In the former limit, we find an unitary transformation which, when applied to the molecular Hamiltonian, provides an effective Hamiltonian without electron-phonon coupling which nevertheless can reproduce all the correct results up to fifth order in the electron-phonon coupling constant. A lattice of such JT molecules is introduced and analyzed in Section III. In Section IV we study the model within a BCS mean field approach. Finally, in Section V, we calculate the phase diagram of the model in one-dimension.

II. THE MOLECULE

The model we are going to discuss describes an array of molecules with two degenerate electronic orbitals \( c_{1\sigma} \) and \( c_{2\sigma} \) (later referred to as “band”), coupled to a two-dimensional molecular vibration (henceforth called phonon) with energy \( \omega_0 \) (\( \hbar = 1 \)). Each molecule is described by the so called E-e Hamiltonian:

\[
H_{mol} = \frac{\omega_0}{2} (\vec{r}^2 + \vec{p}^2) + g\omega_0 \vec{r} \cdot \vec{\tau},
\]

where \( \vec{r} = (x, y) \) is the two-dimensional coordinate of the local phonon mode, and

\[
\vec{\tau} = \frac{1}{2} \sum_{a,b=1,2} \sum_{\alpha=\uparrow,\downarrow} c_{a\alpha}^\dagger \sigma_{ab} c_{b\alpha},
\]

being \( \sigma \) the Pauli matrices.

The Hamiltonian (1) has to be compared with that describing single-band electrons coupled to a non-degenerate phonon

\[
H_{mol} = \frac{\omega_0}{2} (r^2 + p^2) + g\omega_0 rn,
\]

where \( r \) is the one-component phonon coordinate and

\[
n = \sum_{\alpha=\uparrow,\downarrow} c_{\alpha}^\dagger c_{\alpha},
\]

is the local density of single band electrons. In what follows we will show that the additional degrees of freedom of (1) give rise to new interesting properties.

In the absence of electron-phonon coupling, each molecular level of the Hamiltonian (1) with vibronic energy \( m\omega_0 \) and \( n \) electrons is degenerate, with degeneracy

\[
(m+1) \times \left( \begin{array}{c} 4 \\ n \end{array} \right).
\]

The binomial coefficient counts the number of ways of distributing \( n \) fermions among 4 levels (1 and 2, \( \uparrow \) and \( \downarrow \)). These states can be for instance labeled by the total spin \( S \), its \( z \)-component \( S_z \), and by \( \tau_z \) (which is half the difference between the number of electrons in orbital 1 and that one in orbital 2). The factor \( (m+1) \) is instead the degeneracy of each vibrational state and corresponds to the possible values that the vibron angular momentum \( L_z = xp_y - yp_x \) can assume (\( L_z = -m, -m + 2, ..., m \)). When the electron-phonon coupling is switched on, this degeneracy is lifted. The total spin and its \( z \)-component are still good quantum numbers, but now only the \( z \)-component of the total pseudo-angular momentum

\[
J_z = L_z + \tau_z
\]

commutes with the Hamiltonian (1). Notice that for odd number of electrons \( \tau_z \) is half an odd integer, and consequently is \( J_z \). Due to the symmetry \( J_z \rightarrow -J_z \), each state (also the ground state) with odd number of electrons is at least four-fold degenerate (\( \pm J_z, S = \pm 1/2 \)). On the contrary for even number of electrons the starting degeneracy is split and the ground state turns out to be an orbital as well as a spin singlet.

At weak electron-phonon coupling \( g \ll 1 \) each multiplet is split by energy shifts of order \( \omega_0 g^2 \), but different multiplets are still well separated by energy \( \omega_0 \). If we are interested in the behavior of the model at energies \( \ll \omega_0 \),
we can neglect all but the lowest multiplet. Since this is adiabatically connected to the multiplet without excited vibrons \((m = 0, L_z = 0)\), it can be labeled by the electronic quantum numbers only \((S, S_z, \tau_z)\). This suggests that it is possible to define a effective Hamiltonian for this lowest multiplet which acts only on the electronic degrees of freedom and is able to reproduce the energy shifts inside the multiplet. A standard way to derive this Hamiltonian is via an unitary transformation \(U = e^{iS}\). For the non-degenerate model \([3]\), this unitary transformation simply shifts the origin of the harmonic oscillator to a new one, namely \(S = -igpn\). In the degenerate two-band model, the components of the new origin \((g\tau_x, g\tau_y)\) do not commute among themselves, and this gives rise to some of the interesting properties of the model. Up to order \(g^2\), the operator \(U\) for the degenerate model is given by (see e.g. M. Wagner in Ref. 9 for a comprehensive review of unitary transformations in JT models)

\[
U = e^{-ig\vec{p}\cdot\vec{\tau}+ig^2\frac{\vec{x}\cdot\vec{\tau}}{2}}. \tag{4}
\]

The transformed molecular Hamiltonian reads

\[
UH_{mol}U^{-1} = \frac{\omega_0}{2} (\vec{\tau}^2 + \vec{\rho}^2) - \omega_0 g^2 \left(1 - \frac{g^2}{4}\right) L_z \tau_z
- \frac{1}{2} \omega_0 g^2 (1 - \frac{g^2}{2}) \vec{\tau}^2 - \omega_0 g^4 \tau_z^2 + \Delta H, \tag{5}
\]

where \(\Delta H\) contains terms coupling the phonon modes with the electrons and having coupling constants of order \(O(g^4)\). If we are interested in physical quantities with a precision up to \(g^5\), we can neglect \(\Delta H\). The molecular ground state with an odd number of electrons \((n = 1, 3)\) is four–fold degenerate \((J_z = \pm 1/2, S_z = \pm 1/2)\), and its ground state energy is, up to order \(g^4\), \(E_{n=1,3}/\omega_0 = -g^2/4 + g^4/32\). On the other hand, for two electrons, the electron-phonon interaction splits the initial six–fold degenerate ground state state into a multiplet whose lowest member is a non–degenerate singlet \((J_z = 0, S = 0)\). More precisely (in units of \(\omega_0\)):

\[
\begin{aligned}
E_2(J_z = 0, S = 0) &= -g^2 + g^4/2, \\
E_2(J_z = \pm 1, S = 0) &= -g^2/2 - g^4/8, \\
E_2(J_z = 0, S = 1) &= 0.
\end{aligned} \tag{6}
\]

In the strong coupling limit \(g \gg 1\), the situation is quite different. The ground state has the same quantum numbers as in the weak coupling limit, i.e. \(S = 1/2\) and \(J_z = \pm 1/2\) for odd numbers of electrons, and \(S = 0\) and \(J_z = 0\) for even numbers. On the contrary the lowest excited states are identified by the same spin of the ground state but higher \(J_z\) (apart from the trivial case of 0 and 4 electrons, where there is no Jahn-Teller distortion). They are separated from the ground state by an energy of the order \(\omega_0J_z^2/g^2\). In order to describe this limit, Ref. 4 introduced an effective model with a single electronic level which guarantees that the doubly occupied site is always in a singlet state. The larger occupancies were disregarded by imagining a strong on-site repulsion able to cancel the strong polaronic binding energy (of order \(\omega_0g^2\)). The role of the quantum number \(J_z\) was played by a quantum rotator. The main difficulty with this representation is to implement the constraint that \(J_z\) has to be half integer for a singly occupied site and integer otherwise. This condition is automatically verified in the original two-band model, but has to be enforced by imposing a constraint once the effective single-band plus pseudo-spin picture is used.

### III. LATTICE OF MOLECULES

Let us consider a lattice of E-e molecules coupled by the single particle hopping term:

\[
H_{hopping} = -t \sum_{<i,j>} \sum_{\sigma} \left[c^\dagger_{1,i,\sigma} c_{1,j,\sigma} + c^\dagger_{2,i,\sigma} c_{2,j,\sigma}\right]. \tag{7}
\]

Electron hopping between two neighboring molecules modifies both their spin \(S\) and their pseudo angular momentum \(J_z\). Therefore it will mix the ground state configurations of each molecule with the excited states of the others. In the weak coupling limit \(g \ll 1\), if moreover \(tg \ll \omega_0\), we can retain just the hopping processes which mix the states in the lowest multiplet for each electron occupancy. In fact by means of the unitary transformation Eq.(4), we find:

\[
H_{hopping} = -t \sum_{<i,j>} \sum_{\sigma} U \left[c^\dagger_{1,i,\sigma} c_{1,j,\sigma} + c^\dagger_{2,i,\sigma} c_{2,j,\sigma}\right] U^{-1} =
- t' \sum_{<i,j>} \sum_{\sigma} \left[c^\dagger_{1,i,\sigma} c_{1,j,\sigma} \left[1 + \frac{g^4}{8} (n_{2i-\sigma} + n_{2j-\sigma} - n_{1i-\sigma} - n_{1j-\sigma})\right]\right] \tag{8}
\]
\[-\frac{g^4}{8}c_{1,i,\sigma}^\dagger c_{1,j,-\sigma} + c_{2,j,-\sigma}^\dagger c_{2,j,\sigma}^\dagger + n_{2\sigma} n_{2\sigma'} + n_{1\sigma} n_{2\sigma'} - 1 \]
\[-\frac{g^4}{2} \left( c_{1,i,\sigma}^\dagger c_{2,j,\sigma}^\dagger c_{2,j,\sigma} c_{1,j,-\sigma}^\dagger + (1 \leftrightarrow 2) \right),\]

where \( t' = (1 - g^2/8 + 3g^4/64) \), and this effective hopping is intended to give the correct results for \( tg \ll \omega_0 \). The last term in square brackets acts only when a triply occupied site is involved in the hopping process, and is crucial to maintain the particle-hole symmetry around half-filling (two electrons per site). The effective hopping Hamiltonian \( \hat{H} \) plus the molecular term (5) therefore describe the lattice of E\(-\)e molecules for sufficiently small electron-phonon coupling \( g \), even in the interesting anti-adiabatic limit \( t \sim \omega_0 \).

From Eq.(3) we see that the electron–phonon interaction modifies the hopping amplitude according to the occupation of the sites involved in the hopping process. In particular, if we restrict to the lowest-energy molecular states, the hopping amplitude from (or into) a doubly occupied site (\( J_z = S = 0 \)) increases relatively to the hopping from a single occupied site (also in the molecular ground state) to an empty one. For instance the hopping process from a doubly occupied site to a nearest neighboring empty site, relatively to that from a singly occupied site to an empty site is \( T_{2\to0}/T_{1\to0} = (1 + g^4/4)/\sqrt{2} \) for small \( g \) (see Fig. 1), while \( T_{2\to0}/T_{1\to0} \to 1 \) at large \( g \). As soon as this ratio \( T_{2\to0}/T_{1\to0} \geq 1/\sqrt{2} \) (i.e. \( g \neq 0 \)) a two particle bound state appears in one and two dimensions, even if we neglect the polaronic binding energy. For instance the two-particle problem in vacuum is easily solved (in analogy with Ref. 5) and the self–consistency condition for the energy \( E \) reads:

\[
\frac{1}{N} \sum_k \frac{1}{E - 2\epsilon_k} = \frac{1 + g^4/2}{Eg^4/2},
\]

where \( \epsilon_k \) is the hopping energy in momentum space. This equation indeed admits a bound state solution \( E < 2\epsilon_0 \) in one and two dimensions as soon as \( g \neq 0 \). Notice that this bound state is a feature peculiar to the degenerate model and it is absent for the non-degenerate version (3).

At strong coupling the situation is more complicated. In fact the number of lowest excited states, characterized by higher \( J_z \), with excitation energy \( \leq \omega_0 \), grows like \( g \) for large \( g \), and therefore greatly exceed the analogous number in the weak coupling limit (which coincides with the number of states in the lowest multiplet, i.e. six). In order to simplify the analysis, in Refs. 3,5 the excitations into these higher-\( J_z \) states were forbidden. This amounts to assume that the matrix elements due to the hopping processes which mix these states with the molecular ground state configurations, are much smaller than the excitation energies, that is

\[
t \ll \frac{\omega_0}{g^2},
\]

which is therefore the limit of validity of the results found in Ref. 5. Even with this simplification, the model in the strong coupling limit remains analytically quite intractable due to the constraint that \( J_z \) should be half integer for odd occupancy and integer otherwise, as previously discussed. This is the reason why the analysis was done only numerically and in one-dimension.

IV. BCS-MEAN FIELD SOLUTION.

In the previous Sections we have shown how the lattice of E-e molecules can be mapped in the weak coupling limit (\( g \ll 1 \) and \( tg \ll \omega_0 \)) onto the model with the Hamiltonian (3) plus (6) where only electronic degrees of freedom appear. This model can easily be analyzed by standard many-body techniques. For instance we can study within BCS mean-field theory the instability to superconductivity. In order to describe a more realistic system, we also include a generalized on-site interaction including Hund’s rule exchange in the form:

\[
\frac{U}{2} \sum_{\sigma} (n_{1\sigma} n_{1\sigma'} + n_{2\sigma} n_{2\sigma'}) + V \sum_{\sigma\sigma'} n_{1\sigma} n_{2\sigma'} - \Gamma \tilde{S}_1 \cdot \tilde{S}_2,
\]

where \( \tilde{S}_a \) is the spin operator of electrons \( a = 1, 2 \). \( U, V \) and \( \Gamma \) is in fact the minimal set of parameters describing this six–state three–level multiplet of the doubly occupied site.

The BCS wave function we use to minimize the energy is \( |\Phi_0\rangle = \prod_k \left[ u_k + \frac{v_k}{\sqrt{2}} (c_{1k\uparrow}^\dagger c_{2-k\downarrow}^\dagger + c_{2-k\uparrow}^\dagger c_{1k\downarrow}^\dagger) \right] |0\rangle \).
The interaction between the Cooper pairs is given by:

\[ V_{kk'} = V + \frac{3}{4} \Gamma - \frac{1}{2} \omega_0 g^2 + \frac{7}{16} \omega_0 g^4 \]

\[-t g^4 \sum_{i=1,d} \left[ \cos(k_i a) + \cos(k'_i a) \right],\]

where \( k = (k_1, k_2, ..., k_d) \) is the relative momentum of the pair. The BCS equations are:

\[ \Delta_k = -\frac{1}{L^D} \sum_{k'} V_{kk'} \frac{\Delta_{k'}}{2E_{k'}}, \]

\[ E_k = \sqrt{(\epsilon_k - \mu)^2 + \Delta_k^2}, \]

\[ \epsilon_k = -2t' \sum_i \cos(k_i a), \]

\[ n = 1 - \frac{1}{L^D} \sum_k \left( \frac{\epsilon_k - \mu}{E_k} \right), \]

being \( n \) the electron density and \( \mu \) the chemical potential. The form of the BCS equations implies that the gap \( \Delta_k \) depends on the wavevector \( k \) only through the free particle dispersion \( \epsilon_k \) and this dependence is linear. Therefore \( \Delta_k \) can be parametrized by the two unknowns \( \Delta \) and \( \chi \):

\[ \Delta_k = \Delta \left[ 1 + \chi \sum_i \cos(k_i a) \right], \quad (11) \]

and the BCS set of equations reduce to a set of coupled equations for \( \Delta \), \( \chi \) and the chemical potential \( \mu \) which must be solved numerically. The critical line between the superconducting and the normal state can be obtained analytically:

\[ V_c + \frac{3}{4} \Gamma_c = \frac{1}{2} \omega_0 g^2 - \frac{7}{16} \omega_0 g^4 - g^4 \mu + O(g^6). \quad (12) \]

The first two terms on the right hand side represent a negative pairing energy, originating from a gain of molecular zero–point energy upon pairing. Finally the correlated hopping contribution \( g^4 \mu \) provides an additional pairing mechanism (note that \( \mu < 0 \)) which is the analog of that described in Ref. 5 in the electron–pseudospin model. This term, being intersite, is favored by a large coordination number. We recall that this term is originated by the degeneracy of the electronic band and vibronic modes and has no equivalent in a standard non degenerate polaronic model.

V. ONE-DIMENSIONAL PHASE DIAGRAM

It is interesting to compare the properties of the degenerate two-band model with those of a single-band model in one-dimension (1D), where several rigorous results are known for both weak and strong electron-phonon coupling. In the following analysis we will restrict to densities less or equal to one electron per site.

A peculiar feature of 1D systems, which is absent in higher dimensions but for particular band structures and fillings, is the nesting property of the Fermi surface. This induces a strong coupling between the \( 2k_F \)-phonons and the \( 2k_F \) Charge Density Waves (CDW) (Peierls's instability). In fact, as a result of the diverging \( 2k_F \) density-density electronic correlation function, the \( 2k_F \) phonon frequency softens which in turns leads to an increase of the coupling of these phonons with the CDW. The lower the bare \( 2k_F \)-phonon frequency compared to the electron bandwidth, or alternatively the stronger the electron-phonon coupling constant, the more favored the CDW with respect to Singlet Superconductivity (SS) (see e.g. Ref. 12).

A. Non degenerate single–band model

In the standard single-band model \( \| \), the resulting phase diagram has a region at large phonon frequency and small electron-phonon coupling where SS dominates. Upon decreasing the \( 2k_F \)-phonon frequency or increasing the electron-phonon coupling constant, the model has a cross-over to a region where CDW dominates. Further inside
this region a better approach is to represent the $2k_F$ lattice-distortion with its phase and amplitude. The amplitude fluctuations around the finite average value can be neglected. On the contrary the phase fluctuations are gapless and so strongly coupled to the CDW to be practically indistinguishable (the two move together) (see e.g. Ref. [13]). Although the two regimes look different (at weak coupling the amplitude of the lattice distortion is still not developed due to quantum fluctuations) there is no real transition between them and only a cross-over from SS to CDW characterizes the overall phase diagram, as qualitatively drawn in Fig. 2. An additional electron-electron repulsion enlarges the regime of dominant CDW at expenses of SS [2][4]

B. Degenerate two-band model: weak coupling limit

We start our analysis of the two-band model from the limit of weak electron-phonon coupling and high phonon frequency.

a) Two-band model, no electron-electron interaction. If we integrate out the phonon field we obtain the effective retarded electron-electron interaction

$$-\omega_0 \left( \frac{g^2}{2} \right) \frac{\omega_0^2}{\omega_0^2 - \omega^2} \bar{\tau}(\omega) \cdot \bar{\tau}(-\omega).$$

(13)

If $g \ll 1$ and $\omega_0 \gg t$, the effective interaction can be approximated by its unretrarded limit

$$-\omega_0 \frac{g^2}{2} \bar{\tau}(\omega) \cdot \bar{\tau}(-\omega).$$

This route has been recently followed by Shelton and Tsvelik[13] who treat it further by means of bosonization plus Renormalization Group (RG) analysis, in the absence of electron-electron interaction. In the bosonization language, the fermion model is described by sound modes. In the present case one can define four of these modes: symmetric (with respect to the band indices 1 and 2) and anti-symmetric charge and spin sound modes. Shelton and Tsvelik have found that all these modes acquire a gap except for the symmetric charge mode. This remains gapless and is identified by a Luttinger liquid exponent $K = e^{2\varphi} < 1$[13]. The larger the phonon-induced electron-electron interaction $\omega_0g$, the smaller $K$. For $K > 1/2$ the dominant fluctuations are indeed the SS ones, with the pairing operator we have introduced in the previous section. For $K < 1/2$, on the contrary, $4k_F$-CDW dominate. As before, one finds a smooth cross-over from SS at weak coupling to CDW at strong coupling.

b) Two-band model with finite electron-electron interaction. We consider the model in the same weak coupling limit as in Ref. [13] but in the presence of the interaction Eq. (10). It is useful to begin showing how the interaction modifies the energies of the multiplet [13], since the ordering of these levels determines the physical behavior of the model:

$$E_2(J_z = 0, S = 0) = -\omega_0 g^2 + \omega_0 \frac{g^4}{2} + V + \frac{3}{4} \Gamma,$$

$$E_2(J_z = \pm 1, S = 0) = -\omega_0 \frac{g^2}{2} - \omega_0 \frac{g^4}{8} + U,$$

$$E_2(J_z = 0, S = 1) = V - \frac{1}{4} \Gamma.$$

(14)

We see that the $J_z = S = 0$ state remains the lowest energy state until the Hund term $\Gamma$ is so large to make the triplet state favorable or until the inter-orbital Coulomb repulsion $V$ does not exceed the intra-orbital $U$ so much to make the $J_z = 1$ state favorable. In what follows this latter possibility will be disregarded, i.e. we will always assume $U \geq V$.

By including the interaction within the RG approach of Ref. [13] we find that, so long as the $J_z = S = 0$ state remains the lowest energy state, the physical behavior of the model does not change qualitatively with respect to the case in the absence of interaction. The main effect of the interaction is to diminish the Luttinger liquid exponent $K$, which favors CDW against SS. In addition, as the on-site Coulomb repulsions $U$ and $V$ increase, the $4k_F$-CDW (where the charge fluctuates from 0 to 2 electrons) is suppressed in favor of the $8k_F$-CDW (where the fluctuation is between charge 0 and 1).

Analogous results were first obtained by Manini et al. [13] by numerical diagonalization of the effective model at $g \gg 1$ and $\omega_0 \gg tg^2$. They also analyze the model with an additional repulsive interaction [practically their case corresponds to $U = 2V$ and $\Gamma = 0$ in Eq. (10)], part of which cancels the strong polaronic attraction (of order $\omega_0g^2$). Thus the only pairing mechanism they are left with is that induced by the correlated hopping corresponding to our $g^4\mu$, as previously discussed. On the contrary Shelton and Tsvelik only consider the effects of the polaronic attraction, which
is dominant at small $g$. The two apparently different approaches give analogous results since, as we have shown, correlated hopping favors a pairing in the same channel as the polaronic term (i.e. both orbital and spin singlet).

**c) Two-band model, no electron-phonon coupling.** The model with the interaction term (13) but no electron-phonon coupling has also interesting properties. If $\Gamma \neq 0$ we still find gaps in the antisymmetric charge sector and in the spin sectors. Moreover, if $K < 1/2$, we find in addition dominant singlet superconductive fluctuations, which however differ from those we find in the presence of electron-phonon coupling since they are odd by interchanging the two orbitals (which is a way of avoiding the on site repulsion). This curious result which predicts superconductivity for purely repulsive interaction is indeed a common feature of many two-band models in one dimension. For $K > 1/2$ the $4k_F$ CDW fluctuations become dominant, although the pair correlation function is still power-law decaying. In the presence of phonon induced electron-electron interaction (which we still take as unretarded), this phase remains stable as far as the doubly occupied site in a triplet configuration is lower in energy than the singlet one; otherwise, as we already said, the previously discussed regime occur. The two phases are separated by a gapless Luttinger liquid regime with interaction–dependent exponents.

**d) Quarter-filled two-band model.** At quarter filling (one electron per site) $8k_F$–Umklapp scattering is possible and, if $K < 1/2$, the symmetric charge mode gets gapped and the system becomes insulating. This occurs if either the electron-phonon coupling or the on-site repulsion are sufficiently strong. In this commensurate phase all modes are gapped unless the coupling constants have particular values. For instance if the electron-electron interaction and the electron-phonon coupling combine in such a way that the doubly occupied site multiplet (14) is “accidentally” degenerate, then the antisymmetric charge mode and the spin modes are gapless. At weak coupling we in fact realize that all the scattering processes, apart from the Umklapp, are marginally irrelevant.

For strong repulsion, the model can be mapped onto a generalized Heisenberg chain with two species of spin-1/2 per site: the physical spin $\vec{S}$ and the electron pseudo angular momentum $\vec{\tau}$ defined by Eq.(2). This kind of super-exchange Hamiltonians have been quite intensively studied in the context of insulators containing transition metal ions (see e.g. Ref. 7). Practically the derivation of the effective Hamiltonian follows the derivation of the Heisenberg model from the Hubbard model at half filling for $U \gg t$. The important difference is that the state of a virtually doubly-occupied site is not unique. The two electron state can be any of the levels in the multiplet (14). Accordingly we can define three super-exchange couplings: $J_{\text{sing}}$ if the intermediate doubly occupied level has $S = J_\tau = 0$, $J_T$ if it has $S = 1$ and $J_1 = 0$, and $J_1$ if $S = 0$ and $J_1 = \pm 1$. The effective 1D Hamiltonian is:

$$H_{\text{eff}} = \left(\frac{J_{\text{sing}}}{2} - \frac{J_T}{2} + J_1\right) \sum_{<ij>} \vec{S}_i \cdot \vec{S}_j + \left(\frac{3J_T}{2} - \frac{J_{\text{sing}}}{2}\right) \sum_{<ij>} \vec{\tau}_i \cdot \vec{\tau}_j + (J_{\text{sing}} - J_1) \sum_{<ij>} \tau_{zi} \tau_{zj}$$

\begin{equation}
+ (2J_T + 2J_{\text{sing}}) \sum_{<ij>} \left(\vec{S}_i \cdot \vec{S}_j\right) (\vec{\tau}_i \cdot \vec{\tau}_j) + (4J_1 - 4J_{\text{sing}}) \sum_{<ij>} \left(\vec{S}_i \cdot \vec{S}_j\right) (\tau_{zi} \tau_{zj}).
\end{equation}

Similar Hamiltonians have been recently introduced also in connection with fullerenes. For instance, if the polaronic attraction is so strong that the $J_\tau = S = 0$ state for two electrons is much lower in energy than the other levels, then one can assume $J_T = J_1 = 0$. In this case it has been shown in Ref. 8 that the spectrum of $H_{\text{eff}}$ has a gap both in the spin and in the pseudo spin sector and the ground state is a kind of valence bond solid. If, on the contrary, the triplet state energy is lower than the singlet one, the physical spins are ferromagnetically correlated. In this case the Hamiltonian (15) has been recently invoked by Auerbach et al. 17 to explain the weak ferromagnetism plus insulating behavior in TDAE-C$_{60}$. These authors also identify some solvable points in the phase diagram. For instance if $J_{\text{sing}} = J_T = J_1$ the model is SU(4) invariant and is a particular case of a wide class of SU(N) invariant models solved by Sutherland.18 This point corresponds to the situation discussed above where the levels of the two-electron multiplet become degenerate. In this case we indeed find at weak coupling a spectrum with three gapless excitations (the antisymmetric charge mode and the two spin modes) which is in agreement with the exact solution of the effective model at strong coupling.19

**C. Degenerate two-band model: strong coupling limit**

We now consider the limit of low phonon frequency or, equivalently, of strong electron-phonon coupling.

(i) **Weak retardation effects.** We can improve the weak coupling analysis by taking into account a weak retardation. The main consequence of a finite phonon-frequency is its softening induced by the coupling with the CDW. This in turn leads to an increase of the electrons $2k_F$–phonon coupling constant and therefore to a decrease of $K$. A simple
method to describe this effect in the weak coupling or high phonon frequency limit is the two cut-off renormalization group (see e.g. Ref. [12]). By applying this method we find that, as in the standard non degenerate model, a decreasing phonon frequency is equivalent to an increasing coupling constant.

(ii) **Strong retardation effects.** New features appear as soon as the phonon frequency gets too small or the electron-phonon coupling too large. In this case we can no longer apply the weak coupling renormalization group, and we have to resort to some strong coupling approach. However we can qualitatively predict, by simple arguments, what is going to happen in this limit. For an isolated molecule we already saw that the lowest excited states in the strong coupling limit have the same total spin as the ground state (e.g. \( S = 0 \) for two electrons) but higher \( J_z \); their excitation energies vanish at large \( g \) approximately like \( \omega_0 J_z^2/\omega^2 \). When the molecules are coupled, the hopping \( t \), if not too small in comparison with \( \omega_0/\omega^2 \), will clearly mix in the ground state wave function molecular states with higher \( J_z \). The \( z \)-component of the total pseudo-angular momentum \( J_z \), i.e. the sum over all molecules of \( J_z \), is anyway a constant of motion, and remains zero in the ground state. However we expect that an excitation which changes the total pseudo-angular momentum should become gapless in this strong coupling limit. Notice that this regime falls outside that analyzed in Ref. [3]. Even though these authors consider the \( g \gg 1 \) limit, they still assume \( t \ll \omega_0/\omega^2 \) so that higher \( J_z \) states are always separated by a finite gap in their case.

The previous qualitatively scenario can be formally derived by the same approach which is used in the strong coupling limit for a non-degenerate model (see e.g. Ref. [13]). The method consists in solving the mean field equations of the 1D charge and spin sound waves (which are the only coherent excitations in one dimension) strongly coupled to the phonons and then expanding around the solution to take into account quantum fluctuations. In our case we have to describe the \( 2k_F \) lattice distortion by the amplitudes \( \Delta_x = \Delta \cos(\theta) \) and \( \Delta_y = \Delta \sin(\theta) \) and the phases of each phonon component (\( x \) or \( y \)). The two phases are locked to the symmetric charge mode and the three describe a single gapless sound mode. Moreover \( \theta \) gets locked to the antisymmetric charge mode and the two also describe a single gapless mode. The amplitude \( \Delta \), which acquires at mean field level a finite value, feels on the contrary a finite restoring force, so that its fluctuations can be neglected at low temperature. Analogously, the spin modes get gapped.

In conclusion we find that: 1) the gap of the anti-symmetric charge mode vanishes while the spin gaps remain finite; 2) the dominant fluctuations are now inter-band charge density waves or better pseudo angular momentum density waves identified by the \( 2k_F \) components of the operators

\[
\tau^+ = c_{1\sigma}^\dagger c_{2\sigma}, \quad \tau^- = c_{2\sigma}^\dagger c_{1\sigma}.
\]

In a sense we find in this regime an orbitally quasi-ordered ground state (in 1D a continuous symmetry can not be broken).

The vanishing gap in the antisymmetric charge mode can also be inferred from the weak coupling regime. In fact as the electron-phonon coupling increases we find that the operator which couples the charge mode to the spin modes gets more and more relevant and that even if the spin modes remain gapped they will eventually become unable to induce a charge gap. Therefore the two approaches, weak and strong coupling, are perfectly compatible. In comparison to a non-degenerate single-band model, we find that in the degenerate two-band case the increase of the electron-phonon coupling, or equivalently the decrease of the phonon frequency, is accompanied by the closing of a gap in the excitation spectrum.

Notice that, even at quarter filling (one electron per site) the antisymmetric charge mode remains gapless. In fact the \( 8k_F \) Umklapp processes only couple to the symmetric charge mode, which eventually acquire a gap, but do not affect the antisymmetric charge sector. Therefore at filling \( 1/4 \) the difference between the weak coupling regime (where the whole spectrum has a gap, as we previously discussed) and the strong coupling regime (where we find one gapless branch of excitations) is even more pronounced.

**D. Overall phase diagram of the degenerate two-band model**

We are now able to discuss the phase diagram of the two-band model both at weak and strong electron-phonon coupling. The phase diagram is qualitatively drawn in Fig. 3. We find three different regions:

i) at weak coupling or high phonon frequency, the system has dominant SS fluctuations (SS in Fig. 3);

ii) upon increasing the coupling constant or decreasing the phonon frequency, we find a cross-over to a region of dominant \( 4k_F \) CDW (see Fig. 3);

iii) finally, further inside this region, the gap in the antisymmetric charge sector closes and the model has dominant inter-band \( 2k_F \) density waves which can be also interpreted as orbital density waves (\( 2k_F \)-ODW in Fig. 3).
The addition of the on-site repulsion $\Gamma$ does not modify qualitatively this phase diagram until the Hund coupling $\Gamma$ is sufficiently large to make the triplet state for two electrons favorable [see Eq. (14)]. If $\Gamma$ is not so large, we expect that the on-site repulsion simply reduces the region of stability of SS in favor of CDW. Moreover it also suppresses the CDW components where the charge fluctuates between 0 and 2, and increases the components where it fluctuates between 0 and 1. This implies: 1) that the $8k_F$–CDW component is enhanced against the $4k_F$ one; and 2) that the $4k_F$ pseudo angular momentum density wave component is enhanced against the $2k_F$ one.

VI. CONCLUSIONS

In summary we have investigated how level degeneracy and dynamical Jahn–Teller effect influence the phonon-induced attraction in a simplified model of two degenerate bands coupled to a doubly degenerate optical phonon. We have shown that a new intersite attraction is generated to fourth order in the electron-phonon coupling which is not present in a standard one band model. This new process has many advantages with respect to the on-site polaronic attraction, for instance it is robust to the presence of local repulsion and it does not lead to phase separation. However its strength is much smaller, at least in the weak coupling limit we have analyzed, than the on-site polaronic term, so that it is still an open question whether it may play a relevant role as a mechanism for phonon-induced superconductivity.

In one dimension the model can be analyzed in detail in the whole range of the parameters. We have calculated the phase diagram which displays quite new features as compared to the one band model. Together with a standard cross-over from a superconducting region to a charge-density wave regime as the electron-phonon coupling increases (or equivalently the phonon frequency decreases), we have found a new region at strong coupling where a kind of modulated-orbital ordering is present. Such orderings have been already proposed in connection to systems with magnetic ions, but they were mainly ascribed to the strong electronic correlations. We have shown that modulated orbital-ordering may also arise from purely vibrational mechanisms.

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FIG. 1. Hopping processes in the subspace of the molecular ground state configurations. In parenthesis we write the values of the quantum numbers $S_z$ and $J_z$. We recall that the lowest energy configuration of a doubly occupied site is a singlet.

FIG. 2. Qualitative phase diagram of a non-degenerate phonon mode coupled to a single band of non interacting electrons. $g$ is the dimensionless electron-phonon coupling constant, $\omega_0$ is the phonon frequency and $t$ the electron hopping matrix element. SS identifies the superconducting region while $2k_F$-CDW the regime where charge density wave with $2k_F$ oscillations dominate. The spin modes are gapped everywhere in the phase diagram.

FIG. 3. Phase diagram for a two-dimensional phonon mode coupled to a doubly degenerate band of electrons (lattice of E-e molecules). In this case $4k_F$-CDW indicates dominant density waves with period $2\pi/(4k_F)$, while $2k_F$-ODW means orbital density waves with period $2\pi/(2k_F)$. In parenthesis we indicate the density wave components whose amplitude increases as the on-site repulsion gets bigger.
\(T_{20}\) and \(T_{10}\) act on states \((0, 0)\) and \((\pm 1/2, \pm 1/2)\) respectively, transforming them to \((\mp 1/2, \mp 1/2)\) and \((\mp 1/2, \mp 1/2)\) respectively.
$2k_F$-CDW

$\sigma$

$\frac{\omega_0}{t}$

SS
$\omega_0/t$

g

$2k_F$ ODW \ (4k_F ODW)

$4k_F$-CDW \ (8k_F$-CDW$)

SS