Valence-bond states in dynamical Jahn-Teller molecular systems

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We discuss a hopping model of electrons between idealized molecular sites with local orbital degeneracy and dynamical Jahn-Teller effect, for crystal field environments of sufficiently high symmetry. For the Mott-insulating case (one electron per site and large Coulomb repulsions), in the simplest two-fold degenerate situation, we are led to consider a particular exchange hamiltonian, describing two isotropic spin-1/2 Heisenberg problems coupled by a quartic term on equivalent bonds. This twin-exchange hamiltonian applies to a physical regime in which the inter-orbital singlet is the lowest-energy intermediate state available for hopping. This regime is favored by a relatively strong electron-phonon coupling. Using variational arguments, a large-$n$ limit, and exact diagonalization data, we find that the ground state, in the one dimensional case, is a solid valence bond state. The situation in the two dimensional case is less clear. Finally, the behavior of the system upon hole doping is studied in one dimension.
I. INTRODUCTION

Ions or molecules with degenerate electronic orbitals coupled to local vibrations can display a rich variety of phenomena. The most notable of these phenomena is the so-called static Jahn-Teller (JT) effect, i.e., the system gains energy by lowering the symmetry through a static distortion, thereby removing the electronic degeneracy. For finite systems, like a molecule, quantum mechanics can play an important role in that, if the frequency of the relevant vibronic modes is high enough, it can dynamically restore the original symmetry through a quantum superposition of “degenerate” distorted configurations (dynamical JT effect).

Many systems containing JT ions or molecules are found to be insulators with quite a rich variety of spin and orbital ordering effects. Such a richness of exchange effects is due to the interplay between the spin and orbital degrees of freedom.

The simplest cases can be modeled by the so-called $E \otimes e$ JT-coupling, i.e., at each site $r$ a two-fold degenerate electronic orbital is coupled to a two-fold degenerate local vibron. Although conceived as the simplest workable model, such a situation is not totally unrealistic, as higher molecular degeneracies can often be reduced, by the crystal field of the solid state environment, to residual doublets. (If the crystal field symmetry is very low, the degeneracy will be completely removed).

If exactly one electron sits on each JT site, and if the Coulomb repulsion is very large, the system will have an insulating gap, due to Mott-Hubbard correlations, and the low-energy spectrum will consist of spin and orbital excitations. For the $E \otimes e$ case, which we are going to consider, the physics of the insulating state is governed by an exchange hamiltonian involving, besides the actual spin $\mathbf{S}_r$, also a pseudo-spin-1/2 variable $\mathbf{T}_r$, representing the orbital degrees of freedom. Unlike the case of a non-degenerate orbital, where antiferromagnetism is favored, one finds here a rich phase diagram, depending on the energy of the two-particle intermediate states available for virtual hopping. If Hund’s rule coupling is the dominant effect, the lowest doubly occupied site is a spin triplet, and spin ferromagnetism turns out to be favored. Many experimental systems, including possibly the case of TDAE-C$_{60}$, may fit into such a scenario. In the present paper we are going to consider a different regime, i.e., when the coupling to vibrons is strong enough that an inter-orbital singlet state becomes the lowest-energy doubly-occupied virtual state. We are going to argue that new interesting phases can show up in this case. The exchange hamiltonian for this case can be shown to be related to the following spin-model:

\[ H_{ST} = -J \sum_{<rr'>} (2\mathbf{S}_r \cdot \mathbf{S}_{r'} - \frac{1}{2})(2\mathbf{T}_r \cdot \mathbf{T}_{r'} - \frac{1}{2}) \cdot \]

We will show that, in this case, valence bond (VB) states tend to be favored, at least in low enough spatial dimensions.

The paper is organized as follows. Section II introduces the hopping model that we will consider. In section III we will discuss in detail the hamiltonian $H_{ST}$ in Eq. (1). In section IV we study the behavior of the model upon introduction of holes, in one dimension. Finally, section V contains our conclusions, and some open issues.

II. THE MODEL

Suppose that at each site $r$ of the lattice we have two degenerate electronic orbitals and two degenerate phonon modes, of frequency $\omega_0$, both labeled by an orbital quantum number $l = \pm \ell$. Let $c^\dagger_{l \ell}(r)$ be the creation operator for an electron with spin $\sigma$ and orbital quantum number $l$ at site $r$, and $b^\dagger_l(r)$ the phonon operator. In a standard $E \otimes e$ Jahn-Teller problem, the on site linear electron-phonon interaction term can be written as

\[ H_{e-ph}(r) = \omega_0 \sum_{l=\pm} [b^\dagger_l b_l + 1/2] + (g \omega_0/2) \{ T^+ [b^\dagger_l + b_l] + \text{H.c.} \} , \]

where $T = (1/2) \sum \sum \sum \sum c_{l,\ell,\sigma}^\dagger (\sigma)_{l\ell} c_{l,\ell,\sigma}$ is the orbital (pseudo) spin operator, $\sigma$ are Pauli matrices and we have omitted the obvious site-label. We will also consider electron-electron terms, which include a Hubbard intra-orbital repulsion $U$, an inter-orbital repulsion $U_i$, and an exchange (Hund’s) coupling $J_H$,

\[ H_{e-e}(r) = U \sum_{l=\pm} n_{l,\uparrow} n_{l,\downarrow} + U_i \sum_{\sigma,\sigma'} n_{+,\sigma} n_{-,\sigma'} - J_H \mathbf{S}_+ \cdot \mathbf{S}_- , \]

where $\mathbf{S}_l = (1/2) \sum_{\sigma,\sigma'} c_{l,\ell,\sigma}^\dagger (\sigma)_{aa'} c_{l,\ell,\sigma'}$ is the spin operator for the $l$–orbital.
Assume now that there are (small) electronic hopping processes between the different sites described by a standard tight-binding hamiltonian. The total hamiltonian is therefore written as:

\[
H = -t \sum_{<r,r'>} \sum_{i,\sigma} \left[ c_{i\sigma}^\dagger(r)c_{i\sigma}(r') + H.c. \right] + \sum_r H_{\text{site}}(r),
\]

where we have neglected overlap integrals between orbitals with different orbital quantum numbers, and

\[
H_{\text{site}}(r) = H_{e-ph}(r) + H_{e-e}(r).
\]

We will be interested in the limit in which double occupancy of a site is strongly inhibited by the repulsive on-site interactions. The low-energy physics is then described by an effective hamiltonian in which the double occupancy is only treated as a virtual process to second-order in the hopping matrix element. For a two-fold degenerate orbital, there are six possible two-particle states to be considered as intermediate states: an inter-orbital singlet \( |S = 0, T^z = 0 \rangle \), two intra-orbital singlets \( |\pm \rangle = |S = 0, T^z = \pm 1 \rangle = c_{\pm \uparrow}^\dagger c_{\pm \downarrow}^\dagger |0 \rangle \), and an inter-orbital triplet \( |T \rangle = |S = 1, T = 0 \rangle \). For the case of one electron per site, \( n = 1 \), the resulting effective hamiltonian involves two spin-1/2 operators at each site, the spin \( S \) and the orbital pseudo-spin \( T \). The derivation is standard, yielding

\[
H_{\text{eff}} = \sum_{<r,r'>} \left[ (J_S - J_T + 2J_\pm) |S_r \cdot S_{r'} \rangle + \left( 3J_T - J_S \right) |T_r \cdot T_{r'} \rangle + 2(J_S - J_\pm) T^z_r T^z_{r'} \right]
+ \sum_{<r,r'>} \left[ 4(J_S + J_T) (S_r \cdot S_{r'}) (T_r \cdot T_{r'}) + 8(J_\pm - J_S) (S_r \cdot S_{r'}) (T^z_r T^z_{r'}) \right].
\]

The couplings \( J_S, J_T, \) and \( J_\pm \) generalization of the famous antiferromagnetic coupling \( 4t^2/U \) of the non degenerate Hubbard model, are essentially given by \( t^2/\Delta E_0 \) where \( \Delta E_0 \) is the energy difference between a doubly occupied site of type \( \alpha = S, T, \pm \) and two singly occupied sites, and \( t_\alpha \) is an effective hopping matrix element reduced by electron-phonon interactions (Ham’s factor).

In absence of electron-phonon coupling \( (g = 0) \), \( t_\alpha = t \) and \( \Delta E_0^{(0)} = U_i + (3/4)J_H, \Delta E_{T}^{(0)} = U_i - (1/4)J_H, \Delta E_{\pm}^{(0)} = U \). The triplet state is therefore the lowest energy virtual state (under the realistic assumption \( U_i < U \)), and \( J_T \) the largest coupling in the problem. Spin ferromagnetism is the natural outcome of such a scenario. The Jahn-Teller coupling can change this picture considerably. First of all, standard polaronic effects lead to a decrease of the energy of the singlet states, primarily the inter-orbital singlet \( |S \rangle \), with respect to the triplet states \( |T \rangle \). Second, the effective hopping matrix element \( t_\alpha \) turns out to be larger for the singlet \( |S \rangle \) than for the other states. Ref. gives the results for the \( J \)'s obtained from perturbation theory in \( g \), accurate to order \( g^4 \):

\[
J_S = \frac{t^2(1 + g^4/2)}{U_i + (3/4)J_H - (g^2/2 - 7g^4/16)\omega_0}
\]

\[
J_T = \frac{t^2}{U_i - (1/4)J_H + (g^2/2 - 4g^4/16)\omega_0}
\]

\[
J_\pm = \frac{t^2}{U - (3g^4/16)\omega_0}.
\]

In the opposite strong electron-phonon coupling case, \( g \to \infty \), it was shown in Ref. that, again, the most important doubly-occupied state is the inter-orbital singlet \( |S \rangle \), and the model can be mapped into a single-band hamiltonian with a spin-1 variable attached to each site. This also leads to a situation in which, effectively, \( J_S \) is the only coupling left in the problem.

The mean field phase diagram of the model has been studied in Ref., together with a few special points where exact solutions can be obtained in \( D = 1 \). As it turns out, there is a region of the phase diagram, not considered so far, where, as we will argue below, valence bonds (VB) are favored. The physical regime in which this region of relevance is precisely the JT limit in which \( J_S \) is the largest coupling in the problem, i.e., the two-particle inter-orbital singlet has lower energy than the corresponding triplet.

More in detail, let us assume that \( J_S > J_T \) and define \( J = J_S - J_T \). In a bipartite lattice the effective hamiltonian, after performing the canonical transformation \( T^\pm \to (-1)^T T^\pm \), can be written as:

\[
H_{\text{eff}} = H_{\text{ST}} + \Delta H
\]
\[ H_{ST} = J \sum_{<rr'>} \left[ S_r \cdot S_{r'} + T_r \cdot T_{r'} - 4(S_r \cdot S_{r'})(T_r \cdot T_{r'}) \right], \]

and

\[ \Delta H = 4J_T \sum_{<rr'>} \left[ T_r^z T_{r'}^z - (2S_r \cdot S_{r'} + 1/2) T_r^\mu T_{r'}^\mu \right] + 4J_\pm \sum_{<rr'>} (2S_r \cdot S_{r'} - 1/2)(T_r^z T_{r'}^z + 1/4). \]

In the next section we will concentrate on \( H_{ST} \), showing first of all that it certainly has a VB-solid ground state in \( D = 1 \), and suggesting that the same might be true in \( D = 2 \). The presence of a gap in the excitation spectrum implies the robustness of such a phase with respect to a small enough perturbation \( \Delta H \).

Next, we will consider the question of the behavior of a valence bond state upon doping. The resulting generalization of the \( t-J \) model will be discussed, for the \( D = 1 \) case, in section [IV].

**III. ONE ELECTRON PER SITE: THE SPIN HAMILTONIAN.**

As previously discussed, when there is exactly one electron per site (\( n = 1 \)) and one assumes the inter-orbital singlet \( |S\rangle \) to be the only important intermediate two-particle state, the exchange hamiltonian governing the spin and orbital degrees of freedom can be written as

\[ H_{ST} = -J \sum_{<rr'>} (2S_r \cdot S_{r'} - \frac{1}{2})(2T_r \cdot T_{r'} - \frac{1}{2}) = -J \sum_{<rr'>} (P_{rr'}^{(S)} - 1)(P_{rr'}^{(T)} - 1), \]

where \( P_{rr'}^{(S)} = 2S_r \cdot S_{r'} + 1/2 \) is a permutator between the spins at sites \( r \) and \( r' \), and similarly \( P_{rr'}^{(T)} \) for the pseudo-spins. This form will be particularly useful in the following.

This model shows an obvious spin and pseudospin rotation invariance described by the \( SU(2) \otimes SU(2) \) group. However, the full symmetry group displayed by (11) is much larger and includes \( SU(4) \). Indeed, one can show that, in a bipartite lattice, \( H_{ST} \) commutes with the 15 operators

\[ S^a = \sum_r S_r^a, \quad T^a = \sum_r T_r^a, \quad \text{and} \quad L^{\mu\nu} = 2\sum_r (-1)^r S_r^\mu T_r^\nu \]

which generate the Lie algebra \( su(4) \) [11]. Due to the staggering in the \( L^{\mu\nu} \) operators, these generators do not commute with the spatial symmetries which interchange the two sublattices. Therefore, the full symmetry group is even larger than the aforementioned \( SU(4) \). Finally, we notice that this hamiltonian differs from the exactly soluble \( SU(4) \) Sutherland model \( H = J \sum_{<rr'>} P_{rr'}^{(S)} P_{rr'}^{(T)} \) obtained by a natural generalization of the Heisenberg hamiltonian. Rather, it is possible to show that the \( SU(n) \)-invariant model introduced by Affleck [12]

\[ H_n = \frac{1}{n} \sum_{<rr'>} S_{\beta}^\alpha(r) \tilde{S}_\alpha^\beta(r'), \]

is unitarily equivalent to \( H_{ST}/4J \) for \( n = 4 \). Here \( S_{\beta}^\alpha \) and \( \tilde{S}_\alpha^\beta \) generate, respectively, the fundamental and anti-fundamental representations of \( SU(n) \) [13].

In \( D = 1 \), Affleck has shown that \( H_n \), in the limit \( n \to \infty \), has two simple VB-solid ground states, illustrated in Fig. [4]. Moreover, the \( n = 3 \) case has also been shown to have a dimerized ground state, although with a large spin-spin correlation length. [13] As the tendency to dimerization is likely to increase with \( n \), [14] we expect that the \( n = 4 \) case, of interest to us, will also have a VB-solid type of ground state. This expectation will be explicitly shown to be correct in \( D = 1 \).

Let us first show that singlet bonds between \( S \) and \( T \) variables are very natural objects to introduce in our problem, for any \( D \). If we denote by \( (rr')S = 2^{-1/2}(\uparrow_r \downarrow_{r'} - \downarrow_r \uparrow_{r'})S \) a singlet bond formed between the spins at \( r \) and \( r' \), it is easy to show that [14]

\[ (P_{rr'}^{(S)} - 1)(rr')_S = -2(rr')_S \]
\[ (P_{rl}^{(S)} - 1)(rr')_S(l'l'_S) = (r'l)_S(rr')_S. \]

Similar results apply to \( P_{rr'}^{(T)} - 1 \) when acting on valence bonds formed from the pseudo-spin variables, \( (rr')_T \). If we denote by \( (rr')_T = (rr')_S T_{rr'} \) the product of singlet bonds between \( r \) and \( r' \) for both \( S \) and \( T \), and by \( Q_{rr'} = [P_{rr'}^{(S)} - 1][P_{rr'}^{(T)} - 1] \), we find that \( H_{ST} = -J \sum_{<rr'>} Q_{rr'} \) and
First observation: the subspace of valence bond states in which bonds are simultaneously S- and T-singlets is left invariant by the Hamiltonian. In all figures, we will denote by a line such simultaneous S- and T-singlets.) Such a subspace is, however, still overcomplete. In $D = 1$, nevertheless, if we apply $H_{ST}$ any number of times to the valence bond solid in Fig. 1, we generate a subset of valence bond configurations which are linearly independent (although not orthogonal). These are the valence bond configurations associated to non-crossing Lewis diagrams. It is known that such a basis can be conveniently used to work out efficient exact diagonalization algorithms in small chains. The ground state wave function for a chain of $N = 8$ sites, for instance, can be easily obtained by solving a simple $3 \times 3$ problem. Fig. 2 shows the result obtained for the ground state wave function, and the lowest excited state of momentum $\pi$, in terms of VB configurations.

Second observation: as is apparent from Eq. 4, a nearest-neighbor bond contributes a diagonal energy of $-(4J)$, whereas the off-diagonal matrix elements connecting different VB configurations are smaller by a factor 4, i.e., $-J$. For the $SU(n)$-model of Affleck, the off-diagonal matrix element are smaller by a factor $1/n$, which implies that only diagonal energies are retained in the limit $n \to \infty$. The ground states, for $n = \infty$, are therefore the VB configurations with the maximum number ($= N_{s,\text{sites}}/2$) of nearest-neighbor bonds connected by VBs. In $D = 1$, there are only two such states, i.e., the VB-solids in Fig. 1.

To check if the VB scenario remains correct for our $n = 4$ case, we resort to exact Lanczos diagonalizations of chains up to 14 sites, and to Green Function Monte Carlo for longer chains. Fig. 3 shows the finite-size value of the gap $\Delta E/S = 0$ decreasing faster than $1/L$ for $L \to \infty$. The triplet, instead, lies above with a gap $\Delta E \approx -0.218/4$.

Finally, simple variational arguments also point to a VB ground state in $D = 1$, while being, we believe, not conclusive in $D = 2$. A VB phase benefits highly from the large values of $\langle S_r \cdot S_r \rangle = (T_r \cdot T_r) = -3/4$ on the singlet bond, due to the presence of the “square” of the singlet contribution in the quartic term of $H_{ST}$, which enters with a factor 4. Let us compare, for instance, the energy of the following two states: (i) The product of two independent Heisenberg ground states, $|\Psi_{2-H}\rangle = |\Psi_H^{(r)}\rangle \otimes |\Psi_H^{(r')}\rangle$, and (ii) the product of two VB states, $|\Psi_{2-VB}\rangle = |\Psi_{VB}^{(r)}\rangle \otimes |\Psi_{VB}^{(r')}\rangle$ where each VB state has the simple form of a product of dimers on adjacent sites. In $D = 1$ we take

$$|\Psi_{VB}\rangle = (12)(34) \cdots (L-1L),$$

where $(ij) = (\uparrow\downarrow - \downarrow\uparrow)/\sqrt{2}$ denotes a singlet between sites $i$ and $j$. In $D = 2$ we consider the simplest short range VB state: a columnar dimer state, or, equivalently, any state with nearest-neighbor pairs coupled into singlets in an arbitrary manner (there is a huge degeneracy). The energy per site of the two states are:

$$\epsilon_{2-H} = 2H - 4DJ(\epsilon_H/DJ)^2,$$

$$\epsilon_{2-VB} = 2\epsilon_{VB} - 4J(1/2)(-3/4)^2.$$  

Here $\epsilon_H = D\langle S_r \cdot S_r \rangle$ ($r$ and $r'$ nearest neighbors) and $\epsilon_{VB} = -(3/8)J$ are the energy per site of the Heisenberg ground state and of the VB state, respectively. For the Heisenberg model we have $\epsilon_H/J = -(ln2 + 1/4) \approx -0.4431$ (in $D = 1$) and $\epsilon_H/J = -0.66$ (in $D = 2$), whereas for the crude VB state considered here, the expression for $\epsilon_{2-VB}$ turns out to be independent of $D$. The factor $(1/2)$ in the expression for $\epsilon_{2-VB}$ is due to the fact that only half of the bonds in the VB state enjoy the large singlet-singlet pairing $-4J(3/4)^2$. In spite of this reduction, the coefficient of the quartic term is substantially larger for the VB state than for the Heisenberg state in both $D = 1$ and $D = 2$ ($\approx -0.2812(4J)$ for the VB state, to be compared to $\approx -0.1964(4J)$ and $\approx -0.218(4J)$ for the $D = 1$ and $D = 2$ Heisenberg, respectively). In $D = 1$ the VB state wins over the Heisenberg state. Generally speaking, an increase in the coordination number tends to stabilize a Néel-like antiferromagnet with respect to VB states. In $D = 2$, the
previous crude variational estimate would indeed give the Heisenberg state as favored. The VB state considered here is, however, very poor: for instance, its energy per site, neglecting the quartic term, is only $-0.375J$, whereas it is well known that short-range RVB states close in energy to the Heisenberg ground state can be constructed. As a consequence, we believe the present variational estimate to be not conclusive in $D = 2$.

In case the VB picture should be energetically favored, we face the problem of determining the possible orderings of the dimers in the lattice. In principle, either a VB crystal with broken translational symmetry or a homogeneous spin liquid may occur. Following Affleck’s $D = 1$ approach, a possible way of tackling this problem, in $D = 2$, is from the $n \to \infty$ limit. For $n = \infty$, once again, all the states made up of the maximum possible number ($= N_{sites}/2$) of nearest-neighbor S- and T-VBs – we refer to them as NNVB configurations – are degenerate, linearly independent (although not orthogonal) ground states. Contrary to the $D = 1$ case, where only two such states exist (see Fig. 6), in $D = 2$ this implies a huge degeneracy. For $n \to \infty$, however, there are off-diagonal matrix elements connecting different NNVB states (smaller by a factor $1/n$, as previously discussed), which lift this degeneracy to first order. It is straightforward to verify, using Eq. 14, that the effective Hamiltonian within the subspace of NNVB states (to first order in $1/n$) is just the quantum dimer model (QDM) first introduced in Ref. 13.

$$H_{QDM} = -J \sum_{\text{plaquette}} \{ | = \rangle \langle || | + \text{H.c.} \} + V \sum_{\text{plaquette}} \{ | = \rangle \langle | + | || \} \langle || |, \quad (17)$$

for the particular case of $V = 0$. (Here $||$ and = schematically indicate adjacent S- and T-VBs in the $y$ and $x$ direction.) The QDM is known to have a columnar solid phase in a region of parameter space close to $V = 0$. Recently, an exact diagonalization study of the QDM has revealed that such a columnar solid phase has, more precisely, the features of a plaquette RVB, i.e. translational invariance in one direction is spontaneously broken, but the spin-Peierls “columns” are disordered as a consequence of a resonance of parallel bonds in each plaquette. This picture would yield a fourfold degenerate ground state in two dimensions.

We conclude that, for $n \to \infty$, our model has a columnar VB phase in $D = 2$. Given the fact that our crude variational calculation appears to favor a Néel state in $D = 2$, we believe that the issue of the actual behavior of our $n = 4$-case, $H_{ST}$, in $D = 2$ is still open. This issue will be addressed in a future numerical study.

IV. LESS THAN HALF-FILLING.

The motion of holes in a VB state has been the subject of considerable research starting from the early works on high temperature superconductivity. Now, we are able to investigate this problem on the basis of a consistent microscopic model which does have a VB solid as a ground state. This study may shed light on the issue whether holons and spinons decouple in VB states and whether the VB spin background favors effective hole-hole attraction. Therefore, we analyze in some detail the case of filling $n < 1$ in one dimension. For large repulsive interactions (small $J$) the effective Hamiltonian describing the system is simply the analog of the $t - J$ model

$$H_{t-ST} = P_o K P_o - 4J \sum_{<r,r'>} n_r n_{r'} (S_r \cdot S_{r'} - \frac{1}{4})(-T_r \cdot T_{r'} + 2T_r^z T_{r'}^z - \frac{1}{4}) + (3 - \text{site terms}), \quad (18)$$

where $K$ is the hopping part of the original Hamiltonian (Eq. 9), $P_o$ is the projector onto states without double occupancy, and $n_r$ is the occupation number operator. In $D = 1$, analogously to the Hubbard case, the (real-space) wavefunction factorizes, for $J \to 0$, into a spinless fermion part times the wavefunction of a suitable spin hamiltonian $H_{\text{spin}}$ on the squeezed chain

$$\Psi(x_1, \ldots, x_N; \sigma_1, \ldots, \sigma_N, \tau_1 \ldots, \tau_N) = \psi_{SF}(x_1, \ldots, x_N) \Phi(\sigma_1, \ldots, \sigma_N, \tau_1 \ldots, \tau_N). \quad (19)$$

The position of the electrons is determined by the spinless fermion wavefunction $\psi_{SF}(x_1, \ldots, x_N)$, while the spin and orbital ordering is governed by a spin hamiltonian which is obtained by taking the average of $H_{t-ST}$ over the spinless fermion state. The result is simply related, by an overall change of energy scale and a canonical transformation, to the previous spin model $H_{ST}$ (Eq. 11):

$$H_{\text{spin}} = -4Jn[1 - \sin(\frac{2\pi n}{2\pi})] \sum_{<ij>} (S_i \cdot S_j - \frac{1}{4})(-T_i \cdot T_j + 2T_i^z T_j^z - \frac{1}{4}). \quad (20)$$

The physical origin of this factorization relies on a general feature of one dimensional models with nearest neighbor hopping: In the $U \to \infty$ limit, the spatial ordering of the particles is conserved by the dynamical evolution, irrespectively of the spin configuration. Therefore, the hamiltonian can be diagonalized in each subspace defined by a given
spin ordering and the result does not depend on the chosen spin configuration. The effective Hamiltonian governing the charge degrees of freedom is that of a free spinless fermion gas (with suitable boundary conditions which do depend on the spin wavefunction) whose eigenfunctions are \( \psi_{SF} \). The degeneracy among different spin configurations is lifted to \( O(J) \) by the magnetic term in \( \mathcal{H}_{t-ST} \), leading to the complete classification of the eigenstates of \( \mathcal{H}_{t-ST} \) to lowest order in \( J \).

The spin Hamiltonian in Eq. (20), we argued before, has a spin gap. Therefore, we conclude that, while the charge sector is gapless (metallic), for large positive \( \Delta E_S \) and \( n \neq 1 \), the spin sector is gapped at all densities and has a doubly degenerate ground state in the thermodynamic limit. However, such a spin gap is not related to the formation of bound electron pairs. In fact, the charge degrees of freedom behave as free particles with no tendency towards pairing; the superconductive correlations are not enhanced in the ground state and decay as \( \sim x^{-2} \). This state can be rather interpreted as the one dimensional realization of an “itinerant” valence bond state where spinless bond, leaving holons in a Luttinger Liquid state. (The situation is quite similar to the strong coupling phase of the Hubbard model in \( D = 1 \), for \( t' > t/2 \).) The very presence of such a phase is then a remarkable consequence of one dimensional spin–charge decoupling.

The factorization of the wavefunction at \( J \to 0 \) can be used to calculate various physical quantities of this spin-gapped metallic phase, following analogous calculations in the Hubbard case. In particular, density correlation functions just coincide with those of a spinless fermion gas, showing power law decay at large distances (\( \sim x^{-2} \)) while the spin-spin (and pseudospin) correlation still decays exponentially, similarly to the half filled case. Another interesting property which can be evaluated is the one-hole Green’s function providing a quantitative description of the motion of one hole in a short range VB state. The picture of a static VB crystal would yield an exponentially decaying Green’s function in real space, but 1D fluctuations severely affect the asymptotic form of the Green’s function. The calculation can be carried out exactly in the \( J \to 0 \) limit, where the factorization property of all eigenfunctions holds. In fact, in this limit, the energy levels of a single hole in a VB state coincide with those of a free particle in vacuum plus \( O(J) \) corrections depending on the energy of the spin background. Moreover, the energy, to lowest order, just depends on the holon momentum, i.e., on the momentum \( k \) of the spinless fermion part of the wavefunction \( \psi_{SF} \): \( E(k) = 2t \cos k + O(J) \). On the other hand, the holon momentum is related to the total momentum \( p \) of the state by the conservation law: \( p = k + Q \). Here \( Q \) is the momentum of the spin part of the wavefunction \( \Phi \) and is quantized in units of \( 2\pi/(L - 1) \), the spin model being defined on the squeezed chain of \( L - 1 \) sites. Therefore, for \( J \to 0 \), the one-hole energy levels of the model, at a given total momentum \( p \), can be written in terms of the spinon momentum: \( E_{p,Q} = 2 \cos(p - Q) \), i.e., of the momentum of the spin part of the factorized wavefunction. The corresponding density of states coincides with that of a single free fermion:

\[
N(\omega) = \frac{1}{2\pi} \frac{1}{\sqrt{4t^2 - \omega^2}},
\]

with singularities at the band edges \( \omega = \pm 2t \). These singularities are due to the quadratic dependence of the energy spectrum on the holon momentum which will be probably cut-off by the presence of spin excitations to \( O(J) \).

The calculation of the single hole Green’s function

\[
G(p, t) = i \langle \Psi | c_{p,\sigma}^\dagger e^{-iH-E_0-i\delta} c_{p,\sigma} | \Psi \rangle \theta(t)
\]

is conveniently carried out by use of the Lehmann representation of the corresponding spectral function:

\[
A(p, \omega) = \frac{1}{\pi} \text{Im} G(p, \omega) = \sum_s |\langle \Phi_s^h | c_{p,\sigma} | \Phi \rangle|^2 \delta(\omega + E_0 - E_s)
\]

\[
= \sum_Q Z(Q) \delta(\omega - E_{p,Q}),
\]

where, in the last equation, use has been made of the special form of the energy spectrum as \( J \to 0 \). The usefulness of this representation rests on the knowledge of the weight function \( Z(Q) \) which, following Ref. [28], can be written in terms of a non-local correlation function involving only spin (and pseudospin) variables:

\[
Z(Q) = \frac{1}{2} \sum_{j=0}^{L-2} e^{-iQj} \Omega(j)
\]

\[
\Omega(j) = \langle \Phi | (2T_j \cdot T_{j-1} + \frac{1}{2})(2S_j \cdot S_{j-1} + \frac{1}{2}) \cdots (2T_1 \cdot T_0 + \frac{1}{2})(2S_1 \cdot S_0 + \frac{1}{2}) | \Phi \rangle.
\]

Such a correlation function can be evaluated on the ground state of the \( \mathcal{H}_{ST} \) Hamiltonian by Lanczos diagonalization and, similarly to the Heisenberg model case, shows negligible size dependence. Calculations have been carried out up...
to \( L = 18 \) sites, and the results are shown in Fig. 4. A clear singularity in the quasiparticle weight \( Z(Q) \) is visible at the spinon Fermi momentum \( Q_F = \pi/2 \). The analysis of Lanczos data suggests a power law divergence as \( Q \to Q_F^\pm \), in close similarity to the analogous behavior encountered in the gapless Heisenberg model. A quantitative determination of the critical exponent is however precluded by the severe limitation in system size associated to the Lanczos method. In the thermodynamic limit, this singularity gives rise to branch cuts in the analytic structure of the spectral function \( \Sigma(p, \omega) \) along the lines defined by \( |Q_\pm| = \pi/2 \), where \( Q_\pm(p, \omega) = p \pm \arccos(\sqrt{\omega^2 - p^2}) \) i.e. at \( \omega_p = \pm 2\sin p \). The form of this dispersion relation suggests nearest neighbor hopping processes of the hole across the lattice.

The overall picture of hole motion in a Valence Bond state is therefore quite similar to the case of holes in one dimensional quantum antiferromagnets, being characterized by power law tails in the single particle Green’s function at the dispersion energy \( \omega_p \). This behavior can be traced back to the presence of branches of gapless collective modes above the spin gap which allow the decay of the spin 1/2 excitation created by the hole motion. These features of hole propagation should be contrasted to the properties of charges in Ising antiferromagnets, where the excitation spectrum is discrete and the band is dispersionless.

\[ A(p, \omega) = (L - 1) [Z(Q_+(p, \omega)) + Z(Q_-(p, \omega))] N(\omega) \]

V. CONCLUSIONS

In this paper we have discussed in some detail a hopping model of strongly repelling electrons in the presence of local orbital degeneracies not removed by crystal field effects.

For the insulating case (one electron per site and large Coulomb repulsions) we have studied a particular exchange hamiltonian, Eq. (1). It describes the low-energy physics of this system in the regime in which the inter-orbital singlet is the lowest-energy intermediate state available to hopping. This regime tends to be further favored by a relatively strong electron-phonon coupling. At variance with the standard Hund’s rule case (the high spin two-particle state is the lowest-energy intermediate state available to hopping. This regime tends to be further favored by a relatively strong electron-phonon coupling, we find in our case a strong tendency to the formation of a statically ordered Valence Bond (VB) phase. In \( D = 1 \), this has been firmly established by using variational arguments, a large-\( n \) limit, and exact diagonalization results. Given the presence of a sizeable spin-gap, weakly coupled chains should also have a VB ground state.

More uncertain is, instead, the outcome in the isotropic \( D = 2 \) case, where a large-\( n \) approach would predict a columnar VB phase, whereas a crude variational calculation rather points to a Néel-like antiferromagnet. A numerical study, presently under way, will clarify, we hope, this matter.

Finally, we have considered the behavior of the system upon hole doping in the \( D = 1 \) case. The factorization of the wavefunctions, valid in the strong repulsive limit and peculiar to the \( D = 1 \) case, is the crucial ingredient used to tackle the problem. The outcome is a kind of “itinerant” VB state, where charge degrees of freedom are gapless, but the spin and orbital degrees of freedom are gapped and VB-like.

The motivation for our study has been primarily theoretical. Originally inspired by dynamical Jahn-Teller molecular lattices, such as \( C_{60} \) compounds, the ingredients used are, admittedly, extremely idealized, and not easily applicable to an existing realistic situation. In a real JT lattice, both the crystal field effect, and the intermolecular elastic coupling cannot normally be neglected, and may favor a cooperative static JT distortion of all molecules. Second, intermolecular electron hopping tends to be comparable, or even larger in comparison with relevant vibron energies. Apart from this, realistic hopping matrix elements have a strong orientational dependence in more than one dimension, and, in general, there is no reason for neglecting overlap integrals between orbitals with different orbital quantum numbers (see Eq. (3)). Third, a detailed description of the structure of the doubly occupied states at each site brings in correction terms to the exchange hamiltonian which turns out to be, in general, strongly asymmetric in orbital space (see Eq. (4)).

On the opposite side, the exchange hamiltonian we have studied is elegant, parameter-free and prototypical of strong correlations in an orbitally degenerate lattice. The physics uncovered has a definite robustness against “small” perturbations, due to the gap present in the excitation spectrum. The VB gapped state has a clear resemblance to a spin-Peierls state in \( D = 1 \). The spin-gapped metal found upon doping is interesting. The basic ingredients needed for a realistic system to be a candidate VB described in this work are: i) orbital degeneracy not trivially removed by cooperative JT and/or crystal field effects; ii) relatively large molecules with a strong electron-phonon coupling, so as to make the inter-orbital singlet favored as compared to the Hund’s rule triplet; iii) narrow bands with relatively large on-site Hubbard \( U \), so as to stabilize a Mott-Hubbard insulator at exactly one electron per site; iv) reduced dimensionality.

\[ 8 \]
$C_{60}$ charge transfer compounds, based on $C_{60}^-$ ions, are potential candidates to the realization of such a scenario. $C_{60}$ has a triply degenerate $t_{1u}$ molecular orbital, coupled to several intramolecular vibrations, resulting in an important dynamical JT effect. The electron-phonon coupling leads to a substantial pairing energy $\approx 0.1eV$ which is, however, overwon by a substantially larger Hubbard $U \approx 1-1.5eV$, resulting in a Mott insulating behavior. The lattices tend to have anisotropic lattice constants, with a pronounced quasi-one-dimensional character. As for the virtual intermediate states of $C_{60}^2^-$, singlets and triplet are close in energy, at least in solutions. If the triplet prevails, as is possibly the case in TDAE-$C_{60}$, there can be spin ferromagnetism. We believe, however, there is room in some future system for the alternative possibility of a spin gap, and the formation of the spin-orbital VB state described here.

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FIGURE CAPTIONS

FIG. 1. The two VB solid configurations in $D = 1$.

FIG. 2. The ground state (momentum 0, +) and first excited state (momentum $\pi$, -) for $H_{ST}$ on a chain of 8 sites in terms of S- and T-VB configurations. ($\alpha = 0.566 \cdots$, $\beta = 0.416 \cdots$) and ($\alpha = 0.268 \cdots$, $\beta = 0.102 \cdots$), respectively, for the two states.

FIG. 3. Finite size gaps for the lowest excited states of the hamiltonian $H_{ST}$ in $D = 1$ (solid symbols) compared to the Heisenberg chain case (open squares). The data are obtained by exact diagonalization, for chains up to 14 sites, and by Green Function Monte Carlo for longer chains. The excited state for the Heisenberg case is a triplet and $\Delta E/J = \pi^2/(2L) + \cdots$, shown by the dashed line. The solid straight line, extrapolating to a finite value for $L \to \infty (\approx 0.5969)$, is obtained by a quadratic least-square fit to the triplet excitation results. This figure shows that, whereas the triplet excitations are gapped, the singlet gap decreases faster than $1/L$, signalling spontaneous symmetry breaking, consistent with a VB ground state.

FIG. 4. Log-log plot of the $\pi$-component of the Fourier transform of different correlation functions for the hamiltonian $H_{ST}$ in $D = 1$. Open squares refer to $\langle S_i^z S_j^z \rangle$, open and solid circles refer to $\langle (S_i^z S_{i+1}^z)(S_j^z S_{j+1}^z) \rangle$ and $\langle (S_i^z S_{i+1}^z)(T_j^z T_{j+1}^z) \rangle$, respectively. The dashed line has slope 1, for comparison. The dimer-dimer correlations grow fastest with size, again consistent with a VB ground state.

FIG. 5. The function $Z(Q)$ defined, in Eq. 24, determining the single-hole spectral function in the thermodynamic limit (see Eq. 25). The data are obtained from exact diagonalizations of chains up to $L = 18$.

[1] For a review on early work, see, for instance, K. I. Kugel' and D. I. Khomskii, Sov. Phys. Usp. 25, 231 (1982).
[2] R. Englman, The Jahn Teller Effect in Molecules and Crystals (Wiley, London, 1972).
[3] D. P. Arovas and A. Auerbach, Phys. Rev. B 52, 10114 (1995).
[4] The case of TDAE-C$_{60}$ is still quite controversial. First, the weak ferromagnetism observed reveals a strong anisotropy; suggestions have been put forward that the actual exchange mechanism might be of antiferromagnetic nature (Dzyaloshinsky-Moriya type) with an overall canting, responsible for the observed ferromagnetism (see R. Blinc et al. , Phys. Rev. Lett. 76, 523 (1996)). Second, the C$_{60}$ molecules might well be JT distorted, which would make the assumption of unbroken electronic degeneracy invalid. Third, there are recent reports of diamagnetism in this compound (see M. Riccò et al. , Europh. Lett. (to appear)).
[5] M. Airoldi, Ph.D. Thesis (1995) (SISSA, unpublished).
[6] M. Fabrizio, M. Airoldi, and E. Tosatti, Phys. Rev. B 53, 12086 (1996).
[7] A. Auerbach, N. Manini, and E. Tosatti, Phys. Rev. B 49, 12998 (1994); N. Manini, A. Auerbach, and E. Tosatti, ibid. 13008 (1994).
[8] N. Manini, E. Tosatti, and S. Doniach, Phys. Rev. B 51, 3731 (1995).
[9] See, for instance, Ref. 8.
[10] G. Santoro, M. Airoldi, N. Manini, E. Tosatti, and A. Parola, Phys. Rev. Lett. 74, 4039 (1995); G. Santoro, N. Manini, E. Tosatti, and A. Parola, Phys. Rev. B 53, 828 (1996).
[11] See, for instance, J.F. Cornwell, “Group Theory in Physics” Academic Press (1984).
[12] I. Affleck, Phys. Rev. Lett. 54, 966 (1985).
[13] See I. Affleck, J. Phys.: Condensed Matter 2, 405 (1990), and references therein.
[14] P. W. Anderson, Mater. Res. Bull. 8, 153 (1973).
[15] L. Pauling, J. Chem. Phys. 1, 280 (1933).
[16] S. Ramasesha and Z. G. Soos, Phys. Rev. B 32, 5368 (1985).
[17] See for instance: I. Affleck, Les Houches 1988 Fields, strings and critical phenomena.
[18] S. Liang, B. Doucot, and P. W. Anderson, Phys. Rev. Lett. 61, 365 (1988).
[19] D. Rokhsar and S. Kivelson, Phys. Rev. Lett. 61, 2376 (1988).
[20] S. Sachdev, Phys. Rev. B 40, 5204 (1989).
Since we do not have a Bethe-Ansatz solution, we have tested this conclusion numerically from exact diagonalization data.

By *squeezed chain* we mean the ring defined by the sites occupied by the electrons. Clearly the squeezed chain is defined for every fixed real space configuration of the electrons.
