Phase Diagram of Correlated Electrons in a Lattice of Berry Phase Molecules

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A model for correlated electrons in a lattice with local additional spin-1 degrees of freedom inducing constrained hopping is studied both in the low density limit and at quarter filling. We show that in both 1D and 2D two particles form a bound state even in the presence of a repulsive $U < U_c$. A picture of a dilute Bose gas, leading to off-diagonal long-range order (LRO) in 2D (quasi-LRO in 1D), is supported by quantitative calculations in 1D which allow for a determination of the phase diagram.

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Recent work on models with correlated electronic hopping, involving density-dependent hopping matrix elements, has pointed out that superconductivity can arise by purely off-diagonal processes in spite of repulsive short-range interactions [1].

Correlated electronic hopping arises also when additional degrees of freedom participate in the "local physics" at each site, inducing, for instance, *occupation-dependent constraints*. One clear example of the latter situation is realized in molecular crystals, where the additional degrees of freedom arise because of the coupling to intramolecular phonons [2,3]. The basic physics is that, under appropriate conditions, molecules with an *odd* number of electrons have an associated Berry phase and an orbital degeneracy; due to a dynamical Jahn-Teller effect, those with an even number have none [2]. The general question is whether such mechanisms will also lead to superconductivity even in the presence of repulsive diagonal interactions.

The simplest model capturing some of the physics of electronic hopping in the presence of additional local degrees of freedom is a Hubbard-type model with an extra *spin* 1 at each site [3]. The constraint is that the allowed spin-1 states depend on the electron occupancy [3]: An empty or doubly occupied site must have $S^z = 0$, whereas a site occupied by a single electron (either up or down) has an additional twofold (orbital) degeneracy, represented by $S^z = \pm 1$:

$$n_r = 0, 2 \longrightarrow S_r^z = 0, \quad n_r = 1 \longrightarrow S_r^z = \pm 1. \tag{1}$$

The Hamiltonian H is written as follows:

$$H = -\frac{t}{2} \sum_{\langle rr' \rangle} \sum_{\sigma} (c_{r\sigma}^{\dagger} c_{r'\sigma} + \text{H.c.}) \, (S_r^{+} S_{r'}^{-} + \text{H.c.}) + U \sum_r n_{r\uparrow} n_{r\downarrow}, \tag{2}$$

where the $S_r^{\pm}$'s are spin-1 ladder operators at each site, and the remaining notation is completely standard. It is worth stressing that while H, and, in particular, the hopping term, *conserves the constraint* in Eq. (1), the model is still highly nontrivial, even for $U = 0$.

In this paper we will present some results concerning the few-particle problem, the low density region, and the quarter-filling case, which shed light on the basic features of the phase diagram of the model. We will show that in both 1D and 2D the additional spin-1 degrees of freedom lead to a two-electron bound state even in the presence of a repulsive $U < U_c$. Moreover, the model does not show a tendency to phase separation and a picture of a dilute Bose gas, leading to off-diagonal quasi-long-range order (LRO) in 1D (genuine LRO in 2D) is supported at small density by analytical calculations. At quarter filling, a clear superconducting regime is found to survive up to a positive $U \sim t$.

Consider the two-particle problem first. A state in the two-particle Hilbert space with the total z component of the spin $M_{\text{tot}}^z = 0$ (for both the electron spin and the spin-1 states) can be written as $|\Psi\rangle = \sum_{r,r'} [\psi_{+-}(r, r') S_r^{+} S_{r'}^{-} + \psi_{-+}(r, r') S_r^{-} S_{r'}^{+}] c_{r\uparrow}^{\dagger} c_{r'\downarrow}^{\dagger} |0\rangle$, where the vacuum $|0\rangle$ is the state without fermions and with $S_r^z = 0$ at each site. In writing $|\Psi\rangle$ we have taken into account the two possibilities of associating a $S^z = \pm 1$ spin state to the up and down electrons: ψ_{+-} is the amplitude for having $S^z = +1$ associated to the $\uparrow$ electron (and $S^z = -1$ to the $\downarrow$ electron), while ψ_{-+} is the amplitude for the other possible choice. The Schrödinger equation for $\psi_{+-}(r, r')$ is easily shown to be

$$\begin{aligned} E\psi_{+-}(r, r') = & -t \sum_a [\psi_{+-}(r + a, r') + \psi_{+-}(r, r' + a)] \\ & + U \delta_{r,r'} \psi_{+-}(r, r') \\ & - t \left(\sum_a \delta_{r+a,r'} \right) [\psi_{-+}(r, r) + \psi_{-+}(r', r')], \end{aligned} \tag{3}$$

where a denotes a nearest-neighbor vector ($a = \pm 1$ in 1D). A similar equation is obtained for $\psi_{-+}(r, r')$ by just exchanging ψ_{-+} and ψ_{+-} everywhere. The last term in

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Eq. (3) is crucial to the whole story, and deserves a few comments. When the two electrons are far enough in the otherwise empty lattice, the Hamiltonian H simply allows the hopping to a nearest-neighbor site of the "composite" object formed by an electron and the associated spin-1 state [first term in Eq. (3)]. Things are more subtle when two electrons come to the same site r. In such a case, from a doubly occupied site with $S^z_r = 0$ one can reach, upon hopping, two possible final states: either each electron keeps its own spin-1 state or the spin-1 states associated to the two electrons are exchanged. It is precisely this second possibility of exchanging spin-1 states that is responsible for the presence of ψ_{-+} in the equation for ψ_{+-} and vice versa [last term in Eq. (3)].

The Schrödinger equation is easily solved in momentum space, where it reduces to a 2×2 matrix problem. For total momentum $P = 0$, the set of solutions among which the ground state is found satisfies the equation

$$\frac{1}{L^D} \sum_k \frac{1}{E - 2\epsilon_k} = \frac{2}{E + U}, \tag{4}$$

where E is the energy eigenvalue and ϵ_k is the tight-binding dispersion of the free-electron problem ($\epsilon_k = -2t \sum_\alpha \cos k_\alpha$). In the ordinary Hubbard case, the right hand side of Eq. (4) would simply read $1/U$ [4]. A graphical analysis of Eq. (4) readily shows that a bound state solution is present even for $U > 0$ up to $U_c = 4Dt$ in $D \leq 2$. In $D \geq 3$ a finite attractive U is needed to produce a bound state.

The bound state solution can be worked out analytically in 1D. For general values of the total momentum P and for $U \leq U_c = 4t \cos(P/2)$, the ground state energy is given by

$$E_P = -4t \cos(P/2) \, (Z_P^2 + 1)/(2Z_P), \tag{5}$$

with $Z_P = \{-(U/4t) + [(U/4t)^2 + 3\cos^2(P/2)]^{1/2}\}/\cos(P/2)$, and the corresponding ground state wave function is $\psi_{+-} = \psi_{-+} = e^{iP(r+r')/2}[e^{-\kappa|r-r'|} - (1/2)\delta_{r,r'}]$ with $\kappa = \ln Z_P$. At larger values of U, no bound state is present and the energy spectrum is continuous in the infinite lattice. There is still, however, an antibound state. The two-particle solution cannot be generalized to an arbitrary number of particles by the Bethe ansatz because the corresponding scattering matrix does not satisfy the Yang-Baxter relations.

The form of the ground state wave function naturally provides a picture of bound pairs approximately localized on adjacent lattice sites, thereby forming *dimers*. Remarkably, the rather strong attraction responsible for this binding is *generated by the kinetic term alone* via the presence of the additional degrees of freedom. The critical value of the Hubbard repulsion $U_c = 4t$ is considerably larger than the ground state binding energy at $U = 0$: $E_b = 4t\,(Z_0 - 1)^2/(2Z_0) \approx 0.618\,t$, showing that this kind of pairing mechanism is rather insensitive to the presence of on-site Coulomb repulsion. This is explained by its "kinetic" origin which delocalizes the pair on neighboring sites. The same feature is also present in 2D, where $U_c = 8t$: The enhancement is due to the larger coordination of the 2D lattice which provides an even more efficient delocalization of the electron pair.

This interpretation of the two-particle ground state in terms of dimers leads to a simple picture, both in 1D and 2D, of the low density region of the model (2), a picture which we will explicitly verify in 1D: For $U < U_c$, at low densities, the system behaves as a weakly interacting, dilute gas of dimers, which follow boson statistics and may be thought of as bosons with an extended core. In 1D, we can estimate the dimer effective mass from our two-particle calculation, Eq. (5), which at small momentum P gives $E_P \sim E_0 + t_{\rm eff} P^2$ with $t_{\rm eff} = t[3 + (U/4t)^2]^{-1/2}$. The effective mass has a smooth dependence on U varying between $\sqrt{3}$ at $U = 0$ and 2 at $U = 4t$. Dilute dimers are therefore rather mobile and a superfluid ground state must be expected at zero temperature. In 1D, of course, off-diagonal LRO cannot occur and only a long-range power-law decay of the dimer density matrix is possible, while in 2D a genuine Bose condensate will form. In terms of the original electrons this implies a standard strong coupling BCS superconducting ground state with localized Cooper pairs. A similar scenario has also been proposed in the framework of the one-dimensional t-J model, where bound pairs are formed at low density [5] and $2 < J/t < 2.95$. In that case, however, the model is unstable to phase separation, which, in fact, occurs massively at larger values of J/t.

To check whether the superfluid dimer picture is correct and that no phase separation occurs at low density, we have carried out a numerical investigation of the four-particle problem by exact diagonalization of the model (2) in lattices with up to 24 sites. The results for the ground state energy and for the density-density correlation function at $U = 0$ are reported in Fig. 1. The four electrons are sharply localized in two pairs placed at the maximum separation. The origin of this repulsion is purely kinetic and is also reproduced by the ground state wave function of two hard-core bosons in 1D, $\psi(R) \propto |\sin(\pi R/L)|$. The scaling of the energy of four electrons clearly shows that the limiting value is just twice the pair energy $E_0 = -8t/\sqrt{3}$ with $1/L^2$ corrections. Free "hard-core bosons" with the appropriate effective dispersion $t_{\rm eff} = t[3 + (U/4t)^2]^{-1/2}$ give the asymptotic result $L^2(E - 2E_0) \to 2\pi^2 t_{\rm eff}$ marked with a full circle in Fig. 1, and clearly compatible with the data.

A further step in the quantitative characterization of the low density region of the model can be made by using standard field theoretical methods for 1D systems [6]. The analysis of the two- and four-particle problem shows that for $U < U_c$ a spin gap is present in the excitation spectrum of the model while the charge (superfluid) degrees of freedom remain gapless, giving origin to the

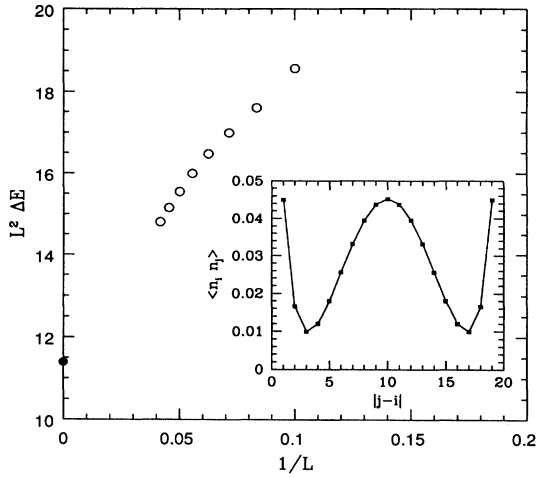

FIG. 1. Size scaling of the ground state energy of the Hamiltonian in Eq. (2) with $U = 0$ and four electrons. $\Delta E = E_L(4) - 2E_\infty(2)$, where $E_L(N)$ is the ground state energy of N electrons in a L-site ring in units of t. The full circle is the exact result for two hard-core bosons in the infinite lattice with $t_{\text{eff}} = t/\sqrt{3}$, fully compatible with the $L \to \infty$ extrapolation of the data. Inset: the density-density correlation function for four electrons in a $L = 20$-site ring at $U = 0$.

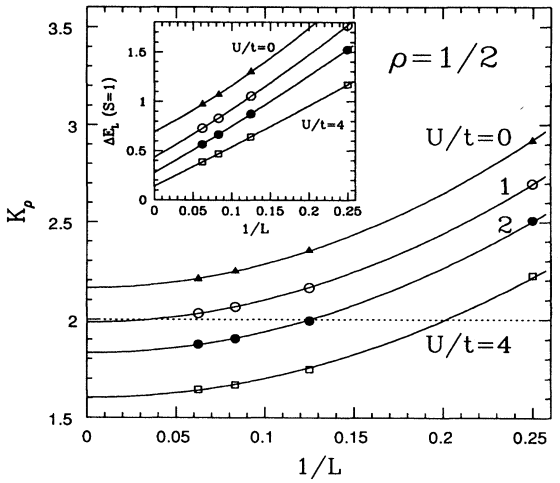

FIG. 2. Size scaling for the exponent K_ρ, obtained from finite size values of the Drude peak D and charge velocity u_ρ at filling $\rho = 1/2$, for $U/t = 0, 1, 2$, and 4. Inset: the spin gap for the same parameters. The continuous lines represent fits of the form $\Delta E = a + b/L + c/L^2$ and $K_\rho = d + e/L^2$. Note the transition from superconductive ($K_\rho > 2$) to CDW correlations ($K_\rho < 2$) for $U/t \approx 1$. The spin gap is always finite.

power-law scaling of the ground state energy shown in Fig. 1. Above U_c a two-electron bound state does not form and the triplet spectrum looks gapless. This actually is not the case at finite density, as can be inferred from the analysis of the $U \to \infty$ limit of the model [7]. The strong coupling expansion of the model in Eq. (2) can be obtained closely following the analogous calculation in the Hubbard model [8]. The resulting Hamiltonian, to $O(t^2/U)$, is defined in the subspace of singly occupied sites where electrons are characterized by *two* internal spin-1/2 degrees of freedom: the usual spin (σ) and a pseudospin (τ). The latter takes into account the two possible states of the original spin 1 allowed by the constraint (1). The resulting Hamiltonian contains a free hopping term (with coupling $-t$) and a spin (and pseudospin) dependent part (with coupling $\propto t^2/U$). In 1D, analogously to the Hubbard model case [9], the wave function factorizes, at $U \to \infty$, for all densities: The position of the electrons is determined by a spinless fermion wave function while the spin (and pseudospin) ordering is governed by the effective spin Hamiltonian

$$H_{ST} = -J_{\text{eff}} \sum_{\langle i,j \rangle} [\vec{\sigma}_i \cdot \vec{\sigma}_j - 1/4][\vec{\tau}_i \cdot \vec{\tau}_j - 1/4], \quad (6)$$

with J_{eff} depending on the electron density $\rho = N/L$ as $J_{\text{eff}} = (8t^2/U)\rho[1 - \sin(2\pi\rho)/2\pi\rho]$. Numerical as well as variational calculations have shown that the Hamiltonian in Eq. (6) is characterized by a *spin gap* of order J_{eff} [7]. Figure 2 (inset) shows the finite size spin gap at filling $\rho = 1/2$ for several values of U. A finite spin gap is quite clear from the $L \to \infty$ extrapolations. We also find that the gap persists to large U and correctly scales with $1/U$. Similar results are also obtained at half filling, where Eq. (6) is the large U effective Hamiltonian. We conclude that our model [Eq. (2)], at arbitrary (finite) density, has a spin gap all the way to $U \to \infty$. In the zero-density limit $\rho \to 0$, however, the spin gap vanishes very fast, like ρ^3, whence the gapless appearance of our previous two-particle results.

The spin (and pseudospin) degrees of freedom are gapped at all U and only the charge degrees of freedom remain gapless. The universality class of the Hamiltonian in Eq. (2) is then given by the Luther-Emery model [10], and the long-range decay of the correlation functions is characterized by power laws which can be obtained by the knowledge of the single exponent K_ρ [6]. This exponent is also related by the Haldane-Schulz equation to the compressibility of the model:

$$L\frac{\partial^2 E}{\partial N^2} = \frac{\pi}{4}\frac{u_\rho}{K_\rho} . \quad (7)$$

The factor 4 on the right hand side takes into account the presence of an additional (pseudospin) degree of freedom which can be attributed to the electron in the present model, due to the additional degeneracy $S_z = \pm 1$ in Eq. (1). Correspondingly, N includes both spin and pseudospin degrees of freedom. As usual, u_ρ represents the charge velocity, i.e., the velocity associated with the branch of gapless excitations. In order to use Eq. (7) for obtaining the low density limit of K_ρ, we should calculate both the ground state energy and the charge velocity at small but finite density. However, assuming a smooth zero density limit, it is possible to get the same information from the two- and four-particle solution.

In fact, at *fixed* N, and $L \to \infty$, the predicted scaling of the energy is $E(N,L) = N\epsilon_0 + \alpha N^3/L^2 - \beta N/L^2 + O(L^{-3})$. Analogously, the large L (i.e., low density) limit of the charge velocity should scale as $u_\rho = \gamma N/L$, where α, β, and γ are model-dependent constants. By means of these asymptotic expressions together with Eq. (7), we get the formal result for $K_\rho = \pi\gamma/24\alpha$. The central charge c [11] of the model can be also expressed in terms of these constants, $c = 6\beta/\pi\gamma$. This will provide a consistency check. At $U > U_c = 4t$, the two-particle analytical result is sufficient to extract the values of the required constants, which turn out to be independent of U: $\alpha = \pi^2/24$, $\beta = \pi^2/6$, and $\gamma = \pi$. This gives $c = 1$, as expected from the universality class of the model, and $K_\rho = 1$. In order to extract the correct large L scaling of the energy in the regime $U < U_c$, the four-particle numerical result is required. By using the estimate of Fig. 1, the parameters governing the asymptotic low density behavior become $\alpha = t_{\rm eff}\pi^2/192$, $\beta = t_{\rm eff}\pi^2/12$, and $\gamma = t_{\rm eff}\pi/2$, which give $c = 1$ and $K_\rho = 4$ independent of $U < 4t$.

The exponents which characterize the decay of the electronic correlation functions are obtained in terms of the parameter K_ρ by bosonization under the assumption that only the charge sector remains gapless [10]. In particular, the density response function at $2k_F$ decays as $x^{-K_\rho/2}$, while the $4k_F$ component behaves as x^{-2K_ρ}. In the derivation of these power laws, we must recall that eight bosonic fields contribute to the physical density operators, and this reduces the exponents by a factor of 2, with respect to the usual Hubbard model case where only four fields occur (right and left movers with two possible values of the spin). At the Luther-Emery fixed point also the superconductive correlations have power-law behavior. By examining the corresponding operator, we get the asymptotic behavior of the s-wave superconductive correlation as $\Delta_s(x) \sim x^{-2/K_\rho}$. At low densities and for $U < 4t$ we have $K_\rho = 4$: The most relevant correlations are the superconductive ones, decaying as $1/\sqrt{x}$. Remarkably, the $1/\sqrt{x}$ behavior is identical with that of a dilute hard-core boson gas, as expected from the physical picture previously discussed. Instead, for $U > 4t$ and $\rho \to 0$, we have $K_\rho = 1$: The correlation with the slowest decay is the density response function at $2k_F$, with an inverse square root behavior, implying a divergence in the CDW susceptibility. Strictly at $U = \infty$ the $2k_F$ response function has vanishing amplitude (as in the Hubbard model) and therefore the corresponding singularity is absent in the exact solution previously discussed: We expect that, at finite U, this additional feature may be detected.

We have also determined K_ρ numerically from the charge velocity u_ρ and from the Drude peak $D = u_\rho K_\rho/(2\pi)$ [6]. Figure 2 shows the results obtained at quarter filling ($\rho = 1/2$). For $U/t < 1$ the $L \to \infty$ extrapolation clearly gives $K_\rho > 2$, i.e., predominantly superconducting correlations. On the contrary, for $U/t > 1$ we have $K_\rho < 2$, i.e., predominant CDW correlations. The crossover between the two regimes is found to take place close to $U \approx t$ at this density. Exactly at half filling ($\rho = 1$) a transition is found at $U_c \approx 0$ between a superconductor ($U < U_c$) and a Mott insulator fully gapped in both spin and charge sectors [7].

The physics of the model in one dimension is now rather clear. A transition occurs at $U_c(\rho)$ [with $U_c(0) = 4t$, $U_c(1/2) \approx t$, and $U_c(1) \approx 0$] between a superconductor ($U < U_c$) and a sliding CDW conductor ($\rho \neq 1$) or Mott insulator ($\rho = 1$). The physics at small U, leading to superconducting correlations, is rather robust and can be generalized to 2D, where true LRO will occur at zero temperature. On the other hand, the CDW state, perhaps akin to a spin Peierls state, should get weaker and disappear in higher dimensions. The large U spin gap is also, probably, a 1D peculiarity.

By extrapolating these results, we can surmise that a correlated hopping model such as Eq. (2) can be expected to give rise to superconductivity in 3D. A pairing mechanism based on correlated hopping is not easily destroyed by a repulsive U, it is more effective at low carrier density, and is apparently immune from the polaron self-trapping, which depresses T_c in strongly coupled electron-phonon systems. More work is now being devoted to investigate the relevance of this type of model to molecular superconductors such as organic 1D metals, Chevrel phases, and metal fullerides.

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