Spin-1 chain doped with mobile $S = 1/2$ fermions

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We investigate doping of a two-orbital chain with mobile $S = 1/2$ fermions as a valid model for $Y_{2-x}Ca_xBaNiO_5$. The $S = 1$ spins are stabilized by strong, ferromagnetic (fm) Hund’s rule couplings. We calculate correlation functions and thermodynamic quantities by DMRG methods and find a new hierarchy of energy scales in the spin sector upon doping. Gapless spin-excitations are generated at a lower energy scale by interactions among itinerant polarons created by each hole and coexist with the larger scale of the gapful spin-liquid background of the $S = 1$ chain accompanied by a finite string-order parameter.

Since Haldane’s famous conjecture about the existence of a spin-gap in one-dimensional integer Heisenberg (HB) spin-chains [1], the intriguing physics of $S = 1$ chains and $S = 1/2$ ladders has been investigated in numerous theoretical and experimental studies and especially hole doping of a spin-liquid is of great importance for the Mott-transition in the context of high-$T_c$ superconductivity. However, doping of a Haldane $S = 1$ chain with mobile holes has only recently been realized in the material $Y_2BaNiO_5$ [3]. In the undoped case, the two active Ni$^{2+}$ orbitals are coupled by a strong fm Hund’s rule coupling $J_H$, giving an almost ideal $S = 1$ HB chain with a large spin gap of $\Delta_{S=1} \approx 100K$ and very weak inter-chain interactions. By substituting Ca$^{2+}$ by Y$^{3+}$, mobile holes can be introduced in the chain. The most remarkable experimental features are a reduction of the resistivity $\rho_{dc}$ by several orders of magnitude, and the creation of states with $S$ between 1 and 3/2 per impurity inside the Haldane gap [4]. Further the temperature dependence of the resistivity no longer follows thermal activation over a barrier.

While doping of $S = 1$ HB chains by static as well as bond impurities [5] has been studied by several authors, only little is known about doping of mobile $S = 1/2$ fermions in $S = 1$ chains. A first theoretical investigation limited to the case of weak hopping amplitudes [6] found states inside the Haldane gap with $S$ larger than $S = 1/2$ per impurity, whereas other studies based on the weak coupling approach find that the spin gap is immediately destroyed upon doping for models with a level difference and fully mobile electrons [7]. Numerically, the spin dynamics of mobile holes in $Y_2BaNiO_5$ have been investigated by exact diagonalization of small finite chains for effective one [8] and two band models [9], and based on the assumption of infinitely strong Hund’s rule couplings $J_H$ states below the Haldane gap have been found.

Among the most interesting properties of these systems is a competition between fm ordering induced by the double exchange (DE) mechanism and antiferromagnetic (af) order due to direct exchange. Other problems are the persistence of the spin-gap and the characterization of the doped phase. In this Letter we would like to address for the first time this competition in an unperturbative manner, with finite values of the Hund’s rule coupling and fully mobile electrons for system sizes significantly exceeding the correlation length of the undoped system. We do so by investigating groundstate properties and various correlation functions by the density matrix renormalization group (DMRG) method [10], and thermodynamic quantities by the thermodynamic DMRG (TDMRG) [11]. This reveals a new hierarchy of energy scales in the spin sector with gapless spin-modes given by the polaron-polaron interactions and a second, much higher lying energy scale stemming from the gapful spin-liquid background of the $S = 1$ chain. We also give first numerical evidence that the spin-gap is immediately destroyed upon doping of mobile electrons in a $S = 1$ chain with level difference. The hierarchy structure found for doping of static holes into the spin-gap background [12] surprisingly persists even in the metallic phase with fully mobile hole doping.

We investigate a model with strong Hund’s rule coupling $J_H < 0$ and a fully occupied lower band, as the $d_{x^2-y^2}$ orbital of Ni$^{2+}$ in $Y_{2-x}Ca_xBaNiO_5$ is almost localized. The results for a model with equal doping in both bands will be published later [13]. Further we assume af couplings $J > 0$ between neighboring sites in the upper $(3d_{x^2-y^2})$ orbital and $J_d > 0$ between neighboring sites in different orbitals. Thus our Hamiltonian reads

$$\mathcal{H}_{as} = -t \sum_{j,\sigma} \mathcal{P} (c_{j,1,\sigma}^\dagger c_{j+1,1,\sigma} + H.c.) \mathcal{P}$$

$$+ J \sum_j \left( \bar{S}_{j,1}\bar{S}_{j+1,1} - \frac{1}{4} n_{j,1} n_{j+1,1} \right)$$

$$+ J_d \sum_j \left( \bar{S}_{j,1}\bar{S}_{j+2,1} + \bar{S}_{j,2}\bar{S}_{j+1,1} - \frac{1}{2} n_{j,1} \right)$$

$$+ J_H \sum_j \bar{S}_{j,1}\bar{S}_{j,2} - \mu_1 \sum_j n_{j,1},$$

where the first index of the double index $j, i$ denotes the lattice site and the second index the orbital, the projection operator $\mathcal{P}$ prohibits double occupancy of a site in order to take account of the strong on-site Coulomb repulsion and the rest of the notation is standard. If not otherwise mentioned we always set $J = J_d$ and assume $J_H \gg J, J_d, t$, typically $-J_H = 10t = 20J = 20J_d$. We have also performed calculations with two different chemical potentials for the upper and lower band, but we find finite hole densities in the lower band only at the high-
est temperatures $T > t$ in that case, and the results are identical to the above case for $T < t$.

The TDMRG allows us to calculate thermodynamical properties in the thermodynamic limit of infinite system size. In general we use finite Trotter-time step sizes of $\Delta \tau = 0.2t$ and extrapolate from the grand canonical ensemble with fixed chemical potential to constant particle density first. We keep between 60 and 80 states per system and environment block, and use a rebiorthogonalization method \[14\] if we encounter numerical instabilities. With the groundstate DMRG we have considered system sizes of up to $2 \times 256$ sites and kept up to 1300 states per system and environment block.

We begin by considering two limits which are easy to understand. The first case is $J = J_d = 0$. Away from half filling, all spins are ferromagnetically aligned by the DE mechanism \[13\] in order to gain kinetic energy. The second case is at half filling, where upon switching on the af couplings $J, J_d$, the system can be mapped to an af $S = 1$ HB chain, with a spin-gap and exponentially decaying of spin-correlations. For any finite value of $J, J_d$, and finite hole doping we will therefore have competition between fn order induced by the DE mechanism and the spin liquid state of the $S = 1$ chain. Let us briefly sketch the picture that emerges from our numerical calculations, before investigating the physical quantities in detail. Each hole doped into the $S = 1$ chain is surrounded by a small fm cloud created by the DE mechanism, and we will call this a polaron in the following. However, in the parameter regions we studied in this paper, the polaron is only a weak local perturbation of the spin-liquid background, and the correlation length remains close to its original value. Among the polarons, $4k_F$ and $2k_F$ charge density wave (CDW) order is then stabilized, and the lowest lying spin excitations are weak magnetic interactions among the polarons. Due to these interactions, there is a spin-singlet groundstate already for very weak couplings $J, J_d \gtrsim 0.2t$ and $J_H = -10t$.

Let us turn to the detailed investigation of physical quantities next and address the question of whether the spin-gap is robust upon doping of holes first. The mapping to the af $S = 1$ HB chain at half filling gives effective couplings $J_e = 3/4J$ of the original $S = 1$ chain by perturbation theory, hence we expect a spin gap of $\Delta_s = 3/4\Delta_{S=1}$ of the original value $\Delta_{S=1} \approx 0.41J$. In good agreement we obtain $\Delta_s = 0.153t \pm 0.005t = 0.306J \pm 0.01J$ from the TDMRG by $\lim_{\tau \to 0} \sqrt{2Tc_{\sigma}/(3\chi)} \to \Delta_s$ \[10\]. Alternatively, we have calculated the spin gap by finite size scaling $\Delta_s = \lim_{L \to 0} \Delta_s(L; N = Ln)$, where $\Delta_s(L; N = Ln) = \Delta_s(L; N) = E_0(L; N; S^z = 1) - E_0(L; N; S^z = 0)$ and $E_0(L; N; S^z)$ is the groundstate energy of the system with $N$ particles on $L$ sites and total $S^z$ component of the spin along the z-direction. However care needs to be taken in order to avoid free $S = 1/2$ spins at the end of the open chain. To keep the free spins out, we have imposed the boundary condition that the upper orbital on the boundary sites remains empty. The result for different values of the hole concentration $n_h$ in the conduction band and $-J_H = 10t = 20J_d$ agrees well with the TDMRG. Here we see that the spin-gap is immediately destroyed upon doping, and by noting that the smallest momentum in the finite open chain is $k_{\text{min}} = \pi/L$ we can calculate the spin-velocity $v_{\sigma}$ from $\Delta_s(L) = v_{\sigma}k_{\text{min}}$. Thus we can determine the $T = 0$ susceptibility by $\chi^0 = \frac{2\pi v_{\sigma}}{\sigma J}$, where $K_\sigma = 1$ due to the SU(2) symmetry. Both results are listed in Tab. \[6\] We compare these findings with the TDMRG results for $\chi(T)$ in Fig. \[8\]. The strong enhancement of $\chi(T)$ at low temperatures suggests the formation of larger magnetic moments upon doping, in agreement with the $T = 0$ results. In the inset of Fig. \[8\] we estimate the effective Curie-constant $\gamma = S(S+1)/3$ created by each hole by subtracting the background of the $S = 1$ chain $\gamma = (\chi - (1-n_h^c)\chi_{S=1})T/n_h^c$. The maximum value of $\gamma \approx 0.5$ near $T = 0.3t$ is nearly independent of the hole doping and corresponds to $S_{\text{eff}} \approx 0.7$, in rough agreement with experimental findings \[3,7\]. By further lowering the temperature, af interactions among the polarons reduce $\gamma$ and finally lead to a singlet groundstate at $T = 0$.

We have checked the rotational invariance by the DMRG from $\sigma(i,j) = S^x_i S^x_j = 1/2(S^+_i S^-_j)$ which vanishes for a singlet groundstate and confirm this result within the numerical calculations.

| $n_h^c$ | $\Delta_s$ | $v_{\sigma}$ | $\chi^0$ |
|--------|-------------|-------------|---------|
| 0      | 0.150t      | -           | 0       |
| 0.0625 | 0.244       | 2.61        |
| 0.125  | 0.201       | 3.17        |

TABLE I. The spin-gap $\Delta_s$ for different values of hole doping $n_h^c$ in the conduction band and $-J_H = 10t = 20J_d$. Also listd is the spin-velocity $v_{\sigma}$ and the susceptibility $\chi^0$ at $T = 0$. The results are obtained after extrapolations to the thermodynamic limit by finite-size scaling.
Next we investigate correlation functions by the DMRG method and start with the particle density in the conduction band $n^c(x)$, which shows Friedel oscillations induced by the open boundary conditions. For small hole densities $n^h_k = 1/16$, and $n^h_k = 1/8$ we only find $\Delta n^h_i/2$ hole pockets (see inset Fig. 2) indicating hole pairing. For larger hole densities however, a weak structure in the hole pockets suggests that the two holes bound to a pair are separated by several lattice spacings. The pair binding energy in the low hole density region can be estimated by $\Delta_{\text{pair}} = 2E_1 - E_0 - E_2 \approx 0.016t$ for $-J_H = 10t = 20J = 20J_d$, where $E_n$ is the groundstate energy with $n$ holes, and confirms pair formation. Also note the very weak amplitudes of the Friedel oscillations. In the Fourier-transform $n(q)$ we only find one peak for very low hole doping $n^h_k = 1/16$ at $k = n^h_k \pi$ and two peaks at $k = n^h_k \pi$ and $k = 2n^h_k \pi$ for larger hole doping $n^h_k = 1/8$. In general, a Tomonaga-Luttinger liquid shows $2k_F$ and $4k_F$ fluctuations, and $2k_F = (n^c + 1)\pi$ for a large Luttinger volume involving the electrons in the lower band. Our observation is consistent with these $2k_F$ and $4k_F$ periods for a large Luttinger volume. By fitting to the Friedel-oscillations for an impurity potential $\delta_n(x) \propto C_1 \cos(2k_F x) e^{-(1+K_p)/2} + C_2 \cos(4k_F x) e^{-2K_p}$, we have determined the single correlation exponent $K_p \approx 0.51 \pm 0.05$ for $n^h_k = 1/8$, indicating dominant CDW correlations. Because of trapped states near the boundaries, these sites have to be discarded for the fit and the uncertainty stems from the fitting ambiguity.

Independently, the correlation exponent $K_p$ can also be determined from the pairing correlations $P_i(f)P^\dagger_{i+x}(f)$, where $P^\dagger_i(f) = \frac{1}{2\sqrt{2}}(c_{i+1,f}^+ c_{i,f+1}^+ + c_{i-1,f}^+ c_{i,f+1}^+)$ is either the singlet ($-$) or triplet pair ($+$) creation operator. The

singlet pairing correlations decay as $P^\dagger_i(f)P^\dagger_{i+x}(f) \propto A_0 \ln(x)^{-1.5} e^{-1/K_p} + A_2 \cos(2k_F x) x^{-1/k_p} e^{-1/K_p}$, and in agreement with the previous estimate we obtain $K_p \approx 0.51 \pm 0.05$ by simultaneously fitting to $f = 2, 4, 6, 8$ (see Fig. 3). Note that the largest amplitudes of the pairing-correlation are obtained for $f = 6$ and $8$, in agreement with the pair structure in $n(x)$.

Finally we turn to the spin-spin correlations shown in Fig. 4. As for the undoped case, all spin-spin correlation functions seem to decay exponentially $S^z_i S^z_{i+x} \propto \cos(2k_F x) e^{-x/\xi}$, and the correlation length $\xi \approx 7.9 \pm 0.1$ for $n^h_k = 1/16$ and $\xi = 11.2 \pm 0.2$ for $n^h_k = 1/8$ remains close to the undoped case $\xi \approx 6.1$. A more conclusive quantity is the string order parameter $g(x) = \langle \sum_{i=1,2} S^z_{x+i} \rangle = \langle \sum_{i=1,2} S^z_{x+i} \rangle$. This characterizes the Haldane $S = 1$ chain. The finite value of $g(x)$ upon doping suggests that the spin-liquid state remains intact. However, for the doped case it is not clear whether $g(x)$ remains finite in the thermodynamic limit, because our system sizes do not seem to be large enough if polaron-polaron correlations would destroy the string correlation.

We finish by summarizing how all the findings including the surprising coexistence of gapless spin-modes with exponential spin-correlations (at intermediate distances) can be reconciled within the polaron picture. The holes which create a small fermion cloud by the DE mechanism are bound to pairs as we see from the charge density, and $2k_F$ and $4k_F$ CDW correlations are dominant with $K_p \approx 0.51$. The amplitudes of the CDW are very weak (see Fig. 3). This and the finite string-order suggest that the polarons are only a weak perturbation of the spin-liquid background of the $S = 1$ chain. Therefore we propose a new model with two very different energy-scales for the spin-excitation. The larger one is of the order
of $\Delta_*$ and stems from the spin-liquid background, giving rise to exponentially decaying spin correlations at the distances we can observe by the DMRG. The second energy scale is very small and consists of the $af$ interactions among polaron-pairs. These are the gapless, lowest lying spin excitations, and at very long distances we expect power-law decay of the spin-correlation functions. Since these interactions are among polaron-pairs, even our largest system-sizes contain only few such pairs and are too small to discriminate between exponential and power-law decay. Note however that $\xi_{\text{spin}}$ increases with doping. In order to estimate the energy scales we finally show the specific heat $c_V$ calculated by the TDMRG in Fig. 5. From the position of the large broad peak near $T \sim 0.3t$ we see that the energy-scale of the spin-liquid remains almost unchanged upon doping, and from the sharp increase of $c_V$ at the lowest temperatures we estimate magnetic interactions among polarons at an energy scale of $T \sim 0.02J$.

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![Figure 4](image1.png)  
**FIG. 4.** Spin-spin correlations $S_i^z S_j^z$ measured from the center and end of the chain for different values of hole doping with $-J_H = 10t = 20J = 20J_d$. Inset: string-correlation function $g(x)$.

![Figure 5](image2.png)  
**FIG. 5.** Specific heat $c_V$ calculated by the TDMRG for $-J_H = 10t = 20J = 20J_d$.
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