Local antiferromagnetic moment induced by Zn impurity in high-T_c superconducting copper oxides: A resonating-valence-bond picture

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(Received 12 March 2006; published 20 June 2006)

Based on a Gutzwiller projected BCS wave function, it is shown that a local $S=1/2$ moment is present around a vacancy site (zinc impurity) in a form of staggered magnetic moments, which is a direct consequence of the short-range resonating-valence-bond pairing in the spin background.

DOI: 10.1103/PhysRevB.73.212504 PACS number(s): 74.20.Mn, 74.25.Ha, 75.20.Hr

Experimentally, it has been observed that a zinc impurity in the high-T_c cuprates generally induces a *free* magnetic moment in its neighborhood, which contributes to an additional Curie-like $1/T$ signature in nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) data.[1–6] In particular, the distribution of such a free moment around the impurity is in the form of staggered (AF) magnetic moments at the copper sites. Namely, if the free moment is polarized, say, by an external magnetic field; its spatial distribution surrounding the zinc atom looks like an antiferromagnetic ordering of spins, with the total sum equal to the magnitude of the free moment.

The induction of a local moment by a nonmagnetic zinc impurity illustrates the strongly correlated nature of the pure system and poses a great challenge to various high-T_c theories. Here two issues are involved. One is why a free moment should be spontaneously induced by a nonmagnetic zinc impurity. The second is that given the fact that a free moment is trapped nearby, why its distribution exhibits a staggered profile around the zinc impurity.

There have been a number of papers on the microscopic origin of the zinc-induced local moment in the framework of the doped Mott insulator approaches.[7–10] Wang and Lee[7] and Liang and Lee[8] attribute the induced local moment to a precursor effect of the AF ordering instability in the pure system. They consider the antiferromagnetic or spin density wave fluctuation in a resonance-valence-bond (RVB) state nearby the zinc impurity. In this picture, the local moment is described by a local spin density wave order parameter, which provides an explanation of the staggered profile of the local moment.[7,8] Qi and Weng[10] used a bosonic RVB theory to study a sudden approximation for the zinc impurity state, in which an electron is annihilated from the zinc-free RVB state. In their picture, the staggered distribution of the local moment induced by the zinc impurity is a result of the short-range AF correlations embedded in the pure system. They also argued that the phase string effect may protect the local moment for a topological reason.

In this paper, we model the Zn impurity by a Gutzwiller projected d-wave BCS wave function[11,12] in the sudden approximation, in which the zinc doped system is constructed simply by locally removing an electron at the zinc site from the pure system. We show that a free moment trapped nearby a Zn impurity will generally exhibit a staggered AF distribution, whereas the unprojected wave function does not. We show an explicit relation between the magnetic moment in the Zn-impurity state and the spin-spin correlation in the impurity-free RVB state. We have also examined a more sophisticated Zn-impurity RVB state, in which the BCS mean field state before the Gutzwiller projection is modified with some relaxation of the surrounding RVB background in the presence of an impurity (vacancy) site. The result is in further support of the sudden approximation. Therefore, the local staggered moment in the Zn-impurity state may be viewed as a consequence of the staggered spatial spin-spin correlation functions in the Zn-impurity free state. From this point of view, the staggered magnetic moments observed in experiments may not be necessarily related to the AF instability. Since the Gutzwiller projection is essential to the staggered spin-spin correlation function, the Zn-impurity effect is a direct probe of the intrinsic RVB state in the cuprate superconductors.

We start by approximately representing the pure system by a Gutzwiller projected d-wave BCS state

$$|\Psi_0\rangle = P_G|\mathrm{BCS}, \qquad (1)$$

where $P_G=\Pi_i(1-n_{i\uparrow}n_{i\downarrow})$ enforces the no double occupancy constraint with $n_{i\sigma}$ denoting the electron number at site i in a two-dimensional square lattice. The Gutzwiller projection transforms the singlet Cooper pairs in $|\mathrm{BCS}\rangle$ into neutral spin RVB pairs at half filling that persist into finite hole doping. Here the mean field state $|\mathrm{BCS}\rangle$ is derived from a renormalized mean field Hamiltonian,[13–15] such as the Hamiltonian given in Eq. (4).

Now we construct a new state $|\Psi_0\rangle_{\mathrm{Zn}}$ by removing *locally* an electron on site i_0 from $|\Psi_0\rangle$. This state may be regarded as a sudden approximation for the *true* ground state $|\Psi\rangle_{\mathrm{Zn}}$ when site i_0 is occupied by a zinc impurity, similar to a construction previously used in the bosonic RVB approach.[10] We note that $|\Psi_0\rangle_{\mathrm{Zn}}$ has the right spin quantum number $(S=1/2)$ to describe a local moment. At the same time, both $|\Psi\rangle_{\mathrm{Zn}}$ and $|\Psi_0\rangle_{\mathrm{Zn}}$ should reduce to $|\Psi_0\rangle$ in a distance sufficiently far away from the zinc site, as a single impurity is not expected to change the thermodynamic bulk properties of the system. Thus, we expect $|\Psi\rangle_{\mathrm{Zn}}$ and $|\Psi_0\rangle_{\mathrm{Zn}}$ should have a finite overlap such that the local states of them around the zinc impurity can be adiabatically connected by some kind of local perturbations, provided the local moment is present in $|\Psi\rangle_{\mathrm{Zn}}$. Namely, if the $S=1/2$ moment is indeed distributed around the zinc impurity in the true ground state, then the "sudden approximation" state $|\Psi_0\rangle_{\mathrm{Zn}}$ should be a good approximation as the first step to describe the related physics.

Without the loss of generality one may define

$$|\Psi_0\rangle_{\mathrm{Zn}} \equiv c_{i_0\uparrow}|\Psi_0. \tag{2}$$

Since $|\Psi_0\rangle$ is a spin singlet state, one has $S^z=-1/2$ in $|\Psi_0\rangle_{\mathrm{Zn}}$, which forms a doublet with the state $c_{i_0\downarrow}|\Psi_0\rangle$. Now let us inspect the distribution of this moment on the lattice by considering the quantity $\langle S_j^z\rangle_{\mathrm{Zn}}$, the average of S_j^z in the state $|\Psi_0\rangle_{\mathrm{Zn}}$. Let $\langle Q\rangle$ be the average of operator Q in the pure RVB state $|\Psi_0\rangle$, we have for the translational and rotational invariant RVB state,

$$\langle S_j^z\rangle_{\mathrm{Zn}} = \frac{\langle c_{i_0\uparrow}^\dagger S_j^z c_{i_0\uparrow}\rangle}{\langle c_{i_0\uparrow}^\dagger c_{i_0\uparrow}\rangle} = \frac{2}{3n}\langle \vec{S}_j \cdot \vec{S}_{i_0}\rangle, \tag{3}$$

where n is the average number of electron per site. Therefore, the moment distribution is determined by the equal-time spin-spin correlation in the pure system. The right-hand side of Eq. (3) can be numerically determined by a variational Monte Carlo (VMC) calculation based on the Gutzwiller projected BCS state. In a system with antiferromagnetic spin-spin coupling on a square lattice, the sign of the spin-spin correlation is alternating in space. Therefore, we expect a staggered magnetic moment in the Zn-impurity state.

To make our discussion more quantitatively, we consider a renormalized Hamiltonian, from which the mean field ground state of $|\mathrm{BCS}\rangle$ in Eq. (5) is derived,

$$\mathbf{H}_{\mathrm{MF}} = -t' \sum_{\langle ij\rangle,\sigma} (c_{i,\sigma}^\dagger c_{j,\sigma} + \mathrm{h.c.}) - \mu \sum_{i\sigma} c_{i,\sigma}^\dagger c_{i,\sigma} + \sum_{\langle ij\rangle} \Delta_{ij}(c_{i,\uparrow}^\dagger c_{j,\downarrow}^\dagger - c_{i,\downarrow}^\dagger c_{j,\uparrow}^\dagger + \mathrm{h.c.}) \tag{4}$$

in which Δ_{ij} denotes the d-wave pairing order parameter.

		-0.008	0.008	-0.008		
	-0.008	0.031	-0.039	0.031	-0.008	
-0.008	0.031	-0.058	0.243	-0.058	0.031	-0.008
0.008	-0.039	0.243	0	0.243	-0.039	0.008
-0.008	0.031	-0.058	0.243	-0.058	0.031	-0.008
	-0.008	0.031	-0.039	0.031	-0.008	
		-0.008	0.008	-0.008		

FIG. 1. The spin distribution of $\langle S_j^z\rangle$ around the zinc site (denoted by the plaquette in the center) in the state $|\Psi_0\rangle_{\mathrm{Zn}}$. The calculation is done on a 12×12 lattice of 22 holes, with $\frac{\Delta}{t'}=0.1$ and $\frac{\mu}{t'}=-0.2$.

This Hamiltonian can be taken as the mean field description of the t-J model, where the parameters t' and Δ_{ij} can be determined by a set of self-consistent equations.[13–15] The results are shown in Fig. 1, which illustrates two things. First, there does exist staggered magnetic moments around the zinc impurity, which are actually determined by the short-range AF correlations already presented in the *pure* system as shown by the right-hand side of Eq. (3). Second, the total moment as the sum of these staggered moments is equal to $S^z=-1/2$, according to the above construction. Namely, the staggered moments spatially distributed around a zinc impurity and a "free" $S=1/2$ total moment can be naturally reconciled within this scheme.

Physically, the local moment around the zinc impurity can be understood as originated from a broken RVB pair, with its one spinon partner (sitting at the site i_0) being removed as the consequence of the Zn substitution and the unpaired partner left behind to contribute to such a free local moment. Here, the Mott physics also plays a crucial role for making such a free moment distributing in the form of enhanced staggered moments, as shown in Fig. 1. By contrast, without the Gutzwiller projection operator P_G, one easily finds that the distribution of magnetic moments is given by

$$\frac{\langle \mathrm{BCS}|c_{i_0\uparrow}^\dagger (S_j^z) c_{i_0\uparrow}|\mathrm{BCS}\rangle}{\langle \mathrm{BCS}|c_{i_0\uparrow}^\dagger c_{i_0\uparrow}|\mathrm{BCS}\rangle} = -\frac{1}{n}[|\langle \mathrm{BCS}|c_{i_0\uparrow}^\dagger c_{j\downarrow}^\dagger|\mathrm{BCS}\rangle|^2 + |\langle \mathrm{BCS}|c_{i_0\uparrow}^\dagger c_{j\uparrow}|\mathrm{BCS}\rangle|^2 \leq 0, \tag{5}$$

which always remains negative and does not show a strong staggered oscillation, as in Fig. 1. Thus, the presence of staggered AF moments around the zinc impurity is a very important feature for an RVB superconductor (Gutzwiller projected BCS state) $|\Psi_0\rangle$, but not for a conventional BCS state $|\mathrm{BCS}\rangle$.

		-0.012	0.021	-0.012		
	-0.009	0.04	-0.035	0.04	-0.009	
-0.012	0.04	-0.058	0.173	-0.058	0.04	-0.012
0.021	-0.035	0.173	0	0.173	-0.035	0.021
-0.012	0.04	-0.058	0.173	-0.058	0.04	-0.012
	-0.009	0.04	-0.035	0.04	-0.009	
		-0.012	0.021	-0.012		

FIG. 2. The distribution of $\langle S_j^z \rangle$ around the zinc site in the state $\mathrm{P_G}\gamma_\uparrow^\dagger|\mathrm{BCS}\rangle_{\mathrm{Zn}}$. The parameters used are the same as in Fig. 1.

The above discussion is based on the assumption that $|\Psi_0\rangle_{\mathrm{Zn}}$ has a finite overlap with the true ground state $|\Psi\rangle_{\mathrm{Zn}}$. Namely, the existence of a local moment is assumed to be around a zinc impurity. If the local moment in $|\Psi_0\rangle_{\mathrm{Zn}}$, created by the sudden approximation from the original ground state $|\Psi_0\rangle$, eventually escapes to infinity (boundary) in the ground state, then $|\Psi_0\rangle_{\mathrm{Zn}}$ and $|\Psi\rangle_{\mathrm{Zn}}$ are orthogonal and the present "sudden approximation" used above will fail. In principle, a RVB state does not prevent such a local moment (spinon) from escaping away to the boundary as it can rearrange the RVB pairings in the bulk. Thus, a more sophisticated approach is needed in order to further demonstrate the stability of the local moment around the Zn impurity.

For this purpose, in the following we consider a modified wave function for describing the local moment. Instead of removing an electron in the projected state of the *pure* system, the impurity state is constructed as a Gutzwiller projected state in which the unprojected mean field state is obtained in the presence of the zinc impurity with a local quasiparticle excitation. Generally, an *s*-wave unitary scatter doped into a *d*-wave superconductor will induce a low-energy *d*-wave resonance state around it, ensured by the *d*-wave pairing symmetry,[16] and if we denote the creation operator of this resonant state as $\gamma_\sigma^\dagger$, then the modified wave function for describing the local moment state is given by $\mathrm{P}_G\gamma_\sigma^\dagger|\mathrm{BCS}\rangle_{\mathrm{Zn}}$, in which $|\mathrm{BCS}\rangle_{\mathrm{Zn}}$ denotes the mean field ground state in the presence of the zinc impurity. Note that here the occupied *d*-wave resonance state will have the right spin quantum number to describe a local moment and at the same time any double occupancy of the same local state, which would destroy the moment, is prohibited by the Gutzwiller projection. The remaining task is to check whether the proposed wave function still exhibits a staggered distribution of the moment. The mean field description of the single zinc impurity at site i_0 is given by H_{MF} of Eq. (4) with the impurity site i_0 excluded.

The mean field ground state of $\mathbf{H}_{\mathrm{MF}}^{\mathrm{Zn}}$ and the *d*-wave resonant state γ_σ can be obtained numerically on the finite lattice. Then one can perform the VMC calculation to implement the Gutzwiller projection which is done on a 12×12 lattice with 22 holes. Figure 2 shows the spin distribution around the zinc site in $\mathrm{P_G}\gamma_\uparrow^\dagger|\mathrm{BCS}\rangle_{\mathrm{Zn}}$. The spin distribution in $\mathrm{P_G}\gamma_\uparrow^\dagger|\mathrm{BCS}\rangle_{\mathrm{Zn}}$ is slightly more extended than that in $|\Psi_0\rangle_{\mathrm{Zn}}$ as a result of the relaxation of the RVB background but otherwise remains quite similar. Since both $\mathrm{P_G}\gamma_\uparrow^\dagger|\mathrm{BCS}\rangle_{\mathrm{Zn}}$ and $|\Psi_0\rangle_{\mathrm{Zn}}$ have the same spin quantum number and show similar spin distribution, it is natural to expect that they are not very different from each other. In fact, we have calculated their overlap by using the VMC, and the result is shown in Fig. 3. From Fig. 3, one sees that the overlap actually saturates to a finite value of 0.8 in the thermodynamic limit. Thus, the two states are indeed very close to each other in terms of both the large wave function overlap as well as the staggered profile of the local moment.

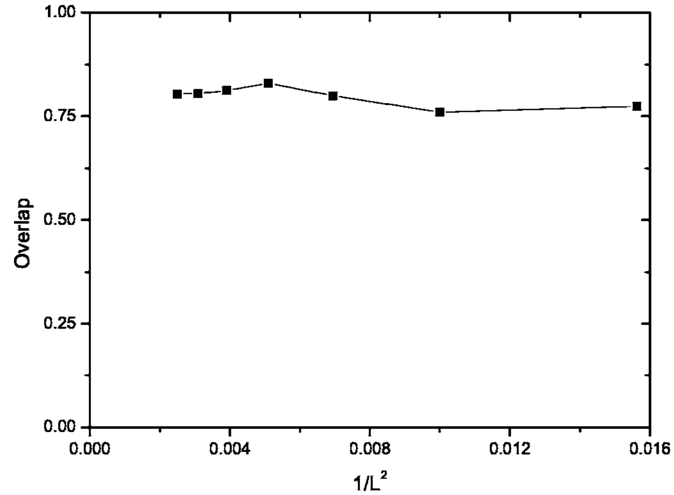

FIG. 3. The overlap between $\mathrm{P_G}\gamma_\uparrow^\dagger|\mathrm{BCS}\rangle_{\mathrm{Zn}}$ and $|\Psi_0\rangle_{\mathrm{Zn}}$ as a function of the inverse lattice size $1/L^2$. The calculation is done with the hole density kept approximately at 15% (for example, 62 holes in the 20×20 lattice). The parameters, $\frac{\Delta}{t'}$ and $\frac{\mu}{t'}$, are the same as in Fig. 1.

Energetically a close competitor of the state $\mathrm{P_G}\gamma_\uparrow^\dagger|\mathrm{BCS}\rangle_{\mathrm{Zn}}$ is the projected mean field ground state $\mathrm{P_G}|\mathrm{BCS}\rangle_{\mathrm{Zn}}$. Since the mean field excitation energy of the resonant state created by $\gamma_\uparrow^\dagger$ is small, we expect that the energy difference between $\mathrm{P_G}\gamma_\uparrow^\dagger|\mathrm{BCS}\rangle_{\mathrm{Zn}}$ and $\mathrm{P_G}|\mathrm{BCS}\rangle_{\mathrm{Zn}}$ to also be small. Indeed, the energy difference in the VMC calculation based on the $t-J$ model is generally very small, although the energy of $\mathrm{P_G}|\mathrm{BCS}\rangle_{\mathrm{Zn}}$ remains to be lower. Thus, strictly speaking, how the local moment can be trapped near the zinc impurity because of the distortion of the RVB order parameter around the impurity is still unsolved in the present approach. In contrast, a topological reason coming from the charge degrees of freedom in the bosonic RVB theory[10] provides the protection of the local moment by responding nonlocally to the presence of a vacancy in the bulk. Whether the underlying physics for the trapping of the local moment is due to the local RVB distortion or some more subtle topological reason needs to be further studied in the present fermionic RVB framework. Nevertheless, once a local moment is trapped around the zinc impurity, a staggered moment profile always emerges, as a direct consequence of the presence of RVB correlations in the pure system.

In summary, we studied two fermionic RVB wave functions describing the zinc doping-induced local moment effect in the doped Mott insulator. We find that the AF staggered profile of the local moment distribution emerges naturally and can be generally attributed to the short-range AF correlations of the RVB structure in the pure system. According to this description, the existence of the induced local moment with a staggered profile in the cuprates provides a strong experimental indication for the underlying RVB structure in the zinc-free systems.

ACKNOWLEDGMENTS

Z.Y.W. thanks X. L. Qi for useful discussions. T.L. is partially supported by NSFC Grant No. 90303009, and Q.H.W. is supported by NSFC Grant No. 10325416 and the Fok Ying Tung Education Foundation Grant No. 91009. Z.Y.W. acknowledges the support from the grants of NSFC and MOE, and FCZ is partially supported by the RGC Grant No. HKU 705704 in Hong Kong. F. Yang is grateful to the BIT-UBF-200507A4219.

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