

Non-magnetic impurities as probes of insulating and doped Mott insulators in two dimensions

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ABSTRACT. We characterize paramagnetic Mott insulators by their response to static, non-magnetic impurities. States with spinon deconfinement (or spin-charge separation) are distinguished from those with spinon confinement by distinct impurity susceptibilities and finite-size spectra. We discuss the evolution of physical properties upon doping to a d -wave superconductor, and argue that a number of recent experiments favor spinon confinement in the reference Mott insulating state.

1. Introduction

Soon after the discovery of high temperature superconductivity, Anderson [1] made the prescient suggestion that the phenomenon is related to the physics of a doped Mott insulator. The parent insulating compound, La_2CuO_4 , is well described at low energies by the excitations of a model of single orbitals on the vertices of the square lattice at a density of one electron per site. The ground state of this model is an insulator, and is known to have antiferromagnetic long-range order. Nevertheless, Anderson argued that the appropriate reference state was a paramagnetic Mott insulator without antiferromagnetic long-range order, often loosely referred to as a “spin liquid”. In the intervening years, much effort has been expended towards finding such spin liquid states, and a number of definite candidates have emerged. There are important qualitative distinctions between these candidates, and we are especially interested in distinguishing states which cannot be deformed adiabatically into each other, and must be separated by a quantum phase transition. In particular, a key property is whether the state allows deconfined $S = 1/2$ spinon excitations or not. If it does, then these neutral, $S = 1/2$ excitations imply that “spin-charge separation” has occurred.

In this paper, we argue that the response of the ground state to non-magnetic impurities is a sensitive probe of spinon confinement, and so is a central distinguishing characteristic of the various paramagnetic Mott insulators. Experimentally, such non-magnetic impurities can be easily created by substituting Zn or Li on the Cu sites, and a large number of such experiments have been carried out on both the

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insulating and superconducting compounds. We will describe the results of some of these experiments here, and argue that they offer evidence that the appropriate reference Mott insulating state to the high temperature superconductors is one in which the spinons are confined; our point of view is therefore contrary to [2]. We will also mention theoretical work [3, 4] which argues that such confined states break translational symmetry by the appearance of spin-Peierls order (which can also be viewed as a “bond-centered stripe”).

The spin excitations of a Mott insulator are usually well described by the Heisenberg Hamiltonian

$$(1.1) \quad H = \sum_{i < j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + \dots$$

where \mathbf{S}_i are SU(2) operators with spin $S = 1/2$ on the sites, i , of some lattice, and the ellipsis represent possible additional multiple spin exchange terms. We will describe cases in which H has a paramagnetic ground state with confined spinons in Section 2 and also discuss their response to non-magnetic impurities. The corresponding discussion for models with deconfined spinons is in Section 3. Finally Section 4 uses the insights gained to review recent experimental and theoretical work on non-magnetic impurities in d -wave superconductors.

2. Confined spinons

Consider the spin-ladder realization of H , as defined in Fig 1c. For the case where the thick lines have J_{ij} much larger than all other exchanges, the state in Fig 1c is a good approximation to the ground state. As the values of J_{ij} on the three sets of links become equal to each other, there is increasing resonance in the ground state between other singlet pairings between the sites, until at a critical point there is an onset of magnetic long-range order. However, the nature of the paramagnetic state remains essentially unchanged all the way up to the critical point. In particular, the lowest-lying excitation is a $S = 1$ particle which is shown schematically in Fig 1d: the columnar pairing of the spin singlets in the environment ensures that the two spin-1/2's at the ends of the broken bond cannot move apart from each other, *i.e.*, the spinons are confined. If we represent the dispersion of the stable $S = 1$ particle by

$$(2.1) \quad \varepsilon_k = \Delta + \frac{c_x^2 k_x^2}{2\Delta} + \frac{c_y^2 k_y^2}{2\Delta}$$

($k = (k_x, k_y)$ is the momentum, Δ is the gap to spin excitations, and $c_{x,y}$ are velocities), then the response to an external magnetic field is determined entirely by the thermally excited density of such particles. A simple calculation then shows that the susceptibility, χ_u , of a sample of area \mathcal{A} is given by [4]

$$(2.2) \quad \chi_u = \frac{\mathcal{A}\Delta}{\pi c_x c_y} e^{-\Delta/T},$$

where T is the absolute temperature, $\hbar = k_B = 1$, and we have absorbed factors of the electron magnetic moment into the definition of the susceptibility.

It is important to keep in mind that the above picture of the confined paramagnet holds not only for anisotropic spin ladders just mentioned, but also for isotropic models in which the Hamiltonian has the full four-fold rotational symmetry of the square lattice about every site [3, 5]. In this case, the model with only nearest neighbor interactions is known to have magnetic long-range order, and so

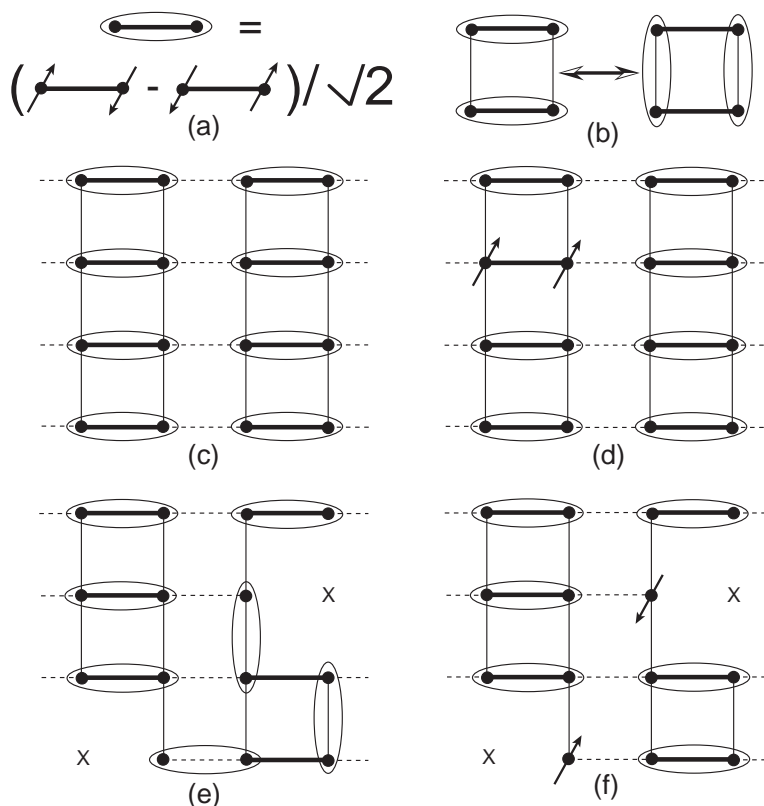


FIGURE 1. (a) Definition of an ellipse as the representation of a singlet bond between a pair of sites. (b) Two different singlet pairings (“dimer packings”) of pairs of spins around a plaquette. The resonance between these will be largest when the exchange constants represented by the thick and thin straight lines are equal. (c) Spin ladder realization of H . The thick, thin, and dashed straight lines represent $J_{ij} > 0$ couplings of differing values. A snapshot of the ground state is shown for the case where the thick lines have the largest J_{ij} . (d) $S = 1$ particle excitation of (2.1) represented by the absence of a singlet bond between a pair of spins; the two free spins propagate throughout the lattice but remain confined to each other. (e,f) Two candidate ground state configurations in the presence of two non-magnetic impurities (represented by the X’s). For a confining paramagnet, the configuration in (f), with two free moments near the impurities, is always preferred once the impurities are sufficiently far apart.

frustrating second neighbor interactions are necessary to access the paramagnetic state. It has been argued that this state *spontaneously* breaks the square lattice rotational symmetry so that the pattern of singlet bonds in one of the four equivalent ground states has the same symmetry as the configuration in Fig 1c [6]. This broken symmetry can be understood in the framework of a “quantum dimer” model

[7] of resonating nearest-neighbor singlet bonds: among all the dimer packings, the columnar pattern of dimers has the maximum number of states which can resonate with it by flipping a pair of singlet bonds as shown in Fig 1b. More technically, the quantum dimer model is dual to a compact U(1) gauge theory [3, 8, 9], and the confining property of this theory implies that translational symmetry is broken. The non-zero spin excitations of such a paramagnet continue to be described by the $S = 1$ particle in (2.1).

Let us now add a non-magnetic impurity. Actually, it is convenient to always deal with systems with an even number of spins, and so we will add two impurities and eventually move them infinitely far apart from each other. These two impurities are represented by the two X's in Figs 1e,f. If we now attempt to construct the ground state of the system with impurities, two distinct possibilities exist. First, we can remain within the subspace of short-range singlet bonds (*i.e.*, the Hilbert space of the quantum dimer model), and this is indicated in Fig 1e. The key property of such a state is that there is a string of 'defect' bonds connecting the two impurities which is out of registry with the global columnar order; so as the impurities move apart from each other, there is an energy cost which grows linearly with the separation between the impurities. This linear energy cost can also be understood within the compact U(1) gauge theory representation of the dimer model, in which the impurities at X appear as static electric charges which are linearly confined by the gauge force. So ultimately, it will always pay for the system to break a singlet bond, and produce two nearly free moments ('spinons') confined around each impurity [10, 3, 11, 12, 13, 14], as shown in Fig 1f. There is a weak effective interaction, J_{eff} , between these moments which is mediated by virtual excitations of the intervening singlet bonds, and is therefore exponentially small in the separation, R , between the impurities. We expect $|J_{\text{eff}}| \sim \Delta e^{-R\Delta/c}$ where c is of order the geometric mean of c_x, c_y . The sign of J_{eff} will be (anti-) ferromagnetic if the impurities are on the same sublattice (opposite sublattices).

The presence of these two weakly interacting moments has strong and distinctive signals in the spectrum and thermodynamics of the model. Upon exact diagonalization of a finite-size system of two impurities, one should find a very low-lying $S = 1$ state, well below the bulk spin gap, which approaches the ground state exponentially fast as the separation between the impurities is increased. For $J_{\text{eff}} < 0$, the $S = 1$ state will eventually become the global ground state. In the presence of a uniform external magnetic field, the free moments contribute a large susceptibility which is easily detectable experimentally; in addition to the bulk contribution in (2.2), we have the impurity contribution

$$(2.3) \quad \chi_{\text{imp}} = \frac{2}{T} \frac{e^{-J_{\text{eff}}/T}}{1 + 3e^{-J_{\text{eff}}/T}}.$$

This has a Curie divergence of two free moments, $\sim 1/2T$, for $T > |J_{\text{eff}}|$ which excludes only an exponentially small low T regime as $|J_{\text{eff}}|$ is so small.

3. Deconfined spinons

We now look for paramagnetic Mott insulators in which non-magnetic impurities do not bind local moments in their vicinity. Clearly, the key effect responsible for confinement in Section 2 was the rigidity of the wavefunction in the space of different singlet bond pairings, produced by the energy gained in the resonance of Fig 1b. We can anticipate that stronger fluctuations will appear in this singlet

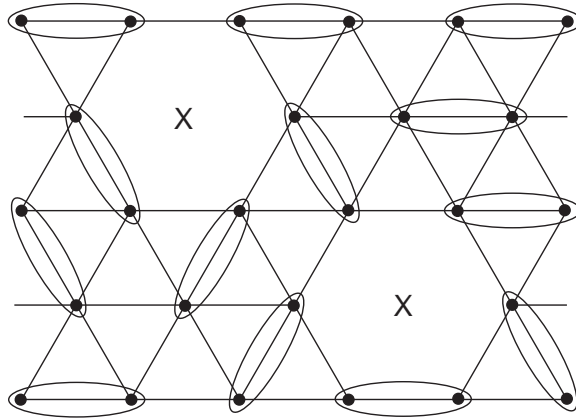


FIGURE 2. Snapshot of the wavefunction on the triangular lattice in the presence of two impurities. The two impurities are not connect by a line of “defect” bonds and are free to move infinitely apart from each other.

pairing space by allowing frustrating exchange interactions in H , *e.g.*, diagonal or second-neighbor bonds on the square lattice will permit resonance around a much bigger class of loops, some of which overlap with each other. More technically, we need the quantum dimer model to be dual to a deconfined gauge theory: the electric charges induced by the non-magnetic impurities will then not be confined to each other, and it will be possible to move the impurities apart with negligible energy cost once they are well separated. In such a situation, even in the presence of the impurities, the ground state will remain within the subspace of short-range singlet bonds, and no nearly-free spinons will be generated. A schematic of such a state with impurities is indicated in Fig 2 for the triangular lattice.

Such paramagnetic Mott insulating states with strong fluctuations in the space of singlet pairings were discussed by a number of investigators under the general umbrella of “resonating valence bond” (RVB) states [15, 1, 16, 7, 17]. However, a clear distinction between deconfined RVB wavefunctions and the confined states in Section 2 was not made. A specific condition for deconfinement was spelt out in Refs. [18, 19, 20]: one needed condensation of a charge ± 2 Higgs field, realized by a dimer on a link with a frustrating interaction, to move the compact $U(1)$ gauge theory into a deconfined phase (the quantum transition between the confined and deconfined states is described by a Z_2 gauge theory [21, 22, 9]). Examples of such deconfined phases were presented in large N computations on frustrated antiferromagnets on the square [18, 19], triangular, and kagome lattices [23]. These phases also have stable, spin-singlet, Z_2 vortex excitations [18, 4] (christened ‘visons’ in recent work [22]), and it is possible that the non-magnetic impurities bind visons in their vicinity[17]; even so, the impurities will be able to move apart as there is no long-range force between two visons. Formation of local moments near the impurities will require the breaking of singlet bonds, and this is suppressed by the presence of the spin gap. Of course, even in the absence of confinement, we cannot completely rule out the possibility that there is an impurity-spinon bound state lower in energy than an isolated impurity and a impurity-vison bound state,

but we consider it unlikely in a situation where short-range RVB states are strongly preferred.

Recently, a couple of plausible candidates for deconfined states have emerged in numerical studies of specific models on the triangular lattice: Misguich, Lhuillier and collaborators [24] examined an extension of H with ring-exchange interactions, while Moessner and Sondhi [25] argued for a deconfined phase for the quantum dimer model.

We close this section by contrasting the spectral and thermodynamic properties of confined states (discussed in Section 2) with the corresponding properties of deconfined states. All specific models for deconfined states discussed so far have been found to have a *pair* of $S = 1/2$ spinon excitations [18, 4]; the two spinons have minima for their dispersion at different points in the Brillouin zone, and the dispersion is described by (2.1) in its vicinity. As in (2.2) we can then compute the susceptibility to a uniform magnetic field

$$(3.1) \quad \chi_u = \frac{\mathcal{A}\Delta}{2\pi c_x c_y} e^{-\Delta/T},$$

which differs from (3.1) by a factor of $1/2$ (also Δ is now the gap to $S = 1/2$, rather than $S = 1$ excitations). A more striking difference appears when we consider the response to two non-magnetic impurities: no local moments form, and so there is no low-lying $S = 1$ state exponentially close to the ground state. Consequently the change in the susceptibility is not large: it is expected to be of order (3.1) with \mathcal{A} replaced by the area of two unit cells. The absence of low-lying $S = 1$ states should also serve as a sensitive diagnostic of deconfinement in numerical studies: it should be interesting to extend the numerical results in [24] in this direction.

4. *d*-wave superconductors

The Bogoliubov quasiparticles of a superconductor have essentially the same quantum numbers as deconfined spinons [26], and so there is no fundamental reason why a non-magnetic impurity in a good *d*-wave superconductor must necessarily bind a $S = 1/2$ moment in its vicinity. However, when one considers incrementally doping a paramagnetic Mott insulator, two distinct possibilities arise.

(A) For the deconfined states of Section 3, both the weak and strong doping limits do not bind moments near the impurity: consequently, we expect a smooth evolution of physical properties with doping, with only a weak magnetic response associated with the impurity.

(B) A quite different picture emerges upon doping the confined states of Section 2. The undoped limit has a $S = 1/2$ near each impurity, while the strongly doped limit does not: we expect that the free $T = 0$ moment will survive in the superconducting state for a finite range of doping (*i.e.*, an isolated moment will exhibit a divergent Curie susceptibility $\sim 1/4T$ even in the superconducting state), and a quantum critical point separates the weak and strong doping limits. On the strong doping side of this quantum critical point, the moment is Kondo screened as $T \rightarrow 0$, and such a regime is continuously connected to a regime, at higher doping, where the moment does not even form at intermediate T . This quantum phase transition is described by a Kondo-like Hamiltonian of a $S = 1/2$ moment exchange-coupled to the gapless Bogoliubov quasiparticles. This model has been much studied [27, 28, 29] in recent years, and it is well established that such a transition does exist in

models without particle-hole symmetry; however, no fundamental understanding of the nature of the critical properties of the transition has yet been achieved.

We wish to argue here that a number of recent experiments on the high temperature superconductors suggest that possibility (B) is the correct one, *i.e.*, the appropriate reference Mott insulating state is the one with spinon confinement, and that non-magnetic impurities in the under-doped superconductor always bind a $S = 1/2$ moment at $T = 0$. The most direct evidence comes from recent NMR measurements of Alloul and collaborators [30] who have measured a Curie-like susceptibility of Li moments in the *superconducting* state of underdoped YBCO; a number of earlier experiments [10, 31] have also seen moments above the superconducting critical temperature in the normal state. Indirect, but strong, evidence comes from our studies of the influence of the non-magnetic impurities on other excitations of the superconductor:

(i) the resonant $S = 1$ spin collective mode broadens dramatically upon doping with a very small concentration of Zn impurities [32], and we have argued [33] that this is naturally explained by the unpaired moments near the impurity. Indeed, the very existence of the spin resonance mode is evidence for confinement in the reference insulating state, as the resonance may be viewed [34] as the continuation of the $S = 1$ particle discussed in Section 2 and Fig 1d.

(ii) STM experiments measuring the quasiparticle tunneling current near Zn impurities in BSCCO have an unusual dependence on bias voltage and spatial location [35], and this is reproduced [28] in the Kondo-like models mentioned above.

Finally, we mention the issue of translational symmetry breaking. We have argued that the translational symmetry breaking must be present in the confined insulator, and it is natural to expect that this will survive in at least the lightly-doped superconducting state [18, 19, 36], and a state with co-existing stripe and superconducting order was discussed early on in [19]. Indeed, it is tempting to relate the stripes in Fig 1c to the stripes experimentally observed in the superconductor [36, 9]. However, at least at very low doping, it seems clear that the magnetic long-range order present in the actual undoped insulator plays an important role in the microstructure of the stripes. But at somewhat larger doping, once the magnetic order disappears, we think it is plausible that the local stripe correlations are bond-centered and look similar to those in Fig 1c. Indeed, a recent photoemission experiment [37] has suggested bond-centering of stripes in this regime.

We reiterate that while local moment formation near non-magnetic impurities is intimately linked with confinement and translational symmetry breaking in the insulating, charge-incompressible state, this is no longer expected to be the case in the superconductor. The latter is compressible and local moments may be present even in a phase without translational symmetry breaking. The main argument for moment formation in the superconductor is based on continuity from the undoped insulator; the quantum critical point at which the moment is quenched with increasing doping can be distinct from the critical point at which bulk translational and rotational symmetries are restored (and also from the point where the ground state becomes a normal metal at large overdoping).

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