Magnetic response of nonmagnetic impurities in cuprates

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(Dated: 10th November 2018)

PACS numbers: 71.27.+a, 75.20.-g, 74.72.-h

A theory of the local magnetic response of a nonmagnetic impurity in a doped antiferromagnet, as relevant to the normal state in cuprates, is presented. It is based on the assumption of the overdamped collective mode in the bulk system and on the evidence, that equal-time spin correlations are only weakly renormalized in the vicinity of the impurity. The theory relates the Kondo-like behavior of the local susceptibility to the anomalous temperature dependence of the bulk magnetic susceptibility, where the observed increase of the Kondo temperature with doping reflects the crossover to the Fermi liquid regime and the spatial distribution of the magnetization is given by bulk antiferromagnetic correlations.

One of the open theoretical questions in cuprates is the understanding of a well established experimental fact that nonmagnetic impurities have a strong effect on superconducting as well as on the normal-state properties of cuprates [1]. Prominent example is the substitution of Cu in CuO2 planes by Zn2+ which acts as a spinless impurity. In contrast to the naive picture of a weak scatterer, Zn2+ impurity depresses superconductivity already at small concentration and represents a strong scatterer for transport properties. In this contribution we mainly address the magnetic effects of an impurity in the non-superconducting phase. NMR experiments show that Zn induces local magnetic moments on the nearest neighbor (n.n.) copper sites [2], as well as on more distant copper neighbors [3,4]. The observed local susceptibility [5,6] is well accounted for by the Curie-Weiss form

\[ \chi_{\text{loc}} \propto \frac{1}{T + \Theta}, \]

whereby \( \Theta \) is independent of the impurity concentration but reveals a clear dependence on doping. Namely, in the underdoped YBaCu3O6+x (YBCO) the behavior is nearly Curie-like, with \( \Theta \sim 0 \), whereas in the overdoped YBCO \( \Theta \) shows a strong increase with doping [7]. In analogy with the Kondo effect in metals \( \Theta \) has been interpreted as a relevant Kondo temperature. Analogous effects in doped cuprates have been established for a Li+1 impurity which is also nonmagnetic [7]. Since it has a different valence the similarity indicates that the additional hole is not trapped near the impurity. By a multi-nuclei NMR imaging it has become also increasingly clear that the spatial distribution of the magnetization around the impurity reflects the antiferromagnetic (AFM) correlations of the bulk system [8].

From the point of theoretical description, it seems well established that a nonmagnetic impurity as, e.g., Zn2+ can be incorporated into a microscopic electronic model of CuO2 planes in cuprates by introducing, e.g., an inert empty site into the \( t-J \) model relevant to cuprates [8], or a local site with a very different local energy within the Hubbard model [8,10]. Impurity-induced moments and a Curie-like susceptibility have been established in disordered spin systems, e.g., spin ladders [11], in the presence of the gap in the spin excitation spectrum. An analogous treatment, assuming a spin gap in underdoped cuprates, also leads to the appearance of a Curie-type susceptibility of an unpaired spin [12]. Kondo effect based on the \( t-J \) model and on the spin-charge separated ground state has been used also to explain strong transport scattering on the impurity site [13]. The 2D Hubbard model with impurities has been analysed using a renormalized random-phase-approximation (RPA) to describe the Knight-shift data in Zn and Li substituted YBCO. Numerical studies confirmed the existence of an induced Curie susceptibility at low doping [12], whereas variational Monte Carlo simulation established equal-time AFM correlations around the impurity [14].

Nevertheless, the understanding of magnetic effects of such an impurity is far from satisfactory. It is clear that in the normal state of cuprates there is at most a pseudogap in underdoped regime, whereas at higher doping spin excitations are gapless and the usual arguments for a Curie-type susceptibility from unpaired spins [12,13] become unfounded. There is also no explanation for the origin and the onset of finite and large Kondo temperature \( \Theta > 0 \) in the overdoped regime. Lacking is also the theoretical answer to the evident question whether the local magnetic response around the impurity is just the reflection of the bulk (as well anomalous) magnetic response, as evidenced by recent experiments [3]. In any case, the \( T \)-dependence of magnetic response outside the spin gap regime has been so far treated only within the RPA [8], which is generally not satisfactory enough to account for anomalous bulk properties.

To address the above issues we present a generalization of the theory of spin response applied to explain anomalous bulk magnetic response [15]. The novel input is the observation that equal-time spin correlations around the impurity are to a large extent unrenormalized. The consequence is that the local magnetic response is an image of the anomalous staggered susceptibility in a homogeneous system, which exhibits also the Curie-Weiss behavior. Consequently, the onset of a finite Kondo scale \( \Theta \) is related to the doping-driven crossover of the bulk spin dynamics from a non-Fermi-liquid spin dynamics to a Fermi-liquid one [16].

Let us start with an approach to the spin response of a homogeneous doped AFM. The dynamical spin susceptibility
\[ \tilde{\chi}_q(\omega) = -\langle S^z_q, S^z_q \rangle / \omega \text{ can be expressed within the memory function formalism as} \]

\[ \tilde{\chi}_q(\omega) = \frac{-\eta_q}{\omega^2 + \omega M_q(\omega) - \omega_q^2}, \quad (1) \]

where \( \eta_q = -i\langle [S^z_q, \tilde{\chi}_q(\omega)] \rangle \) with \( \omega_q = \eta_q/\chi_q \) and \( \chi_q = \tilde{\chi}_q(\omega = 0) \) is the static susceptibility. \( \omega_q \) represents the collective-mode frequency in the case of low damping \( \gamma_q \sim M''(\omega_q) < \omega_q \). However, in cuprates the collective mode is found to be overdamped throughout the normal phase, i.e., \( \gamma_q > \omega_q \). Following the evidence from the analysis of microscopic models, such as the planar \( t-J \) model \([15,17]\), we assume also constant \( \eta_q \sim \eta \) and \( \sqrt{\gamma_q} \sim \gamma \) in the region of interest near the AFM wavevector \( q \sim Q = (\pi, \pi) \). \( \eta \) is closely related to energy, so it is quite \( T \)-independent and only smoothly dependent on doping. In a doped AFM damping \( \gamma \) emerges from the decay of a spin collective mode into electron-hole excitations and is also assumed to remain finite and large at low \( T \rightarrow 0 \) in the normal state \([17]\). Hence, the main \( T \)-variation enters Eq. (1) via \( \chi_q \).

The central idea of the theory of the anomalous scaling in doped AFM \([19]\) is that a nontrivial dependence \( \chi_q(T) \) is driven by the fluctuation-dissipation relation for the equal-time correlations

\[ \frac{1}{\pi} \int_0^\infty d\omega \cosh \frac{\omega}{2T} \chi''_q(\omega) = \langle S^z_q S^z_q \rangle = C_q. \quad (2) \]

There exists an extensive evidence from analytical \([21]\) and numerical work on the \( t-J \) model at finite hole concentration \( c_h > 0 \) that \( C_q \sim \Theta_q \sim C(\kappa^2 + \hat{q}^2) \) \( \hat{q} = q - Q \), and the AFM correlation length \( \xi = 1/\kappa \) saturates at low \( T \). Similar conclusions emerge from an analysis of inelastic neutron scattering on YBCO \([18,19]\). The relation \([22]\) then leads to a strongly \( T \) dependent \( \chi_q(T) \) which is at heart of the non-Fermi liquid behavior observed in underdoped cuprates, in contrast to the usual Fermi liquid where \( \chi''_q(\omega) \) is essentially \( T \)-independent.

Let us first consider the behavior of \( \chi_q(T) \). Performing the high-\( T \) expansion in Eq. (2) we get

\[ C_q \sim T \chi_q + \frac{1}{\pi} \int_0^\infty d\omega \frac{\omega}{6T} \chi''_q(\omega) = T \chi_q + \frac{\eta_q}{12T}. \quad (3) \]

where we have taken into account the definition of \( \eta_q \) as the second frequency moment of the shape function \( \chi''_q(\omega)/\omega \).

The high-\( T \) expansion is thus consistent with the Curie-Weiss behavior \( \chi_Q = C_Q/(T + \Theta_Q) \) where \( \Theta_Q = \eta_Q/12C_Q \). Since in a doped AFM, as represented, e.g., by the \( t-J \) model, \( C_q \propto 1/c_h \) \([14]\) we get quite small scale \( \Theta_Q \propto c_h \). On the other hand, the expansion is valid only for \( T > \Theta_q \). At \( T = 0 \) we get \( \chi_Q(T = 0) = \eta_q/(\gamma \omega_p) \) \([15]\), where \( \omega_p \sim \gamma e^{-2\xi} \) and \( \xi = \pi \gamma C_Q/2\eta \).

In Fig. 1 we present \( C_Q/\chi_Q(T) \) as follows from the solution of Eqs. \([1,2]\) for fixed \( \eta = 0.6 \) and \( \gamma = 0.5 \) \([15]\) (note that \( t \sim 400 \text{ meV} \) for cuprates) but varying \( \kappa = 0.5 \sim 1.5 \) (in units of inverse lattice spacing). By way of Eq. (3) \( \kappa \) also determines \( \tilde{k} \) which enters the low-\( \omega \) behavior of \( \chi''_q(\omega) \). For the range of \( \kappa \) considered, \( \kappa/\tilde{k} \sim 2 \) so that \( \tilde{k} \) roughly corresponds to the experimental range of values in underdoped YBCO \([13]\). Note that the Curie-Weiss law is obeyed down to \( T \sim \Theta_Q \). The deviation appears (to lower values for given parameters) on approaching \( T \rightarrow 0 \). \( \Theta_K = C_Q/\chi_Q(T = 0) \) can be interpreted as the relevant Kondo temperature and its variation with \( \kappa \) is presented in the inset of Fig. 1. On increasing \( \kappa \) (note that \( \kappa \propto \sqrt{\gamma t} \)) we are facing quite an abrupt transition from a Curie behavior at \( T \rightarrow 0 \) to a Curie-Weiss variation with finite and rapidly increasing \( \Theta_K > 0 \) \([16]\). Such a behavior is also consistent with experimental results for \( 1/\chi_Q(T) \) obtained from the analysis of NMR 1/T2G(T) relaxation in various cuprates \([16]\).

Figure 1: \( C_Q/\chi_Q \) vs. \( T \) (both in units of \( t \)) for various \( \kappa \). The inset shows the variation of Kondo \( \Theta_K \) with \( \kappa \).

Let us turn to a doped AFM with an added nonmagnetic impurity, as relevant to \( \text{Zn}^{2+} \) replacing planar \( \text{Cu} \) in \( \text{CuO}_2 \) planes. To be more specific we have in mind the planar \( t-J \) model, where the impurity is represented as an empty site at the origin \( i = 0 \). In analogy with the homogeneous system, Eq. (4), we consider the equal-time local correlations \( C_{ij} = \langle S^z_i S^z_j \rangle \) as an essential input. In general, \( C_{ij} \) differ from correlations in an homogeneous system without any impurity where \( C_{0ij} = C^0(\textbf{R}_i - \textbf{R}_j) \). (Furtheron we label the homogeneous quantities by the superscript 0.) However, it appears characteristic for strongly correlated electrons in low-doped AFM that at least shorter-range \( C_{ij} \) close to the impurity deviate modestly from unperturbed \( C_{0ij} \). This is partly plausible since, e.g., the n.n. correlations \( C_{ij} \) are governed by the minimization of the exchange energy. On the other hand, insensitivity of \( C_{ij} \) around the impurity can be interpreted as an effective spin-charge decoupling, where the empty site represents just a free spinon not affecting nearby spin correlations \([12,13]\).

In support of the above conjecture we perform an exact-diagonalization calculation of \( C_{ij} \) within the \( t-J \) model with an empty site. As an example of a doped AFM we present in Fig. 2 results for a system \( N = 20 \) sites at \( T = 0 \) with
$N_h = 2, 3$ mobile holes and $J/t = 0.3$. We show some nonequivalent n.n. and next n.n. correlations $C_{ij}$ around the impurity. We notice that even on sites neighboring the impurity at least shorter-range $C_{ij}$ are nearly the same as in the bulk, or even enhanced as noted also by others \[14\].

\[\begin{align*}
C_{ij} &= \sum_{i,j \neq 0} C_{ij}^0 - 2 \sum_i C_{ij}^0 \neq 0 = C_{ij}^0 = 1 - c_h, \quad (4)
\end{align*}\]

\[\sum_{i,j} = \langle \frac{S_i^z S_j^z} {N_h} \rangle = 0. \] Eq. (4) reproduces for $c_h \ll 1$ the proper moment of the impurity corresponding to $S_{tot} = 1/2$ \[8, 12\].

\[\begin{align*}
\chi_i(\omega) &= -[\omega^2 \delta + \omega M(\omega) - \bar{\delta}]^{-1} \eta,
\end{align*}\]

where $\bar{\delta} = \frac{\eta}{\eta}^{-1}$. Again, the local fluctuation-dissipation relation

\[\frac{1}{\pi} \int_0^{\infty} d\omega \text{cth} \frac{\omega}{2T} \chi''_i(\omega) = C_{ij}, \]

is used to fix $\chi_i$.

The next step in an inhomogeneous system is to diagonalize the correlation matrix $C_{ij} = \sum_{\lambda} C_{ij} (\gamma_\lambda^i)^* v_\lambda^i$ where $\sum_{\lambda} C_{ij} v_\lambda^i = C_{ij} v_\lambda$. From the sum rule \[5\] it then follows that one can simultaneously diagonalize the susceptibility matrix $\hat{\chi}_i(\omega) = \sum_{\lambda} \chi_\lambda(\omega) (\gamma_\lambda^i)^* v_\lambda^i$ with

\[\hat{\chi}_\lambda(\omega) = -\frac{\eta_\lambda}{\omega^2 + i\gamma_\lambda \omega - \delta_\lambda}, \]

where we have for simplicity assumed the diagonal form of $(M_{ij}, \eta_{ij}) \sim \sum_{\lambda} (\gamma_\lambda^i, \eta_\lambda) (\gamma_\lambda^j)^* v_\lambda^j$ as well. In analogy with the homogeneous system, the local magnetic response around the impurity will be determined by the behavior around $\lambda \sim \Lambda$ for which $C_{ij} = \max$. In this region we assume constant $\gamma_\lambda \sim \gamma$ and $\eta_\lambda \sim \eta$. Clearly, this is based on the assumption that damping is quite local and not affected significantly by the impurity. On the other hand, $\eta_{ij}$ can be explicitly calculated and is expressible in terms of equal-time correlations \[17\].

In a system with a nonmagnetic impurity a spin polarization around the impurity induced by a homogeneous magnetic field, gives rise to the susceptibility $\chi_i$ on site $i$

\[\chi_i = \sum_j \chi_{ij} = \sum_{\lambda} \chi_{ij}(\gamma_\lambda^i)^* v_\lambda, \quad v_\lambda = \sum_j v_j^\lambda. \]

In the case of a n.n. site $\chi_i$ is directly related to the Knight shift on the $^7$Li impurity and of $^{89}$Y near the Zn impurity \[9\].

Another relevant quantity is the (average) uniform susceptibility $\bar{\chi} = \sum_{\lambda} \chi_\lambda v_\lambda^2/N$ which yields the impurity-induced contribution $\Delta \chi = \bar{\chi}_i - \chi_{0} = -\chi_{0}$.

We first give an approximate solution to the impurity problem via the perturbation calculation. Here, $C_0 = C_0' + C_0''$ with the perturbative part $C_0' = -1/4$ and $C_0'' = -C_0'''$. The unperturbed eigenvectors are the homogeneous ones, $v_i^\lambda = \exp(i\kappa r_i)/\sqrt{N}$, and the lowest order calculation gives

\[\Delta v_\lambda = \frac{1}{N} \sum_{q \neq 0} v_\lambda^q \frac{\mu^2 - C_0' - C_0''}{C_0 - C_0' q^2}. \]

where $\mu = \sqrt{1/4 - c_h}$ is the effective local moment. The impurity-induced correction to the local susceptibility is thus

\[\Delta \chi_i = \sum_q \Delta \chi_q v_q^i v_q^i + \chi_0 (\Delta v_q^i v_q^i + v_q^i q^2 \Delta v_q^i q^2), \]

and can be expressed as $\Delta \chi_i = \Delta \chi/N + \chi_i$, i.e., as a sum of the perturbed uniform susceptibility $\Delta \chi = N \Delta C_q = 0, q = 0 = -\mu^2/T$, whereas

\[\chi_i = \sum_q e^{i q r_i} \chi_0 \mu^2 - C_0' q^2} - 1]. \]

It is evident that $\Delta \chi$ corresponds to a free spin with the moment $\mu \sim 1/2$ (at low doping) introduced by the impurity. Nontrivial is the spatial distribution of $\chi_i$. Since the main contribution in Eq. \[11\] arises from $q \approx Q$ and $C_0' \gg \mu^2$, we obtain from Eq. \[11\] $\chi_i \sim -\chi_{0i}$, i.e., the local response is just the intersite susceptibility of a homogeneous system, being the Fourier transform of $\chi_0^q$.

In Fig. 3a we present results for $1/\chi_1$ for the n.n. site. We use Eq. \[11\] with $\chi_0^q$ determined via a self-consistent solution to Eqs. \[11, 12\]. To be consistent with the $t$-$J$ model on a 2D square lattice we take here the form $C_0^0 = a/(\kappa^2 + \zeta_q) - b$ with $\zeta_q = 2(\cos(qx) + \cos(qy) + 2)$ whereas $a, b$ are chosen...
such that $C_{q=0}^{0} = 0$ and $C_{q}^{0} = 1/2$. As in the case of homogeneous $\chi_{Q}$ in Fig. 1, we notice that the behavior is close to the Curie-Weiss form $1/\tilde{\chi}_{1} \propto T + \Theta_{1}$ with a qualitative transition from $\Theta_{1} \sim 0$ for $\kappa < 0.7$ to finite and large $\Theta_{1}$ for $\kappa > 1$. Deviations from the Curie-Weiss dependence are understandable since Eq. (11) includes contributions from all $q$ where $\Theta_{q} > \Theta_{Q}$. Nevertheless the behavior at $q \sim Q$ is dominant since considered $\kappa$ are quite large. It should be reminded that the essence of the theory of anomalous scaling of spin response in underdoped cuprates [15] lies in the fact that anomalous $\omega, T$ dependence appears for $T > T_{K} \sim 0$ even for substantial and $T$-independent $\kappa$.

In summary, we have presented a theory for the magnetic response of nonmagnetic impurities in doped AFM. It is based on the assumptions, and also evidence, that certain quantities are not substantially modified in the vicinity of an impurity. This is in particular the case of correlations $C_{ij}$, but also of the collective mode amplitude $\eta$ and damping $\gamma$. Note that such assumptions would not be valid within a normal Fermi liquid but are rather the consequence of strong correlations, i.e., $C_{ij}$ exhibit a kind of charge-spin separation.

Within the present theory the local spin response around the impurity clearly reflects the one in the homogeneous system which is also anomalous. Or alternatively, the measurements of the impurity-induced susceptibility allow for the reconstruction of the bulk $\chi_{Q}$ and corresponding correlation length $\xi$, as has been established in some other systems with the spin gap [23].

We have also shown that $\chi_{Q}$ in a doped AFM follows quite well the Curie-Weiss behavior. Consequently also local $\tilde{\chi}_{i}$ exhibit similar behavior, although with some deviations due to contributions from $q \neq Q$. In any case, deviations from $\chi_{i} \sim A_{i}/(T + \Theta_{i})$ diminish as we consider further neighbors or when the perturbation by the impurity is less local (or weaker). From the theory it is clear that $A_{i}$ is related to AFM correlations $C_{0i}^{0}$. Even more important, the transition from the regime with Kondo scale $\Theta_{i} \sim 0$ to a finite and fast increasing $\Theta_{1}$ reflects the crossover from a non-Fermi liquid to a more normal Fermi-liquid regime.

Authors acknowledge the support of the Ministry of Education, Science and Sport of Slovenia under grant P1-0044.

[1] H. Alloul, J. Bobroff, A. Mahajan, P. Mendels and Y. Yoshinori, AIP Conf. Proc. 483, 161 (1999) (cond-mat/9905424).
[2] A. V. Mahajan, H. Alloul, G. Collin, and J. F. Marucco, Phys. Rev. Lett. 72, 3100 (1994).
[3] S. Ouazi, J. Bobroff, H. Alloul, and W. A. MacFarlane, cond-mat/0307728.
[4] M.-H. Julien, et al., Phys. Rev. Lett. 84, 3422 (2000).
[5] P. Mendels et al., Europhys. Lett. 46, 678 (1999).
[6] J. Bobroff, et al., Phys. Rev. Lett. 83, 4381 (1999).
[7] J. Bobroff, et al., Phys. Rev. Lett. 86, 4116 (2001).
[8] D. Poilblanc, D. J. Scalapino, and W. Hanke, Phys. Rev. Lett. 72, 4116 (1994).
[9] N. Bulut, Physica C 363, 260 (2001); Y. Ohashi, J. Phys. Soc. Jpn. 70, 2054 (2001).
[10] Th. A. Maier and M. Jarrell, Phys. Rev. Lett. 89, 077001 (2002).
[11] M. Sigrist and A. Furusaki, J. Phys. Soc. Jpn. 65, 2385 (1996).
[12] G. Khaliullin, R. Kilian, S. Krivenko, and P. Fulde, Phys. Rev. B 56, 11882 (1997).
[13] N. Nagaosa and P. A. Lee, Phys. Rev. Lett. 79, 3755 (1997).
[14] S.-D. Liang and T. K. Lee, Phys. Rev. B 65, 214529 (2002).
[15] P. Prelovšek, I. Sega, and J. Bonča, Phys. Rev. Lett. 92, 027002 (2004).
[16] J. Bonča, P. Prelovšek, and I. Sega, cond-mat/0403325.
[17] I. Sega, P. Prelovšek, and J. Bonča, Phys. Rev. B 68, 054524 (2003).
[18] A. V. Balatsky and P. Bourges, Phys. Rev. Lett. 82, 5337 (1999).
[19] K. Kakurai et al., Phys. Rev. B 48, 3485 (1993).
[20] R. R. P. Singh and R. L. Glenister, Phys. Rev. B 46, 11871 (1992).
[21] F. Tedoldi, R. Santachiara, and M. Horvatić, Phys. Rev. Lett. 83, 412 (1999).