Visualizing the particle-hole dualism in high temperature superconductors.

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Recent Scanning Tunneling Microscope (STM) experiments offer a unique insight into the inner workings of the superconducting state of high-Tc superconductors. Deliberately placed inside the material impurities perturb the coherent state and produce additional excitations. Superconducting excitations — quasiparticles — are the quantum mechanical mixture of negatively charged electron (–e) and positively charged hole (+e). Depending on the applied voltage bias in STM one can sample the particle and hole content of a superconducting excitation. We argue that the complimentary cross-shaped patterns observed on the positive and negative biases are the manifestation of the particle-hole dualism of the quasiparticles.

The dual particle-wave character of microscopic objects is one of the most striking phenomena in nature. While posing deep philosophical problems, the dualism is ubiquitous in the microworld. Most notably, the two-slit experiments of Stern and Gerlach revealed the interference and, hence, the wave nature of electrons. In the condensed matter systems, such explicit visualization of the wave nature of the constituent electrons was missing until just recently. The breakthrough came when the researchers from the IBM labs realized that the best way to elucidate the electrons inside a material is to place an impurity in an otherwise perfect crystal structure. By building corrals of the impurities on the clean surface, and observing the generated patterns through the scanning tunneling microscope (STM), the experimenters were able to demonstrate the laws of the wave optics using the conduction electron waves.

The analog of the conduction electrons in the superconductors are the quasiparticles. Unlike electrons, the superconducting quasiparticles do not carry definite charge. Like the Cheshire cat, the quasiparticle is a combination of an electron and its absence ("hole"). And much like the Cheshire cat, the superconducting quasiparticles have never been seen in nature. Until now. In the series of beautiful experiments J.C. Davis’ group observe just that — the interference of the superconducting quasiparticles, which depending on the way one looks at them show their electron or hole parts.

Pan et al. explore the structure of the superconducting state in Bi$_2$Sr$_2$CuO$_2$ high-temperature superconductor in the vicinity of Ni and Zn impurities. To visualize the local quasiparticle states they employ the STM technique. There is one aspect of the electron tunneling into the superconducting state that makes it qualitatively different from the tunneling in conventional metals. The STM tip contains only the regular electrons which carry a unit of charge (–e). On the other hand, quasiparticles that live inside the superconductor do not possess a well-defined charge. Upon entering the superconductor, an electron that arrived from the normal STM tip must undergo a transformation into the Bogoliubov quasiparticles native to the superconductor. The detailed process of conversion of an electron into a quasiparticle is a deep theoretical problem. Another example of such process occurs in the case of the tunneling into fractional quantum Hall liquid, where the natural quasiparticles carry a fractional, but well defined, charge.

The most striking experimental observation that Pan et al. make is that close to the impurity additional electronic states are generated, with the energies inside the superconducting gap. That such states should exist in conventional (s-wave) superconductors was first predicted by Shiba and others in the late 1960’s, while for the unconventional (d-wave) superconductors these states were predicted and intensively studied in. Experimentally, these intra-gap states in conventional (Nb) superconductor were previously observed in IBM experiments.

The low-lying impurity states are produced when the local impurity is sufficiently strong so as to significantly disturb the superconducting order parameter in its neighborhood. It has been found theoretically that in the conventional superconductors an impurity that doesn’t have its own magnetic moment, or “spin,” should not produce states inside the gap. On the other hand, in the d-wave superconductors, even a potential (spinless) impurity produces two states located symmetrically above and below the chemical potential.

In the latest experiments, Pan et al. see the impurity states inside the gap. However, the most surprising is the spatial structure of the impurity states. For a Ni impurity, the positive-energy state, which corresponds to adding an electron, has the largest weight at the impu-
urity site, smaller weight on the next-nearest neighbors and even smaller weight on the nearest neighbors. The negative-energy state, which corresponds to removing an electron, shows a complimentary pattern: The impurity state is evenly distributed between the impurity’s four nearest neighbors, with almost no weight at the impurity site, or at the next-nearest neighbors.

In this paper we show how this highly non-trivial impurity state structure can be accounted for by using the particle-hole dualism of quasiparticles in superconducting state. We implement simple but realistic model of the doped cuprate superconductor with potential impurity. We demonstrate that the alternating intensity of the impurity states is the manifestation of the quantum wave nature of the quasiparticles scattering from the impurity.

\[ H_0 = -t \sum_{\langle i,j \rangle,\sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} - V \sum_{\langle i,j \rangle} n_i n_j, \]  

were a quantum-mechanical operator \( c_{i\sigma}^\dagger \) creates an electron on site \( i \), the operator \( c_{j\sigma} \) eliminates an electron from the site \( j \), and \( n_i = c_{i\uparrow}^\dagger c_{i\uparrow} + c_{i\downarrow}^\dagger c_{i\downarrow} \) represents the electron density on site \( i \). The electron spin, \( \sigma \), can point up or down. This model, referred to as the \( t-V \) model, is known to produce the d-wave pairing for the electron densities close to one electron per lattice site. The model, however, is invalid very close to the half-filled case (exactly one electron per Cu site) where the cuprates are no longer superconductors, but rather antiferromagnetic insulators. For the model parameters we use \( t = V = 300 \text{ meV} \). Such choice ensures that the electronic band structure of the cuprates is accurately represented, and the superconducting gap in the electronic density of states is on the order of \( 0.1t = 30 \text{ meV} \). The local impurity is introduced by modifying the electron energy on a particular site. The corresponding correction to the Hamiltonian is

\[ H_{imp} = V_{imp}(n_{0\uparrow} + n_{0\downarrow}) - S_{imp}(n_{0\uparrow} - n_{0\downarrow}). \]  

Qualitatively, the spatial distribution of tunneling intensity can be understood as follows. Let us define the respective amplitudes of particle and hole parts of the Bogoliubov quasiparticle, \( u_n(i) \) and \( v_n(i) \) for site \( i \) and for particular eigenstate \( n \). They obey the normalization condition \( \sum_n |u_n(i)|^2 + |v_n(i)|^2 = 1 \) for any fixed site \( i \). Consider now a site where, say, \( u_n(i) \) is large and close to 1. It follows therefore that for the same site the \( v_n(i) \) would have to be small, since the normalization condition is almost fulfilled by \( |u_n(i)|^2 \) term alone. Similarly, for the sites where \( v_n(i) \) has large magnitude, \( u_n(i) \) would have to be small. Recall now that large \( u(i) \) component would mean that quasiparticle has a large electron component on this site. Hence the electron will have large probability to tunnel into superconductor on this site and the tunneling intensity for electrons (positive bias) will be large. Conversely, for those sites the hole amplitude is small \( |v(i)| \ll |u(i)| \) and the hole intensity (negative bias) will be small. Similarly, for sites with large hole amplitudes \( |v(i)| \gg |u(i)| \) the electron amplitude will be suppressed and this site will be bright on the hole bias. Therefore if there is a particular pattern for the large particle amplitude (sampled on positive bias) on certain sites \( i \), the complimentary pattern of bright sites for hole tunneling (on negative bias) will develop as a consequence of the inherent particle-hole mixture in superconductor. This is the main physics, we believe, behind the cross rotation upon bias switch.

Our numerical results are summarized on Fig. 1 where the particle and hole like intensity is plotted near the impurity site.

To model the high-temperature superconductors we utilize the highly-anisotropic structure of the cuprates and focus on a single layer of the material. In the simplified model, the conduction electrons live on the copper sites, \( i \), and can hop to the neighboring sites, \( j \), with a certain probability measured by the quantity \( t \). In addition to that, the electrons that occupy the neighboring sites feel mutual attraction of a strength \( V \). Formally, this model is represented by the Hamiltonian,

FIG. 1. Impurity state patterns for a positive (left) and negative (right) bias. Impurity strength is \( V_{imp} = -3t \), doping 14%.
The important aspect that we include in the treatment of the impurity problem is the absence of the particle-hole symmetry. The particle-hole symmetry is lost as soon as we depart from the half-filled insulating part of the cuprate phase diagram, and hence is related to the amount of doping. While the asymmetry is not large, it results in two important effects. First, it leads to redistribution of the spectral weight among the impurity sites and its neighbors; second, it changes the position of the impurity level. The first effect is closely analogous to the Friedel oscillations, which occur in the vicinity of an impurity in a normal metal. An impurity essentially plays a role of a boundary condition imposed on the scattered electronic states. Since the most important states are in the vicinity of the Fermi level, these states oscillate in space with the corresponding filling-dependent Fermi wave vector. This generates oscillation in the electronic density of states. Similar phenomenon occurs for impurities in the cuprates. However, it is compounded by the superconducting character of the quasiparticles, as well as the anisotropy imposed by the Cu-O lattice. Figure 2 demonstrates the high sensitivity of the impurity state intensity on the doping.

Similarly, the effect of changing the impurity level position by the particle-hole asymmetry (doping) has important consequences. In the particle-hole symmetric case, the impurity levels approach the chemical potential as the strength of the impurity increases. In the limit of an infinitely strong impurity (“unitary” limit), the levels lie exactly at the chemical potential. For a finite doping, the position of the levels changes. In figure 3 we show how the impurity level position, \( \omega_0 \), changes as a function of doping for two different impurity strengths. Analytically, the change can be estimated from the non-self-consistent \( T \)-matrix approximation. One finds that for non-zero chemical potential \( \mu \) (with \( \mu = 0 \) at the half filling), the impurity levels are shifted by an amount proportional to \( \mu/W \), where \( W \) is the bandwidth. Hence neglecting this effect can cause an error in the impurity strength estimate. In fact, in a doped superconductor the impurity levels can cross the chemical potential at a finite impurity strength. While this effect turns out to be not very important in the case of Ni impurity in BSCO, we believe that it is indeed relevant for Zn in BSCO. Unlike Ni, the Zn impurity levels appear to be very close to the chemical potential. If we neglect the particle-hole asymmetry, this would suggest that Zn impurity is in the unitary limit. However, inclusion of the asymmetry shift would lead to a finite impurity strength, and would imply high sensitivity of the Zn level position on the doping. One of the characteristics of the unitary impurity states is that their spectral weight tends to zero on the impurity site, with the maxima positioned on the nearest neighbors. On the contrary, in the experiment, the spectral weight is maximized on the impurity site. This suggests that neither Ni nor Zn is in the unitary limit. More data on doping dependence of the position of Zn level inside the gap would help to clarify how relevant the particle-hole asymmetry effect is.

![FIG. 2. Doping dependence of the impurity state intensity pattern. The impurity strength is \( V_{imp} = -3t \). Each square represents a lattice site. The left-column patterns are for the positive bias and the right column is for the negative bias. The first row is the large doping case — 20% (\( \omega_0 = 0.0661 \)); the second row is the low doping case — 7% (\( \omega_0 = -0.0347 \)). Notice how the positive and negative bias patterns get interchanged as a function of doping.](image1)

![FIG. 3. Doping dependence of the impurity level position. The red line is for \( V_{imp} = -3t \); blue line is for \( V_{imp} = -2t \); the dashed line shows the level of the bulk d-wave gap obtained from the 16x16 lattice calculation (the infinite lattice result for the gap is about 50% larger).](image2)
fully local, and may include, for instance, modification of
the hopping parameters in its vicinity and interactions
with other bands, present in Cu-O plane. Accounting for
such effects would require a number of extra fitting pa-
rameters, which would reduce credibility of the obtained
results. Hence, we restrict our attention to the Ni impuri-
ties, where the only fitting parameter needed is the local
impurity strength. We find that for an attractive impu-
rity with a strength around $V_{\text{imp}} = -3t = -900 \text{ meV}$
and the average fillings of about 0.85 electrons per site
(15% doping), the impurity levels are situated within the
gap with the intensity distribution that corresponds to
the experimental pattern around Ni impurity (figure 1).
By including a weak spin part of the impurity interac-
tion, $S_{\text{imp}} = 0.2t = 60 \text{ meV}$, we reproduce the fine
energy splitting of the impurity peaks also observed in the
experiment of Pan et al. [1]. The site-dependent spectral
intensities are shown in figure 1.

![Figure 1](image_url)

FIG. 1. Inclusion of a weak, $S_{\text{imp}} = 0.2t$, spin component of
the impurity potential causes the spin-degenerate spectral
density peaks to split. The red line is the spin-up branch and
the blue is the spin down. The bottom left chart represents
the spectral density at the impurity site; top-right —
on the next-nearest neighbor; top-left and bottom right —
nearest neighbors. Due to the ferromagnetic coupling of
the impurity spin and conduction electrons, the spin-up level lies
lower than spin down. The energy (horizontal axis) is in the
units of $t$. Impurity strength $V_{\text{imp}} = -3t$, doping 14%.

That the spin part should be present in the interaction
follows from the atomic structure of the Ni$^{2+}$ that substi-
tutes for Cu in the copper-oxygen layer and believed to
have spin $S = 1$. The strength of the conduction electron
– Ni spin coupling is extremely hard to determine from
the first principles. The close analysis of the Ni impurity
states in the superconductor enabled us to extract the
approximate strength of both the potential and the spin
coupling between Ni impurity and electrons in BSCO.

Based on our theoretical analysis we can make the fol-
lowing predictions for the properties of Ni impurities in
BSCO: (1) For the lower-doped BSCO samples, the Ni-
induced peaks should shift closer to the chemical poten-
tial, and the patterns should change according to Fig. 1.
(2) In the presence of the in-plane magnetic field, there
should be Zeeman splitting of the peaks on the scale of
0.1 $\text{ meV}$/Tesla. For some impurities, Zeeman splitting
will enhance, and for the others suppress the intrinsic
peak splitting due to the impurity spin (this effect de-
PENDS on the relative alignment of the impurity spin and
the external magnetic field); (3) for a similar potential
strength impurity, but with a larger value of spin (Mn),
the peak splitting in zero magnetic field should increase.

In conclusion, we find that a simple effective model
well describes rich physics of the STM images near Ni
site. The model we adopted here is the simplest effective
model of the real material, where only the on-site impu-
riety effects are considered. As such, the model does not
address many aspects of the impurity influence on the
electronic states of the host material. Surprisingly, even
such a simple model exhibits a very rich set of phenom-
ena as a function of doping and impurity strength. We
find that to explain the experimental data we need to in-
clude both the non-magnetic scattering of carriers from
Ni site as well as spin interaction between carriers and
the impurity spin. The most striking feature observed in
the experiment — the rotation of the “impurity cross” as
a function of bias — appears to be a universal feature of
the theoretical model. This rotation is the manifestation
of the quantum-mechanical nature of the quasiparticles
in the superconducting state, and is a consequence of the
unique particle-hole composition of the quasiparticles.

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