Quasi-Particle Bound States around Impurities in $d_{x^2-y^2}$-wave Superconductors

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Abstract

Zn and Ni impurities in the hole-doped high-temperature superconductors are known to have strong effects on thermodynamic and transport properties. A recent scanning tunneling microscope study of Zn-doped Bi2212 (Pan et al., Nature 403, 746 (2000)) has provided high-resolution images of the local density of states around non-magnetic impurities in $d_{x^2-y^2}$-wave superconductors. These pictures contain detailed information about the spinor wave functions $u(r)$ and $v(r)$ of bound states with energy $E_0 \sim \Delta/30$, centered at the Zn-sites. We show that this type of wave function follows from the solutions of the Bogoliubov-de Gennes equations for $d_{x^2-y^2}$-wave superconductors.
Introduction: Impurity-doping of anisotropic superconductors has turned out to be a valuable probe, setting them apart from conventional superconductors with an s-wave order parameter. For example, doping of high-temperature superconductors, such as YBCO, LSCO, and BCCO, with non-magnetic impurities has contributed greatly to establish the underlying $d_{x^2-y^2}$-wave order parameter in these systems. [1–3] In particular, an analysis of the thermodynamic and transport properties in these compounds suggests that Zn-impurities can be modeled with a scattering potential in the unitary limit. [2,4] On the other hand, little is known experimentally about the local real-space structure of the impurity bound states around the Zn-sites, in spite of numerous theoretical studies on this question. [5–7] Very recently, Pan et al. have provided detailed scanning tunneling microscope (STM) images of the local tunneling conductivity, fixed at $\pm E_0$, where $E_0 \approx \Delta/30$ is the binding energy of the impurity bound state around a Zn site in Bi2212. The corresponding wave function exhibits a fourfold symmetry, associated with the underlying CuO$_2$ lattice.

In the context of conventional s-wave superconductors, this type of bound state, in this case associated with a magnetic impurity, has been predicted by Shiba. [9] Recently, this idea has found experimental support by STM studies in the vicinity of Fe and Gd impurity atoms on the surface of Nb superconductors. [10]

The objective of this paper is to present a simple solution of the Bogoliubov-de Gennes equations for $d_{x^2-y^2}$-wave superconductors [11,12] in the presence of a single impurity. This corresponds to an experimental situation where the impurity concentration is dilute enough, such that interactions between the impurities can be neglected. Within this approach, we obtain a wave function which resembles very accurately the fourfold symmetry which has recently been observed around Zn-impurities in Bi2212 [8], where the energies of the associated bound states are very small ($|E_0|/\Delta \ll 1$). We believe that this image of the local tunneling conductivity around the Zn-site, as seen by STM, provides strong evidence for $d_{x^2-y^2}$-wave symmetry. Therefore, this method can also be used to test anisotropic order parameters in organic superconductors, and may serve as a straightforward tool to explore the underlying symmetry in other new superconductors where the nature of the
order parameter is still under debate.

We also study the case of Ni impurities which may be modeled by a weaker scattering potential, close to the Born limit. In this case, we find that although $|v(r)|^2$ is not much different from the Zn-case, $|u(r)|^2$ is rotated by $\pi/4$ with respect to the strong-scattering limit corresponding to Zn. Finally, we find that for impurities with an impurity potential of intermediate strength, the lowest harmonic in $|u(r)|^2$ is suppressed, and therefore a dominant eight-fold symmetry may be expected instead of the four-fold symmetry, observed in the weak and strong scattering limits.

**Bogoliubov-de Gennes equations and bound state wave functions:** The Bogoliubov-de Gennes (BdG) equations for $d_{x^2-y^2}$-wave superconductors in the continuum limit are given by

$$Eu(r) = \left(-\frac{\nabla^2}{2m} - \mu - V(r)\right)u(r) + \frac{1}{p_F^2}\Delta(\partial_x^2 - \partial_y^2)v(r),$$  
(1)

$$Ev(r) = -\left(-\frac{\nabla^2}{2m} - \mu - V(r)\right)v(r) + \frac{1}{p_F^2}\Delta(\partial_x^2 - \partial_y^2)u(r),$$  
(2)

where $\mu$ is the chemical potential, and $V(r) > 0$ is the impurity potential, centered at the site $r = 0$.

Let us first consider the case of Zn impurities where the energy of the bound states is known to be very small, $E_0 \simeq 0$. In the following, we use a variational ansatz for the solutions of the BdG equations:

$$u(r) = A \exp\left(-\gamma r\right)\left(J_0(p_F r) + \sqrt{2}\beta J_4(p_F r) \cos (4\phi)\right),$$  
(3)

$$v(r) = \sqrt{2}A\alpha \exp\left(-\gamma r\right)J_2(p_F r) \cos (2\phi),$$  
(4)

where $J_l(z)$ are Bessel functions of the first kind, and $p_F$ is the Fermi momentum. ($A$ is the global normalization factor for the wave functions which can be neglected.) Note that for Bi2212 it is believed that $p_F \simeq 0.7\AA^{-1}$. This implies that $p_F a \simeq 2$. The coefficients $\alpha$, $\beta$, and $\gamma$ are determined variationally. Inserting Eqs. 3 and 4 into Eqs. 1 and 2, we find

$$E = K - V - \frac{1}{\sqrt{2}}\Delta\alpha,$$
\[ E\alpha = -K\alpha - \frac{1}{\sqrt{2}}\Delta(1 + \frac{\beta}{\sqrt{2}}), \]
\[ E\beta = K\beta - \frac{1}{2}\Delta\alpha, \]

where

\[ K \equiv \int_0^\infty drr \left[ (\partial_r \exp(-\gamma r)J_l(p_Fr))^2 + (l \exp(-\gamma r)J_l(p_Fr)/r)^2 \right]/2m \int_0^\infty drr (\exp(-\gamma r)J_l(p_Fr))^2 - \mu \simeq \frac{\gamma^3}{mp_F}, \]
\[ V \equiv \int_0^\infty drr \exp(-2\gamma r)J_0^2(p_Fr)V(r) \simeq (2\pi \gamma p_F) \int_0^\infty drr \exp(-2\gamma r)J_0^2(p_Fr)V(r). \]

In general, \( K \) in Eq. 6 depends on which Bessel function \( J_l(p_Fr) \) is used. However, in the limit \( \gamma/p_F \ll 1 \), \( K \) reduces to \( \gamma^3/(mp_F) \) for all \( J_l(p_Fr) \) with \( l \ll p_F/\gamma \). In the approximation for \( V \), only the dominant s-wave component \((l = 0)\) of the scattering potential \( V(r) \) has been considered. In the usual convention, which is used in this paper, a positive sign of \( V(r) \) corresponds to the attraction of electrons by the impurity. In impurity-doped Bi2212 the charge carriers are holes, and hence the opposite sign has to be chosen.

For the case of a Zn-impurity (strong scattering limit), we may assume that \( E \simeq 0 \). This gives \( K \simeq V/2, V \simeq 3\Delta/2 \approx \sqrt{2}\Delta \), \( \alpha \simeq \sqrt{2}(V - K)/\Delta \), and \( \beta \simeq -\sqrt{2} \). These choices yield the approximate parameter set \( \alpha \simeq 1, \beta \simeq -1/\sqrt{2} \), and \( \gamma \simeq p_F(\sqrt{2}p_F\xi)^{-1/3} \simeq 0.3p_F. \)

The tunneling conductance is given by

\[ \frac{dI}{dV}(r) \propto \text{sech}^2 \left( \frac{eV - E_0}{2T} \right)|u(r)|^2 + \text{sech}^2 \left( \frac{eV + E_0}{2T} \right)|v(r)|^2. \]

Thus, at small temperatures, the local tunneling conductance around the impurity site is dominated by \(|u(r)|^2\) for a fixed binding energy \( E_0 \) and by \(|v(r)|^2\) for \(-E_0\). In Figs. 1 and 2 images of \(|u(r)|^2\) and \(|v(r)|^2\) are shown. Both \(|u(r)|^2\) and \(|v(r)|^2\) have a four-fold symmetry, and extend in the directions of the Cu-O bonds. This strongly resembles the images seen by the STM experiments. Furthermore, weaker higher-harmonic satellite peaks are observed in \(|u(r)|^2\), along the \((\pm \pi/4, \pm \pi/4)\) directions, in accordance with the experiments. Note that with our sign convention for the scattering potential \( V(r) \), the roles of \(|u(r)|^2\) and \(|v(r)|^2\) are interchanged for the hole-doped cuprates. Thus, in Bi2212 our \(|u(r)|^2\) corresponds to a bound state at \(-E_0\) and \(|v(r)|^2\) to a bound state at \(E_0\).
Now let us turn to the case of Ni impurities. Ni is considered to be a weak scatterer. Therefore we may assume that $V(r) \to 0$, and consequently $\alpha \simeq 2\beta(K - E)/\Delta$ and $\beta \simeq \sqrt{2}(1 - 4(E^2 - K^2)/\Delta^2)^{-1}$. So, if $E^2 > K^2 + \Delta^2/4$ the coefficient $\beta$ turns out to be positive, which is most likely the case for Ni. Indeed, a sufficiently large magnitude of $\alpha$ implies that $E^2 \gg K^2 \simeq 0$ and $E \simeq \sqrt{3}\Delta/2$. This gives $\alpha \simeq -\sqrt{3}/2$, $\beta \simeq 1/\sqrt{2}$, and $\gamma \simeq 0.1p_F$. The squares of the wave functions $u(r)$ and $v(r)$ are shown in Figs. 3 and 4. Comparing with the corresponding images for the strong scattering limit, we note that $|v(r)|^2$ is qualitatively similar in both cases, whereas $|u(r)|^2$ appears to be rotated by $\pi/4$ with respect to the case of Zn impurities.

For impurities with a scattering potential $V(r)$ of intermediate strength, the coefficient $\beta$ in the wave function $u(r)$ is found to be greatly enhanced. Consequently, the higher-harmonic term in $u(r)$ (Eq. 3), containing a $\cos(4\phi)$-modulation dominates the tunneling response at positive binding energies $+E_0$. In this case, an eight-fold instead of a four-fold symmetry should be observed in $|u(r)|^2$, as shown in Fig. 5. On the other hand, the shape of $|v(r)|^2$ is not affected. The weaker satellite peaks in Fig. 1 can be viewed as strong-coupling precursors of this phenomenon. It would be interesting to test this particular prediction of an eight-fold symmetry in $|u(r)|^2$ experimentally, using appropriate candidate impurity atoms with intermediate scattering strengths.

**Conclusions:** In summary, we observe that (i) using the Bogoliubov-de Gennes equations for single impurities in $d_{x^2-y^2}$-wave superconductors in the continuum limit is a very useful approach. (ii) Both Zn and Ni impurities produce bound states with a four-fold symmetry, localized around the impurity sites. (iii) Impurities with intermediate scattering strength may have a bound state with a dominant eight-fold symmetry. The simple analysis of the BdG equations we have presented in this work provides a semi-quantitative picture of the spatial structure of bound states in anisotropic superconductors.

Recent experiments suggest that the electron-doped high-temperature superconductors NCCO and PCCO also have a $d$-wave order parameter. [16–18] On the other hand, the effects of Zn and Ni doping in the electron-doped systems appear to be opposite from the
hole-doped case, i.e. Ni impurities lead to a stronger suppression of the superconducting ordering temperature than Zn doping. \[19\] It is therefore likely that the roles of Zn and Ni are interchanged in the electron-doped high-T\(_c\) cuprates. Furthermore, there are indications that the \(\kappa-(ET)_2\)-salts have a d-wave superconducting order parameter as well. \[20,21\] Therefore, similar studies of impurity bound states in these compounds would be of great interest.

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FIG. 1. Spatial variation of the local tunneling conductance, centered at a strong-scattering impurity, such as Zn, in a $\text{d}_{x^2-y^2}$-wave superconductor. In this figure, the dominant contribution $|u(r)|^2$ at the positive bound state resonant frequency $+E_0$ is shown.

FIG. 2. Spatial variation of the local tunneling conductance, localized around a strong-scattering impurity, such as Zn, in a $\text{d}_{x^2-y^2}$-wave superconductor. Here the dominant contribution $|v(r)|^2$ at the negative bound state resonant frequency $-E_0$ is shown.
FIG. 3. Spatial variation of the local tunneling conductance, centered at a weak-scattering impurity, such as Ni, in a $d_{x^2-y^2}$-wave superconductor. In this figure, the dominant contribution $|u(r)|^2$ at the positive bound state resonant frequency $+E_0$ is shown.

FIG. 4. Spatial variation of the local tunneling conductance, localized around a weak-scattering impurity, such as Ni, in a $d_{x^2-y^2}$-wave superconductor. Here the dominant contribution $|v(r)|^2$ at the negative bound state resonant frequency $-E_0$ is shown.
FIG. 5. Spatial variation of the local tunneling conductance, centered at an impurity of intermediate scattering strength. Here the dominant contribution $|u(r)|^2$ at the positive bound state resonant frequency $+E_0$ is shown. In contrast to the weak and strong scattering limits, a dominant eight-fold symmetry is observed.