Impurity effect in electron-doped high-$T_c$ superconductors

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Abstract

The quasiparticle states around a nonmagnetic impurity in electron-doped high-$T_c$ superconductors are studied systematically based on the Bogoliubov–de Gennes equations. In the antiferromagnetic state, one in-gap impurity resonance state is revealed. As the impurity scattering potential increases, the resonance peak shifts to the gap edge and finally disappears for a strong impurity. The antiferromagnetic order and superconducting order coexist when the doping density increases. In this coexisting state, the in-gap resonance peaks are rather robust and appear in pairs that are lying symmetric with the Fermi energy. The peak positions and intensities strongly depend on the impurity potentials and the next-nearest-neighbour hopping constants. For a rather strong impurity, the resonance peaks shift to near the gap edge. When further increasing the doping density, the system is in the pure superconducting state. The resonance peaks still appear in pairs, with the peak intensities being weaker compared to those in the coexisting state. The two resonance peaks may occasionally merge into one zero-energy peak for both the coexisting state and the pure superconducting state. The spin-resolved LDOS are also investigated and may be used to detect possible antiferromagnetic order.

1. Introduction

High-$T_c$ superconducting (SC) materials have attracted tremendous attention since their discovery [1]. At present, a full understanding of this family of materials is still far from complete. Generally, the materials are quasi-two-dimensional compounds with the CuO$_2$ planes being conducting planes. The parent compounds are antiferromagnetic (AF) Mott insulators, and superconductivity is achieved by doping either holes or electrons into the parent system. However, the properties of electron-doped materials are quite different from those of hole-doped materials. Based on angle-resolved photoemission experiments, it was revealed that there are two disconnected Fermi surface pockets [2, 3], and thus, an effective two-band model may be required to describe electron-doped SC materials. Theoretically, several two-band models have indeed been proposed to account for low-energy properties [4–7]. Possible microscopic origins have been intensively discussed. Based on the $t - J$-type model, it was proposed that the magnetic band-folding effect induced by the magnetic correlation can account for this two-band feature [5, 6]. Alternatively, the two-band feature can be explained based on the $t - U - J$ model, and the two energy bands arise from the upper Hubbard band and the Zhang–Rice singlet band [7]. Another prominent feature of electron-doped materials is the electronic–hole asymmetry, which can be clearly observed from the doping/temperature phase diagram [8], namely, the AF region in electron-doped materials is considerably wider and the SC region is rather narrow. In hole-doped materials, the SC region and the AF region are completely separated. Many experiments have proposed that AF order and SC order may coexist in electron-doped samples [9]. Several possible explanations have been proposed to account for such asymmetric behaviour. This behaviour may be explained based on the Fermi surface topology or the picture of the van Hove singularities [10, 11]. The next-nearest-neighbour hopping may also play an important role in the electron–hole asymmetry [12].

The impurity effect has been an important tool for studying SC properties [13]. Experimentally, scanning tunnelling microscopy (STM) is a powerful technique for studying the single point-like impurity effect since it...
can investigate the quasiparticle density of states at the atomic scale. It was revealed by STM experiments that low-energy bound states exist near the impurity in hole-doped high-$T_c$ superconductors [14–16]. Theoretically, there are two effective methods for investigating the local density of states (LDOSs) of SC systems with a point-like impurity and comparing the numerical results with the STM experimental results. The first method is based on the $T$-matrix method and treats the impurity as a site potential [17, 18]. The second method is based on the Bogoliubov–de Gennes (BdG) equations [19–23]. Indeed, the impurity effect in hole-doped materials was previously studied intensively based on both methods. With the $T$-matrix technique, the LDOS is expressed in an analytic way. Therefore, the existence and origin of the impurity states may be discussed based on the pole of the Green’s function. In contrast, the advantage of the BdG technique is that it calculates the SC order parameter in a fully self-consistent manner. In particular, due to the pair-breaking effect, the order parameters near the impurity are strongly suppressed. This effect is typically ignored in the $T$-matrix method, whereas it is reproduced by the BdG technique. It was proposed that the suppression effect is also important and would enhance the intensity of the bound states. The peak width and position also depend on the amplitude of the suppression [24]. Thus, this suppression effect needs to be considered to provide a more accurate numerical result.

At present, most of the knowledge about the impurity effect of high-$T_c$ superconductors comes from the results on hole-doped samples. A systematic theoretical study for the impurity effect in electron-doped materials is still lacking. The impurity effect based on the $T$-matrix approximation is studied in [25–27]. The bound states in AF/SC coexisting states are revealed. Thus far, there are no theoretical studies about the impurity effect in electron-doped samples based on the BdG technique. Note that for another family of high-$T_c$ SC materials, i.e., the iron-based superconductors, the impurity effect of the AF state is studied based on both the BdG technique and the $T$-matrix method by the same group and starting from the same model Hamiltonian [28, 29]. Qualitatively different results have been reported. Therefore, for the electron-doped cuprates in which AF order exists for a rather large doping region, it is necessary to reexamine the impurity effect using a fully self-consistent method. Moreover, note that the value of the next-nearest-neighbour hopping constant $t'$ is important for determining the properties of electron-doped superconductors, and this value should be material dependent [9, 12]. It is insightful to study the impurity effect with different values of $t'$. Another important issue is the impurity effect with different impurity scattering potentials. Previously, only positive scattering potentials were considered when studying the impurity effect in electron-doped materials [25–27]. In fact, both negative and positive potentials are possible in real materials. In hole-doped high-$T_c$ superconductors, the impurity effects for the negative potential and the positive potential are completely different when a considerable $t'$ term is considered [13]. This also indicates that it is rather necessary and important to study the impurity effect with different values of $t'$ and impurity scattering potentials.

In this paper, motivated by the above considerations, we have studied theoretically the impurity effect in electron-doped high-$T_c$ superconductors based on the BdG technique. Starting from the $t-U-V$-type model, the LDOS spectra near the impurity in the pure AF state, the AF/SC coexisting state, and the pure SC state are calculated. The bound states with different next-nearest-neighbour hopping constants and impurity scattering potentials are also discussed.

The remainder of this paper is organised as follows. In section 2, we introduce the model and work out the formalism. In section 3, we perform numerical calculations and discuss the obtained results. Finally, we provide a brief summary in section 4.

2. Model and Hamiltonian

We start with an effective Hubbard-type model on a two-dimensional square lattice by assuming that onsite repulsive interactions are responsible for the AF term and that the nearest-neighbour attractive interactions generate SC pairing [23, 30, 31]. At the mean-field level, the Hamiltonian is expressed as

$$H_{SC} = - \sum_{ij}(t_{ij}c_{i\uparrow}^\dagger c_{j\downarrow} + \text{h.c.}) + \sum_{ij}(\Delta_{ij}c_{i\downarrow}^\dagger c_{j\uparrow} + \text{h.c.}) + \sum_{k\sigma}(U\langle n_{k\sigma}\rangle - \mu)c_{k\sigma}^\dagger c_{k\sigma} + V_s\sum_{\sigma}c_{k\sigma}^\dagger c_{k\sigma},$$

where $i$ and $j$ are lattice site indices, $\sigma$ and $\bar{\sigma}$ represent the electron spin with $\sigma = \uparrow, \downarrow$, $c_{i\sigma}^\dagger$/$c_{i\sigma}$ are quasiparticle creation/annihilation operators. $n_{k\sigma} = c_{k\sigma}^\dagger c_{k\sigma}$ is the particle number operator. $t_{ij}$ is the hopping integral between the sites $i$ and $j$. $\Delta_{ij}$ is the SC pairing order parameter. $\mu$ is the chemical potential. $U$ is the strength of the onsite repulsive interaction. In the present work, we assume a point-like impurity at the site $1_0$, and $V_s$ is the impurity scattering potential.

The above Hamiltonian can be written as a $2N \times 2N$ matrix ($N$ is the number of lattice sites). Then, it can be diagonalized by solving the BdG equations [19–23, 30, 31].
The pairing potential \( E_{ij} \) is determined self-consistently, where the pairing parameter \( \Delta_{ij} \) is the components of the Sl(2) order parameter. For a d-wave pairing symmetry, the SC pairing occurs between the nearest-neighbour sites. The pairing order parameter \( \Delta_{ij} \) is chosen as 1.2 and 2.64 to obtain a quanitatively correct phase diagram. The numerical results are obtained on a 36 × 36 lattice with periodic boundary conditions. A single impurity is placed on the site (18, 18). A 20 × 20 supercell is used to calculate the LDOS.

3. Results and discussions

The amplitudes of the SC order parameter and the AF order as a function of the doping density are plotted in figure 1 (without the impurity, the order parameters are spatially uniform with \( \Delta \equiv \Delta \) and \( m \equiv m \)). As shown, at very low doping densities, the system is in the AF state. The amplitude of the AF order decreases and the SC order and AF order coexist as the doping density increases. For the overdoped region, the AF order is suppressed completely, and only SC order exists. The dome-shaped SC order is analogous to that in the hole-doped cuprates. Here, one may observe that the SC order appears at a doping of approximately \( x = 0.01 \). Then, the SC region is larger compared with the real material of electron-doped high-\( T_c \) superconductors. In fact, at

![Figure 1. The amplitudes of the SC and AF order parameters as a function of the doping density without the impurity.](image)
the mean-field level, the theoretically obtained SC region is generally larger because various fluctuations are neglected. It is expected that the ground state properties, such as the LDOS near the impurity, are qualitatively correct at the mean-field level.

In the presence of a point-like impurity, the possible resonance peaks generally appear at the nearest-neighbour site or next-nearest-neighbour site of the impurity. We have verified numerically that the results are qualitatively the same for these two sites for all of the parameters that we considered, except that the resonance peaks for the nearest-neighbour site are stronger. Thus, in the following presented results, we focus on the LDOS spectra at the nearest-neighbour site of the impurity. The doping densities are taken as 0, 0.1 and 0.2, which correspond to the pure AF state, the AF/SC coexisting state, and the pure SC state, respectively.

We first study the impurity effect in the pure AF state. The entire LDOS spectra with different impurity scattering potentials \( V_s \) and next-nearest-neighbour hopping constants \( t' \) are plotted in figure 2. Without the impurity \( V_s = 0 \), the bulk LDOS reaches zero at low energies, indicating that the system is fully gapped and that the parent compound is indeed insulating. For the case of \( t' = 0 \), as shown in figure 2(a), one sharp resonant bound state is observed in the presence of the impurity. As the impurity potential is positive, the resonance peak also appears at positive energy. The peak intensity decreases and the peak shifts to higher energy as the impurity potential increases. As the peak shifts to near the gap edge, the intensity of the resonance peak is small (for the case of \( V_s = 10 \)). When further increasing the impurity potentials, the resonance peak disappears completely (not presented here). The features of resonance peaks for negative potentials are similar to those for positive ones, except that they appear at negative energies. Such symmetric behaviour is due to the particle–hole symmetry for the case of \( t' = 0 \) and \( x = 0 \).

As the \( t' \) term is considered, the particle–hole symmetry of the normal state Hamiltonian is broken. Then, the symmetry of the bound states between negative and positive potentials is also broken, as shown in figures 2(b)–(d). Generally, the bound states are stronger for negative scattering potentials. Overall, however, the qualitative feature of the impurity effect does not change, i.e., there is only one in-gap bound state, with the peak shifting to the gap edge for the stronger impurity potential. For rather strong impurity potentials, the bound state disappears. We note that the gap magnitude is rather important for the impurity effect in the AF state. Based on self-consistent calculations, we found that the AF gap decreases as \( t' \) increases. Consequently, as \( t' \) becomes larger, the bound state will disappear for weaker potentials. Numerically, one can change the on-site interaction \( U \) to control the AF gap. We also found similar results when \( U \) is changed (not presented here), namely, the in-gap bound state disappears for smaller potentials if \( U \) is reduced.

The ground state of the AF state consists of an alternating series of spin-up and spin-down quasiparticles. The LDOS spectra \( \rho_{i\sigma} \) should depend on the dominant spin of the site \( i \). The spin-resolved LDOS spectra at the site \( i \) \([i = (17, 18)\) are presented in figure 3. At this site, the spin-up electronic state is occupied and the spin-down electronic state is nearly empty. As shown, the spin-up LDOS spectra are relatively strong at the negative energy, whereas they are significantly suppressed at the positive energy. For the spin-down quasiparticles, the LDOS spectra at the negative energy are suppressed and only positive spectra appear. In fact, in the pure AF state

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**Figure 2.** The LDOS spectra at the nearest-neighbour site of the impurity in the pure AF state \( (x = 0) \). From bottom to top, the impurity scattering potentials are \(-10, -5, -3, 0, +3, +5\), and \(+10\).
near the half-filled region, the spin-up electron density ($n_{\uparrow}$) equals the spin-down hole density ($1 - n_{\downarrow}$), and the energy for electrons/holes should be negative/positive. This particle–hole transformation picture can soundly explain the above numerical results. Note that the spin-resolved LDOS in the pure AF state is not presented in previous studies, and we expect that our numerical results can be verified by future experiments.

We now study the impurity effect in the AF/SC coexisting state. The LDOS spectra with different parameters are shown in figure 4. As shown, the impurity resonance peaks are robust and exist for all of the parameters that we considered. This is different from the case of the pure AF state, where the impurity state disappears for strong impurities. The resonance peaks appear in pairs that are lying symmetrically at the positive and negative energies. The intensities of the two peaks are significantly different, with one peak typically being rather weak and the other being strong. This result is also different from those of the pure AF state. In general, there is one
pair of resonance peaks for most of the parameters that we considered, whereas when $t'$ increases, one additional pair of resonance peaks may appear for weak positive impurity potentials, as shown in figures 4(c) and (d) ($t' = 0.2 V_i = +3$, and $t' = 0.25 V_i = +3, +5$). The existence of two pairs of in-gap resonance peaks was not reported in previous studies \[25–27\]. As $t'$ is large enough, the two peaks from one pair may be close to the Fermi energy, and occasionally, they may merge to one low-energy peak near the Fermi energy ($t' = 0.25, V_i = -5$).

Here, the positions and intensities of the resonance peaks clearly depend on $t'$. They are typically different for positive and negative scattering potentials. Interestingly, however, for rather strong impurity scattering potentials ($V_i = \pm 100$), the impurity states are qualitatively the same for different $t'$, i.e., the resonance peaks appear near the gap edge with the peak at the positive energy being much stronger. Furthermore, this result does not depend on the sign of the potentials.

The spin-resolved LDOS spectra in the coexisting state at site $i = (17, 18)$ are presented in figure 5. At this site, spin-up quasiparticles are dominant over spin-down quasiparticles. Impurity resonance peaks exist for both the spin-up LDOS and the spin-down LDOS spectra. Interestingly, for all of the parameters that we considered, significant imbalance exists for spin-up and spin-down spectra. As observed, the spin-down LDOS is strongly suppressed, and the entire LDOS is mainly contributed by the spin-up one. This feature can be used to detect the existence of AF order. In fact, for the pure SC state, the spin-down LDOS should equal the spin-down one from the symmetry analysis. Our numerical results suggest that the spin-resolved STM experiment may be a powerful tool for differentiating different states of electron-doped high-$T_c$ superconductors.

Let us turn to study the impurity effect in the pure SC state. The corresponding LDOS spectra are presented in figure 6. Similar to the cases of the coexisting state, the resonance peaks also appear in pairs in this case. Their strengths are weaker than those of the coexisting state. The resonance peaks disappear for rather weak potentials ($V_i \leq 3$, not presented here). Moreover, the positions of the resonance peaks also strongly depend on the parameters. In contrast to the cases of the coexisting state, even for a strong impurity, the resonance peaks in this case still depend on the value of $t'$. However, for a strong impurity, the resonance states are qualitatively the same for negative or positive potentials, and this result is similar to that of the coexisting state. One important feature that has attracted considerable attention is the number of in-gap peaks. It was concluded that the two in-gap peaks are always separated and that the merged resonance peak may not occur for the pure SC state. Thus, it was proposed that this feature can be used to differentiate the coexisting state and the pure SC state \[25\]. However, our results are significantly different from those in \[25\]. As shown, for the case of $t' = 0$, one in-gap zero energy peak is revealed for the strong impurity potentials ($V_i = \pm 100$). As $t'$ increases, two in-gap peaks were observed for strong potentials. The two peaks may indeed merge for some positive weak potential ($V_i = +5$). However, the impurity effects for positive potentials and negative potentials are different when the potential strengths are weak. For negative potentials, the intensities of the resonance peaks are significantly suppressed by the $t'$ term. The two peaks do not merge if a considerable $t'$ term is considered.

![Figure 5](image-url) The spin-resolved LDOS spectra at the nearest-neighbour site of the impurity (spin-up dominant site) in the AF/SC coexisting state ($x = 0.1$). From bottom to top, the impurity scattering potentials are $-100$, $-10$, $-5$, $-3$, $0$, $+3$, $+5$, $+10$, and $+100$.
In the presence of the pairing order parameter $\Delta$, the SC quasiparticle energy band is particle–hole symmetric, i.e., the eigenvalues of the BdG equations appear in pairs with $E$ and $-E$. Consequently, the impurity resonance peaks should also appear in pairs or merge to a single zero-energy resonance peak. Previously, similar results have also been presented in other families of superconductors [28, 32]. This result is rather useful and may help to identify the existence of the SC pairing of the system.

For rather strong potentials, as shown in figures 4 and 6 it appears that the resonance states depend weakly on the signs of the impurity potentials. This is also an interesting result, but note that it should not be considered to be a general conclusion. For the case of $t' = 0$ and $\mu \neq 0$, the normal state energy band is particle–hole asymmetric. Therefore, there is no apparent conclusion for the impurity effect with different signs of potentials. The impurity effect has also previously been studied in iron-based SC materials. Note that for this family of SC materials, the impurity resonance state strongly depends on the sign of the potentials, even for rather strong potentials [28].

It is insightful to compare our present results with those in hole-doped high-$T_c$ SC materials. For hole-doped SC compounds, the LDOS spectra at the nearest-neighbour site of the impurity with different parameters are plotted in [13]. To summarise, in hole-doped ones, the impurity resonance peak is generally close to the Fermi energy. When $t'$ is zero or small, two resonance peaks appear for weak potentials ($V_i = \pm 3$). The two peaks merge and only one zero energy peak is observed as the impurity potential increases ($V_i = \pm 5, \pm 10$). When $t'$ increases, the resonance peaks for negative potentials and positive potentials are different. For negative potentials, the impurity effect strongly depends on $t'$. For large $t'$, the two peaks are always separated, even for a strong potential. For positive potentials, the main results do not change qualitatively with different $t'$. For electron-doped materials, the results are qualitatively consistent with those of hole-doped materials when $t'$ is zero, as is presented in figure 4(a). However, as $t'$ increases, the properties of the impurity resonance states are notably significantly different for both weak and strong potentials. This result also indicates that the value of $t'$ is important for obtaining a qualitatively correct understanding of the impurity effect in high-$T_c$ superconductors.

Finally, we would like to clarify whether different states can be differentiated based on the impurity effect. Clearly, the spin–resolved LDOS is able to differentiate these three states. For the case of the entire LDOS spectra, the impurity effect in the AF state is different from that in the other two states. In the AF state, the position of the resonance peak monotonically changes with the impurity scattering potentials. Moreover, it is easily determined from the other two states according to the number of in-gap peaks. However, the differences between the coexisting state and the pure SC state are not clear. There are some weak features that may be verified further. Generally, the energies of the resonance peaks in the pure SC state are typically closer to the Fermi energy compared with those in the coexisting state. Moreover, significant differences exist for the intensities of the two resonance peaks in the coexisting state, namely, one resonance peak is rather strong and the other is quite weak.
For the pure SC state, the intensities are smaller but the intensities of the two peaks have the same order of magnitude. These features may help to distinguish different states in electron-doped SC materials.

4. Summary

In summary, we study systematically the impurity effect in electron-doped high-$T_c$ superconductors based on the BdG equations. The LDOS spectra in the pure AF state, the AF/SC mixture state, and the pure SC state are presented. In the pure AF state, only one resonance impurity peak exists for weak impurity potentials. This peak shifts to the gap edge as the impurity potential increases and finally disappears for a strong impurity. In the AF/SC coexisting state, the impurity resonance peaks appear in pairs, which lie symmetric at positive and negative energies. For larger next-nearest-neighbour hoping, the two peaks may merge for some potentials. For rather strong impurities, the impurity resonance peaks shift to near the gap edges. The spin-resolved LDOS spectra in these two states are also investigated and may be used to detect the existence of AF order. In the pure SC state, similar to the cases of the coexisting state, the resonance peaks also appear in pairs and may merge for some of the parameters. The differences between the impurity effect of the three states are discussed. We expect that the impurity effect could be used to detect different states of electron-doped high-$T_c$ superconductors.

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