Single nonmagnetic impurity resonance in FeSe-based 122-type superconductors as a probe for pairing symmetry

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received 30 November 2012; accepted in final form 13 February 2013
published online 14 March 2013

PACS 74.70.Xa – Pnictides and chalcogenides
PACS 74.62.En – Effects of disorder
PACS 74.20.Pq – Electronic structure calculations

Abstract – We study the effect of a single nonmagnetic impurity in A_yFe_{2-x}Se_2 (A = K, Rb, or Cs) superconductors by considering various pairing states based on a three-orbital model consistent with the photoemission experiments. The local density of states on and near the impurity site has been calculated by solving the Bogoliubov-de Gennes equations self-consistently. The impurity-induced in-gap bound states are found only for attractive impurity scattering potential, as in the cases of doping of Co or Ni, which is characterized by the strong particle-hole asymmetry, in the nodeless \( d_{x^2-y^2} \) wave pairing state. This property may be used to probe the pairing symmetry of FeSe-based 122-type superconductors.

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Introduction. – The FeSe-based 122-type A_yFe_{2-x}Se_2 (A = K, Rb, or Cs) high-\( T_c \) superconductors have been the focus of intensive attention due to their distinctive high transition temperatures (\( \sim 30 \text{K} \)) [1–4] and novel Fermi surface topology. Angle-resolved photoemission spectroscopy (ARPES) [5–9] and density functional theory (DFT) calculations [10–13] show that there is no hole pocket around the Γ-point of the Brillouin zone (BZ), and large electron pockets are observed around the \( M \)-point which is located at the corners of the folded BZ [5]. Effort has been made to investigate the pairing symmetry of the Fe-based superconductors. The popular \( s_{\pm} \) pairing symmetry in iron pnictide 1111-type superconductors in which the hole pockets are at the Γ-point, has been predicted by spin-fluctuation theory [14,15]. However, for FeSe-based 122-type superconductors, due to the absence of the hole pockets, nodeless superconducting (SC) gap can be originated from various pairing symmetries. Spin-fluctuation theory predicted \( d_{x^2-y^2} \) wave pairing state [16–19], while \( s \) wave pairing state was argued to be more favorable against strong disorder [20]. Moreover, a co-existence candidate of anisotropic \( s \) and \( d_{x^2-y^2} \) wave pairing symmetries has also been predicted [21]. These results reveal the competitive nature of the pairing state in these novel superconductors.

The response of a SC system to impurities can be a probe for the SC pairing symmetry [22]. The local electronic states can evidently be influenced by impurities. In a multi-band SC system, the SC order parameter may or may not be sensitive to the existence of impurity [23]. Doping of Co and Zn in iron pnictide 1111-type superconductors has been realized by several experimental groups [24–28]. Theoretically, the effects of impurity in iron pnictide superconductors have also been investigated intensively [29–37]. The calculated results of the \( T \)-matrix method based on a four-band model show the in-gap impurity resonance states [33] for \( s_{\pm} \) wave pairing symmetry, and results obtained by solving the Bogoliubov-de Gennes (BdG) equations in the framework of a detailed five-orbital model also demonstrate that the \( s_{\pm} \) wave pairing symmetry is characterized by a bound state in the vicinity of the Fermi level in the presence of a single nonmagnetic impurity [34]. However, for FeSe-based 122-type superconductors, the impurity resonance bound state, which is located away from the Fermi level, were obtained only in \( d_{x^2-y^2} \) wave pairing state [38].

In this work, we use self-consistent BdG equations to study the effect of a single nonmagnetic impurity in FeSe-based 122-type superconductors modeled by a three orbital Hamiltonian. The local density of states (LDOS) and the real-space SC order parameters are calculated. It has been reported that the effective on-site impurity potentials can be repulsive or attractive which is related to the energy difference between the impurity 3\( d \) levels and...
Fig. 1: (Color online) The Fermi surface in the extended BZ. The nodal lines of the gap function for anisotropic s and \(d_{x^2-y^2}\) wave pairing symmetry are plotted with green and red lines, respectively.

Fe 3d level for various impurity atoms. Realistic estimation of the impurity potential in iron pnictide superconductors predicts that the potential difference for Zn, Co, and Ni are negative, whereas for Mn it is positive [39]. Therefore both repulsively (positive) and attractive (negative) scattering potentials have been considered in our calculation which may simulate different dopants, such as Zn, Co, Ni, and Mn etc. Responses of isotropic s, anisotropic s, and \(d_{x^2-y^2}\) wave pairing states to impurity are examined, respectively.

Model and methodology. – We describe the SC system with a single nonmagnetic impurity by a three-orbital Hamiltonian

\[
H = H_0 + H_{\text{pair}} + H_{\text{imp}}
\]

and the hopping, pairing, and impurity terms read

\[
H_0 = \sum_{i,j,\alpha,\beta,\sigma} t^{ij}_\alpha \tilde{a}_{i\alpha\sigma} \tilde{a}_{j\beta\sigma} - \mu \sum_{i,\alpha,\sigma} \tilde{a}_{i\alpha\sigma}^\dagger \tilde{a}_{i\alpha\sigma},
\]

\[
H_{\text{pair}} = \sum_{i,j,\alpha,\beta} \left( \Delta^{ij}_{\alpha\beta} \tilde{a}_{i\alpha\sigma}^\dagger \tilde{a}_{j\beta\sigma} + \text{h.c.} \right),
\]

\[
H_{\text{imp}} = U_s \sum_{i,\alpha,\sigma} \tilde{a}_{i\alpha\sigma}^\dagger \tilde{a}_{i\alpha\sigma},
\]

where \(\tilde{a}_{i\alpha\sigma}^\dagger\) (\(\tilde{a}_{i\alpha\sigma}\)) denotes the creation (annihilation) operator of electrons with spin \(\sigma = \uparrow, \downarrow\) and orbital \(\alpha\) at site \(i\). \(t^{ij}_\alpha\) are the hopping integrals and \(\mu\) is the chemical potential. A single nonmagnetic impurity is located at site \(i\).

Results of DFT calculation demonstrate that the electronic structure in the vicinity of the Fermi level is dominated by \(d_{xz}\), \(d_{yz}\), and \(d_{xy}\) orbitals [13], therefore it is feasible to describe the band structure by introducing an effective three-orbital model [40]. The independent parameters of the hopping model (in unit: eV) are \(t^{11/22}_{ij} = 0.0\), \(t^{13}_{ij} = 0.4\), \(t^{11}_{i+\hat{x},j} = 0.05\), \(t^{11}_{i+\hat{x},j+\hat{y}} = 0.01\), \(t^{11}_{i+\hat{x}+\hat{y},j} = 0.02\), \(t^{13}_{i+\hat{x},j+\hat{y}} = 0.01\), \(t^{13}_{i+\hat{x}+\hat{y},j} = 0.01\), \(t^{13}_{i+\hat{x},j} = t^{13}_{i+\hat{x},j} = 0.2\), \(t^{13}_{i+\hat{x}+\hat{y},j} = t^{13}_{i+\hat{x}+\hat{y},j} = 0.1\), where \(\hat{x}(\hat{y})\) denote the unit vectors along \(x(y)\) directions of the lattice coordinate. Figure 1 shows the heavily electron-doped Fermi surface obtained with a chemical potential \(\mu = 0.312\) eV corresponding to a filling factor \(n = 4.23\) and it turns out that the bandwidth of the model is 2.83 eV. The SC gap function stemming from the mean-field decoupling of the pair scattering process \(V^{\alpha\beta}_{ij} \tilde{a}_{i\alpha\sigma}^\dagger \tilde{a}_{j\beta\sigma}^\dagger \)

is expressed as

\[
\Delta^{ij}_{\alpha\beta} = V^{\alpha\beta}_{ij} \langle a_{ij\beta\sigma} a_{ij\alpha\sigma} \rangle.
\]

The diagonal condition of the Hamiltonian is the BdG equation

\[
\sum_{j,\beta} \left( \frac{h^{\alpha\beta}_{ij}}{\Delta^{\alpha\beta}_{ij}} \Delta^{\alpha\beta}_{ij} - h^{\alpha\beta}_{ij} \right) \left( u^{\alpha\beta}_{n,j} \right) = \epsilon_n \left( u^{\alpha\beta}_{n,j} \right),
\]

where

\[
h^{\alpha\beta}_{ij} = t^{\alpha\beta}_{ij} - \mu \delta_{ij} \delta_{\alpha\beta} + U_s \delta_{ij} \delta_{\alpha\beta}
\]

and the gap equation is represented as

\[
\Delta^{\alpha\beta}_{ij} = -\frac{V^{\alpha\beta}_{ij}}{2} \sum_n \left( u^{\alpha\beta}_{n,i} v^{\alpha\beta}_{n,j} + u^{\alpha\beta}_{n,j} v^{\alpha\beta}_{n,i} \right) \tanh \left( \frac{\epsilon_n}{2k_B T} \right).
\]

Single static impurity in a uniform superconductor which manifests itself as a point-like imperfectation can be regarded as a localized orbital-independent on-site scattering potential \(U_s \delta_{R_i R_0}\) with the impurity at \(R_0\) in orbital representation, provided that the Coulomb interaction is screened at length scales comparable to the lattice spacing [22]. Both positive and negative scattering potential \(U_s\) are considered in our calculation, and by checking the results obtained from several different values, it has been found that \(U_s = \pm 6.0\) eV can be regarded as the unitary limit.

The absence of the hole pockets of the FeSe-based 122-type Fermi surface around the \(\Gamma\)-point eliminates the possibility of nodes. Calculation pertaining to the magnetic exchange couplings reveals that the leading pairing is originated from the intra-orbital pairing, whereas the inter-orbital components are found to be significantly small [40]. Consequently, the \(s\) and \(d_{x^2-y^2}\) wave pairing symmetries are considered for intra-orbital pairing only in order to investigate their responses to a single nonmagnetic impurity scattering. For isotropic \(s\) wave pairing,

\[
V^{\alpha\alpha}_{ij} = -g_0 \delta_{ij}
\]

for anisotropic \(s\) wave pairing,

\[
V^{\alpha\alpha}_{ij} = \frac{g_1}{4} \left( \delta_{i+\hat{x},j+\hat{y}} + \delta_{i+\hat{x},j} + \delta_{i+\hat{x}+\hat{y},j} + \delta_{i+\hat{x}+\hat{y},j} \right),
\]

and for \(d_{x^2-y^2}\) wave pairing,

\[
V^{\alpha\alpha}_{ij} = \frac{g_2}{2} \left( \delta_{i+\hat{x},j+\hat{y}} + \delta_{i+\hat{x}+\hat{y},j} + \delta_{i+\hat{x},j} + \delta_{i+\hat{x}+\hat{y},j} \right),
\]

where \(g_{0,1,2}\) are pairing amplitudes for each pairing symmetry. The pairing patterns in real space result in specific
Fig. 2: (Color online) The LDOS for the anisotropic s wave pairing state for repulsive scattering potential $U_s = 0.5$ eV (a), $U_s = 0.8$ eV (b), $U_s = 2.0$ eV (c), and $U_s = 6.0$ eV (d). LDOS for impurity, NN, and NNN sites are plotted in red (solid), green (dashed), and blue (dotted) lines, respectively. The spectrum of the clean system is also shown in black (dashed and dotted) line for comparison.

pairing symmetries of the gap function in the $k$-space as for the isotropic s wave channel $\Delta^{\alpha\alpha}(k) \sim \Delta_0$, for the anisotropic s wave channel $\Delta^{\alpha\alpha}(k) \sim \cos(k_x)\cos(k_y)$, and for the $d_{x^2-y^2}$ wave channel $\Delta^{\alpha\alpha}(k) \sim \cos(k_x) - \cos(k_y)$ in the extended BZ, respectively. The pairing amplitudes are taken to be $g_0 = 0.3$ eV, $g_1 = 1.0$ eV, and $g_2 = 0.5$ eV which guarantees that the SC coherence length $\xi \leq 4a$, where $a$ is the lattice constant.

The energy spectrum of the quasiparticle i.e., the LDOS at site $i$ is calculated via

$$\rho_i(\epsilon) = \frac{1}{N_{orb}} \sum_{n,\alpha} |u_{i\alpha}|^2 |\delta(\epsilon - \epsilon_n) + |v_{n\alpha}|^2 |\delta(\epsilon + \epsilon_n)|, \quad (10)$$

where the prefactor comes from taking the average of three orbitals. The Lorentzian smearing method is used to visualize the LDOS with a broadening width $\sigma = 0.001$. All the self-consistent calculations are performed on a $20 \times 20$ lattice with a periodic boundary condition at temperature $T = 0.1$ K, and the single impurity is located at the center of the lattice.

Results and discussion. – For the isotropic s wave pairing state, the existence of impurity does not change much of the superconducting properties. Similar results are also obtained in refs. [29,34], which demonstrates that there is no in-gap bound state for such a pairing symmetry, whereas the order parameter on the impurity site are suppressed evidently.

Results of the anisotropic $s$ pairing symmetry are shown in fig. 2 for repulsive scattering potentials and in fig. 3 for attractive cases, respectively. The SC coherence peak is located at $\pm 0.044$ eV, and the typical resonating states induced by the impurity appear for both cases at $\pm 0.028$ eV for $U_s = 0.5$ eV and $\pm 0.025$ eV for $U_s = -1.0$ eV, respectively. The resonance peaks move towards the gap-edge as the amplitude of the scattering potential increases for repulsive interaction, while for attractive cases, the resonating peaks maintain at the gap-edge for small value of scattering potential $U_s = -0.5$ eV, as shown in fig. 3(a). Additionally, it has been noticed that the resonating states for positive interaction $U_s = 0.5$ eV is very robust in comparison with other values of $U_s$. At unitary limit, the characteristics of the spectrum for both repulsive and attractive interaction tends to be identical since the electrons cannot hop to the impurity site, regardless of the detailed feature of the scattering interaction. We note that the resonating states within the SC gap, as compared with the clean cases, appear always in pairs which are located symmetrically with respect to the Fermi level. The magnitudes of the LDOS of the resonating states at $E = \pm 0.028(\pm 0.025)$ eV for $U_s = 0.5(-1.0)$ eV, for instance, may not be the same, but they are of the same order. Therefore, we may interpret them as the SC pairing states influenced by the impurity.

The response of $d_{x^2-y^2}$ wave pairing state to impurity scattering in cuprate superconductors has been investigated intensively, and the study of the impurity effects in superconductors has been considered as an effective method to reveal the pairing symmetry of the superconductivity [22]. In figs. 4 and 5, we show the LDOS for the $d_{x^2-y^2}$ wave pairing state for positive and negative scattering potentials, respectively. As we can see from the figures, the in-gap bound states are only found for

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states are observed when the scattering potentials are small enough as $|U_s| \leq 0.4$ eV, which is physically justified that the impurity-induced bound states would become small and vanish as the amplitude of scattering interaction decreases. Decomposed LDOS analysis demonstrates that the contribution of $d_{xy}$ orbital is larger than that of $d_{xz}$ and $d_{yz}$ orbitals which indicates the significance of the multi-orbital feature of Fe-based superconductors. In passing, we note that the single impurity-induced in-gap bound state, for the $d_{xy}$ wave pairing state, is found near the Fermi energy for a moderate scattering potential $U_s = -1.0$ eV. This is reminiscent of the cuprates, where the emergence of the impurity-induced bound states, as a result of the nodal $d_{x^2-y^2}$ wave pairing state, is characterized by its low-lying feature.

We now discuss the asymmetry of the impurity states between attractive and repulsive potentials. In a superconducting state, the quasiparticle at the Fermi surface has exact electron-hole symmetry in the sense it carries no net electric charge, $\langle |u(\vec{q})| \rangle = \langle |v(\vec{q})| \rangle$. Away from the Fermi surface, the quasiparticle is either more electron-like (outside the Fermi surface) or more hole-like (within the Fermi surface). In a usual superconducting state, the gap function is approximately symmetric with respect to outside or inside the Fermi surface. Therefore, quasiparticles outside or within the Fermi surface have similar energies, and there is an approximate electron-hole symmetry in responding to a charged impurity. Since a repulsive potential to an electron means an attractive potential to a hole, we expect an asymmetry in the impurity bound state between attractive and repulsive potentials with respect to an electron. This is what we usually also find in study of the impurity bound state. The situation in a FeSe-based superconductor is however, very different. As we can see from fig. 1, the gap $\Delta(\vec{k})$ vanishes along the zone diagonal, well outside the electron Fermi surfaces. Therefore, electron-like quasiparticles (outside the Fermi surface) contributes more to the impurity state than the hole-like quasiparticles (inside the Fermi surface), and there is lack of electron-hole symmetry in the electronic structure. Our results for existence of the bound impurity state for attractive potential but not for repulsive potential may be understood as the strong electron-hole asymmetry. Mathematically, the amplitude of the density of the impurity-induced bound states is determined by the Bogoliubov quasiparticle weights $|u_n^i|^2$ and $|v_n^i|^2$, and the asymmetry of LDOS of the bound states in fig. 5 demonstrates a strong violation of the particle-hole symmetry. We note that using $T$-matrix method, the impurity-induced bound states in (K,Tl)Fe$_2$Se$_2$ superconductors have been predicted by Zhu et al. [38] in the case of $d_{xy}$ pairing state. Our results, which are obtained from a microscopic orbital-featured Hamiltonian, are qualitatively similar to the findings in the previous work [41] except that additional information has been revealed that the emergence of the impurity-induced bound state requires an attractive on-site scattering interaction which
originates from the effective potential difference between the impurity-3d and Fe-3d $t_{2g}$ electrons.

In Fig. 6, we plot the distribution of the order parameter in real space at unitary limit of the impurity scattering. It shows a color mapping of the cross shaped $[22]$ suppression of the order parameters which occurs prominently along the NNN directions for anisotropic $s$ wave and NN directions for $d_{x^2-y^2}$ wave pairing state, respectively.

Additionally, the subtle mechanism of the substitution of Co and Ni for Fe remains a controversial question in Fe-based superconductors. The effective impurity potential induced by various dopants which can be ascribed to the difference of the on-site ionic potential, together with the modification of the Fermi surface caused by the rigid shift of the band structure, has been investigated from both theoretical and experimental perspective $[39,42,43]$. The isovalence of Co and Fe in the Ca(Fe$_{0.94}$Co$_{0.06}$)$_2$As$_2$ compound has been pointed out and a binding energy shift (0.25 eV) has also been observed, which reveal the complexity of the impurity nature of Co $[43]$. Inspired by this finding, one may anticipate that the doping of Ni in iron pnictide or chalcogenide superconductors may be another promising alternative since the effective impurity potential, as reported by Nakamura et al. $[39]$, is higher than that of Co. The impurity-induced bound states observed in our calculations in the state of $d_{x^2-y^2}$ wave pairing when the scattering potential is within the range $U_s = -0.5 \div -6.0$ eV may simulate the cases of Ni and Co doping in FeSe-based 122-type superconductors.

In summary, using a three-orbital model, we present a comprehensive investigation of the effects of a single nonmagnetic impurity in $A_2$Fe$_{2-y}$Se$_2$ ($A = $ K, Rb, or Cs) superconductors by means of the BdG theory. The in-gap bound states have been found for $d_{x^2-y^2}$ wave pairing state. For the anisotropic $s$ wave pairing state, the observed resonating states are typically SC pairing states influenced by impurity. The locations of the bound states for $d_{x^2-y^2}$ pairing symmetry, moving towards the Fermi energy from the gap-edge as the amplitude of the scattering potential increases from 0.5 to 1.0 (eV), appear uniquely for attractive interaction. Due to the absence of the hole pocket, strong violation of the electron-hole symmetry occurs, which results in that no impurity-induced bound state emerges for repulsive scattering interaction. Therefore, distinguishable responses to a single nonmagnetic impurity, in terms of LDOS on and near the impurity site, would be an approach to examine the pairing symmetries of FeSe-based 122-type superconductors.

We acknowledge financial support from Hong Kong RGC HKU 706809 and NSFC 11274269.

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