In-gap Bound States Induced by Interstitial Fe Impurities in Iron-based Superconductors

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Based on a two-orbit four-band tight binding model, we investigate the low-lying electronic states around the interstitial excess Fe ions in the iron-based superconductors by using T-matrix approach. It is shown that the local density of states at the interstitial Fe impurity (IFI) possesses a strong resonance inside the gap, which seems to be insensitive to the doping and the pairing symmetry in the Fe-Fe plane, while a single or two resonances appear at the nearest neighboring (NN) Fe sites. The location and height of the resonance peaks only depend on the hopping $t$ and the pairing parameter $\Delta_I$ between the IFI and the NN Fe sites. These in-gap resonances are originated in the Andreev’s bound states due to the quasiparticle tunneling through the IFI, leading to the change of the magnitude of the superconducting order parameter. When both $t$ and $\Delta_I$ are small, this robust zero-energy bound state near the IFI is consistent with recent scanning tunneling microscopy observations.

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The discovery of different families of the iron-based superconductors provided us a new platform to study high temperature superconductivity [1-6]. It has been reported that the superconducting transition temperature $T_c$ can reach as high as 55K [2]. Similar to the cuprate superconductors, the iron-based superconductors also have a layer structure and the superconductivity comes from the Cooper pairs in the Fe-Fe plane, while a single or two resonances appear at the nearest neighboring (NN) Fe sites. The location and height of the resonance peaks only depend on the hopping $t$ and the pairing parameter $\Delta_I$ between the IFI and the NN Fe sites. These in-gap resonances are originated in the Andreev’s bound states due to the quasiparticle tunneling through the IFI, leading to the change of the magnitude of the superconducting order parameter. When both $t$ and $\Delta_I$ are small, this robust zero-energy bound state near the IFI is consistent with recent scanning tunneling microscopy observations.

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It is known that the impurity effects play a crucial role in exploring superconductivity [21]. The strong zero-energy bound state (ZBS) at the Zu ion and the fourfold symmetric electronic states around the single impurity, observed by scanning tunneling microscopy (STM) [22], demonstrate that the superconducting order parameter in the cuprates has a d-wave symmetry. The in-gap resonances induced by a nonmagnetic impurity was also used to confirm the $s_{++}$ pairing symmetry in the iron-based superconductors [18]. It is clear that these resonance peaks are originated in the Andreev’s bound states due to the quasiparticle scattering between the Fermi surfaces or parts of the Fermi surface with opposite phases of the superconducting order parameter.

Very recently, Yin et al. also used STM to study the electronic states near the interstitial excess Fe ions in the iron-based superconductor Fe(Fe,Se) [23]. The as-grown Fe(Fe,Se) single crystals usually contain a large amount of excess Fe ions situated randomly at the interstitial

FIG. 1: (Color online) Schematic lattice structure of the Fe-As/Se/Te layers with each unit cell containing two Fe (A and B) and two As/Se/Te (A and B) ions. The As/Se/Te ions A and B are located just below and above the center of each face of the Fe square lattice, respectively. Here, $t_1$ is the nearest neighboring (NN) hopping between the same orbitals of the IFI and the NN Fe sites. $t_2$ and $t_3$ are the next nearest neighboring hoppings between the same orbitals mediated by the As/Se/Te ions B and A, respectively. $t_4$ is the nearest neighboring hopping between the different orbitals. The IFI is situated at the symmetric position of As/Se/Te ion about the Fe-Fe plane. $t$ and $\Delta_I$ are the hopping and the pairing parameters between the same orbitals of the IFI and the NN Fe sites, respectively.
sites, which are the symmetric points of the Te/Se ions about the Fe-Fe plane (see Fig. 1). They found that the differential conductance at the interstitial Fe impurity (IFI) also has a strong ZBS. The height of this resonance decays rapidly with the distance from the IFI and vanishes at about 10 Å. It is especially surprising that the ZBS at the IFI is not affected by a magnetic field up to 8 Tesla. Such a ZBS induced by out of the superconducting plane impurities was never reported before, and its origin is unclear up to now.

In this work, we provide an explanation for the interesting observation of the robust ZBS. Because the big family of the iron-based superconductors has a similar energy band structure, here we employ the two-orbit four-band tight binding model presented in Ref. [18] to explore the origin of the ZBS near the IFI. We remember that this energy band structure was constructed by starting two degenerate orbitals $d_{xz}$ and $d_{yz}$ per Fe ion and two Fe ions in each unit cell, and fitted well the ARPES observations. Because the asymmetry of the above and below As/Se/Te ions in the Fe-As/Se/Te surface layer was taken into account, the model naturally explained several important STM observations, e.g. in-gap impurity resonances [18,24], the bound state at negative energy in the vortex core [25,26], the domain walls [27-30], etc., and especially repeated the phase diagram measured by nuclear magnetic resonance and neutron scattering experiments [31-33].

It is obvious that the IFI is different from the nonmagnetic, magnetic, and Kondo impurities in the superconducting plane. Because Fe ion is assumed to possess two electron channels, the electrons in the Fe-Fe plane can tunnel through the IFI. Now we know that superconductivity in the iron-based superconductors originates from electron pairing between the next nearest neighboring Fe sites. So only one electron of a Cooper pair can arrive at the IFI in the superconducting state. Therefore, the Hamiltonian describing the IFI in the iron-based superconductors has the form

$$H = H_0 + H_{BCS}$$

$$-t \sum_{\alpha \sigma} \{ c_{\alpha \sigma}^+ \{ c_{\alpha_0,000\sigma} + c_{B_0,000\sigma} + c_{\alpha_0,100\sigma} + c_{B_0,100\sigma} \} + h.c. \}$$

$$+ \Delta_I \sum_{\alpha} \{ c_{\alpha \uparrow}^+ \{ c_{\alpha_{\uparrow},000\downarrow} + c_{\alpha_{\downarrow},000\uparrow} + c_{\alpha_{\uparrow},100\downarrow} + c_{\alpha_{\downarrow},100\uparrow} \}$$

$$+ c_{\alpha \downarrow}^+ \{ c_{\alpha_{\downarrow},000\uparrow} + c_{\alpha_{\uparrow},000\downarrow} + c_{\alpha_{\downarrow},100\uparrow} + c_{\alpha_{\uparrow},100\downarrow} \} + h.c. \}, \quad (1)$$

where $H_0$ is the four-band four-orbit tight binding model proposed in Ref. [18], $H_{BCS}$ is the mean field BCS pairing Hamiltonian in the Fe-Fe plane, $c_{A(B)\alpha,ij\sigma}^+$ $(c_{A(B)\alpha,ij\sigma})$ creates (destroys) an $\alpha$ electron with spin $\sigma$ (=$\uparrow$ or $\downarrow$) in the unit cell $\{ i, j \}$ of the sublattice $A$ ($B$), $\alpha = 0$($1$) represents the degenerate orbital $d_{xz}$ ($d_{yz}$), and $t$ and $\Delta_I$ are the hopping and pairing parameters between the same orbitals of the IFI and the nearest neighboring (NN) Fe sites, respectively.

We note that the sub-Hamiltonian $H_0 + H_{BCS}$ can be diagonalized by suitable transformations. Introducing first the Fourier transformation $c_{A(B)\alpha,\pm \sigma} = \sum_{k, \tau, \vec{r}} c_{A(B)\alpha,\tau,0} e^{ik_{xy} \delta \vec{r}}$ with $N$ the number of unit cells and the canonical transformations $c_{A\alpha, \pm \sigma} = \sum_{uv} (-1)^{\nu} a_{u,v,k} \phi_{u,v,k}$ with $u, v = 0$ and 1, $a_{u,v,k} = \frac{1}{2} (c_{A, u,v,k} - \epsilon_{B,k})$ and $(-1)^u \sqrt{2} (c_{A, u,v,k} - \epsilon_{B,k})^2 + \epsilon_{T,k} + \epsilon_{T,k}^*$, $c_{A, u,v,k} = -2(t_2 \cos k_x + t_3 \cos k_y), \epsilon_{B,k} = -(t_2 \cos k_y + t_3 \cos k_x), \epsilon_{T,k} = -t_1 [1 + e^{ik_x} + e^{ik_y} + e^{-ik_x}], \epsilon_{T,k}^* = -t_1 [1 + e^{-ik_x} + e^{-ik_y} + e^{ik_x}]$, and $\Gamma_{u,v,k} = \sqrt{2} (c_{A, u,v,k} + \epsilon_{B,k} e^{ik_x}), \epsilon_{T,k}$, and then the Bogoliubov transformations $\phi_{u,v,k} = \sum_{\alpha=0,1} (-1)^\nu \xi_{u,v,k} \psi_{u,v,k}$ and $\phi_{u,v,k}^* = \sum_{\alpha=0,1} (-1)^\nu \xi_{u,v,k}^* \psi_{u,v,k}^*$ with constants $\xi_{u,v,k}$ to be determined below, the total Hamiltonian $H$ finally becomes

$$H = \sum_{\nu \alpha} (-1)^\nu \Omega_{\nu \alpha} \psi_{\nu \alpha}^+ \psi_{\nu \alpha}$$

$$+ \frac{1}{\sqrt{N}} \sum_{\nu \alpha \sigma \tau} (M_{\nu \alpha \sigma \tau} c_{\nu \alpha \sigma}^+ \psi_{\nu \tau \sigma} + N_{\nu \alpha \sigma \tau} c_{\nu \alpha \tau}^+ \psi_{\nu \tau \sigma}^+ + h.c.), \quad (2)$$

where $\Omega_{\nu \alpha} = \sqrt{(E_{\nu \alpha} - \mu)^2 + \Delta_{\nu \alpha}^2}, \quad E_{\nu \alpha} = \frac{1}{2} (\epsilon_{A, k} + \epsilon_{B, k}) - 2(-1)^\nu t_2 \cos k_x + \cos k_y + \epsilon_{T,k} + \epsilon_{T,k}^*, \quad M_{\nu \alpha \sigma \tau} = (-1)^\nu \Xi_{\nu \alpha \tau} \{ (-1)^\nu \xi_{\nu \alpha \tau} \psi_{\nu \alpha \tau} + \Delta_I \xi_{\nu \alpha \tau} \psi_{\nu \alpha \tau} \}, \quad N_{\nu \alpha \sigma \tau} = (-1)^\nu \Xi_{\nu \alpha \tau} \{ \Xi_{\nu \alpha \tau} \psi_{\nu \alpha \tau}^+ + (-1)^\nu \Delta_I \xi_{\nu \alpha \tau} \psi_{\nu \alpha \tau} \}, \quad \Xi_{\nu \alpha \tau} = [1 + e^{ik_x}] a_{\nu \alpha \tau,0,k} + [1 + e^{-ik_x}] e^{ik_x} \Gamma_{\nu \alpha \tau,0,k} \xi_{\nu \alpha \tau} \psi_{\nu \alpha \tau} = \Delta_{\nu \alpha} \psi_{\nu \alpha \tau}^+ / (2 \Omega_{\nu \alpha}), \quad \xi_{\nu \alpha \tau}^2 = \frac{1}{2} [1 + (-1)^\nu (E_{\nu \alpha} - \mu) / \Omega_{\nu \alpha}].$ Here, $\mu$ is the chemical potential to be determined by doping and $\Delta_{\nu \alpha}$ is the superconducting order parameter in the Fe-Fe plane. We can see from the Hamiltonian (2) that the hopping $t$ may form new electron-fermion pairs while the pairing parameter $\Delta_I$ can also induce a hopping term. In other words, new quasiparticles are excited if electrons tunnel through the IFI. It is expected that such a novel mechanism produces the ZBS observed by the STM [23].

The Hamiltonian $H$ in Eq. (2) has a quadratic form of the fermionic operators and can be exactly solved by using the T-matrix approach [18,21]. The analytic expression of the LDOS near the IFI has been obtained at different bias voltages. In our calculations, we have used the energy band parameters: $t_1 = 0.5, t_2 = 0.2, t_3 = -1.0$, and $t_4 = 0.02$. We note that the iron-based superconductor Fe(Se,Te) in the STM experiment [23] has a small gap of about 1.5 meV. In order to clearly observe the change of the impurity resonance peaks with the bias
voltage, here we employ a large gap, i.e. 5.8 meV, in the electron-doped BaFe$_2$-xCoxAs$_2$ [34,35], where the excess Fe or Co ion is also regarded as an IFI. In Fig. 2, we plot the LDOS at the IFI as a function of the bias voltage eV under different $t$ and $\Delta_I$ for the $s_{+-}$ pairing symmetry at the chemical potential $\mu = -0.54$, where there are two Fermi surface sheets around $\Gamma$ point. Obviously, when $t$ or $\Delta_I$ is small, i.e. $<\sim 3$ meV, the LDOS has a strong resonance peak at zero energy, and the superconducting coherence peaks do not show up. With increasing $t$ or $\Delta_I$, the sharp zero energy resonance peak moves toward positive or negative energy, respectively, and the superconducting coherence peaks appear at the symmetric bias voltages in Fig. 2(a) and (b). The height of the coherence peak at the positive energy is higher (lower) than that at the negative energy for the parameter $t$ ($\Delta_I$). We note that when $t <\sim 4$ meV and $\Delta_I = 0$ meV, where the coherence peak at the negative energy disappears, the LDOS at the IFI has a single- or double-peak structure at the positive energies, very similar to the STM observations in the black regions of the superconducting BaFe$_2$-xCoxAs$_2$ sample [35]. When $t = \Delta_I = 3$ and 5 meV, the LDOS possesses the strong ZBS and the symmetric coherence peaks, shown in Fig. 2(c). However, the superconducting energy gap at the IFI is smaller that in the bulk, i.e. $\Delta_0 = 5.8$ meV, and becomes larger if $t$ or $\Delta_I$ increases. When $t$ is large enough to neglect $\Delta_I$, the superconducting energy gap at the IFI is equal to $\Delta_0$, and there is no in-gap bound state in Fig. 2(d).

Fig. 3 shows the LDOS at the NN Fe sites of the IFI for the $s_{+-}$ pairing symmetry under $\mu = -0.54$. When $t(\Delta_I) \sim 2$ meV and $\Delta_I(t) = 0$ meV, there is a ZBS appeared in the LDOS (see Fig. 3(a) and (b)). With increasing $t$ or $\Delta_I$, the single resonance splits into two peaks at symmetric energies. The resonance peak at positive energy has higher height than that at negative energy. It is interesting that the curves of the LDOS in Fig. 3(a) are same with those in Fig. 3(b) if $t$ and $\Delta_I$ are replaced each other. In other words, $t$ and $\Delta_I$ play the same role for the LDOS at the NN Fe sites of the IFI. This is the result that the Cooper pairs in the Fe-Fe plane tunnel through the IFI. We note that when $t = \Delta_I$, there is always a ZBS. If $t = \Delta_I$ is large, a strong resonance peak shows up at positive bias voltages in Fig. 3(c). However, for $t >> \Delta_I$, the in-gap resonances move outside of the superconducting energy gap (see Fig. 3(d)).

In order to understand the variation of the in-gap bound states with the doping, we plot the LDOS curves near the IFI for the $s_{+-}$ pairing symmetry under $\mu = -0.3$ and -0.45, where there is no Fermi surface sheet and one Fermi surface sheet around $\Gamma$ point, respectively, in Fig. 4. Obviously, in both cases, the LDOS at the IFI in Fig. 4(a) and (b) has a sharp zero energy resonance, and the superconducting coherence peaks are completely suppressed when $t = \Delta_I$. Meanwhile, there is only a ZBS at the NN Fe sites of the IFI in Fig. 4(c) and (d). The larger the parameter $t = \Delta_I$, the higher the zero energy resonance peak.

Now we investigate the low-lying electronic states induced by the IFI under different pairing symmetry in the bulk. In Fig. 5, we present the LDOS near the IFI at different physical parameters for the $s_{++}$ pairing symmetry. After comparing Fig. 5 with Fig. 2(c), Fig. 3(c), and Fig. 4, we find that the LDOS curves for the $s_{++}$ pairing symmetry are identical with those for the $s_{+-}$ pairing symmetry in the presence of the same physical
The nearest neighboring Fe sites in (c) and (d) as a function of the bias voltage eV under different $t$ and $\Delta_I$, for the $s_{++}$ pairing symmetry $\Delta_{\alpha \mathbf{k}} = \frac{1}{2}\Delta_0(\cos k_x + \cos k_y)$ with $\Delta_0 = 5.8$ meV.

In summary, we have explored the impact of the IFI on the electronic states in the iron-based superconductors. This IFI is dealt as two electron channels with the orbital index $\alpha$, which can also break the Cooper pairs when electrons tunnel through it. It is undoubted that re-forming new Cooper pairs with different magnitudes of the superconducting order parameter produces the in-gap resonances, which are determined by $t$ and $\Delta_I$ and are independent of the pairing symmetry in the bulk. This implies that the resonance peaks induced by the IFI are not affected by a magnetic field. Obviously, the origin of these in-gap bound states is due to the Andreev reflection with the change of the magnitude rather than the phase of the superconducting order parameter, which is never reported in the superconductivity literature. We note that when both $t$ and $\Delta_I$ are small, the LDOS near the IFI always has a single resonance peak at zero bias voltage, which is also irrelevant to the doping. Such a robust ZBS is consistent with recent STM observations in the iron-based superconductor Fe(Te,Se) [23].

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