Spin-polarized zero-bias peak from a single magnetic impurity at an s-wave superconductor: first-principles study

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Magnetic impurities at surfaces of superconductors can induce bound states referred to as Yu-Shiba-Rusinov (YSR) states within superconducting gaps. Understanding of YSR states with spin-orbit coupling (SOC) plays a pivotal role in studies of Majorana zero modes. Spin polarization of a zero-bias peak (ZBP) is used to determine its topological nature. Here we investigate the YSR states of single magnetic impurities at the surface of Pb using the fully relativistic first-principles simulations including band structure of Pb and five 3d orbitals of the impurity in the superconducting state. We show that for single Fe and Co impurities, strong SOC can induce a ZBP with rotation of the impurity magnetic moment and that the ZBP has large spin polarization in contrast to effective model studies. Conditions for a ZBP from a single magnetic impurity are discussed. Our results are relevant to longer atomic chains considering their canting and noncollinear magnetism.

Introduction

When magnetic impurities are present at surfaces of superconductors, quasiparticle excitations can appear within superconducting (SC) gaps due to exchange coupling between the impurity magnetic moments and the conduction electron spins. These excitations referred to as Yu-Shiba-Rusinov (YSR) states [1–3] have drawn lots of attention due to ongoing search for Majorana zero-energy modes (MZMs) [4–6] in long ferromagnetic atomic chains at s-wave superconductors with strong spin-orbit coupling (SOC) [7–22]. Magnetic properties of adatoms at superconductors were shown to be measured using YSR states in scanning tunneling microscopy/spectroscopy (STM/S) with much higher resolution [23]. YSR states can be also used to understand pairing symmetries [24–27]. So far, YSR states have been mostly studied using effective models [1–3, 11, 12, 14–17] based on single orbitals without realistic band structures and/or spin-orbit coupling (SOC) of SC substrates. In long ferromagnetic atomic chains, zero-energy bound states, i.e. zero-bias peaks (ZBPs), arising from the ends of the chains are interpreted as topological MZMs when they have particle-hole symmetry and significant spin polarization, while ZBPs with zero spin polarization are considered to be topologically trivial [13, 15, 16]. For long Fe atomic chains on SC Pb, a spin-polarized ZBP was experimentally observed only at the ends [12, 14–17], whereas that was not the case for long Co chains [18]. Single interstitial Fe impurities at SC Fe(Te,Se) revealed zero-energy bound states [22] without an external magnetic field, and their origins are under active study [38, 39]. Given the intriguing results, first-principles studies of YSR states in the presence of SOC would shed light into the search for MZMs in a wider range of systems.

As a first step toward achieving the goal, we study the YSR states of a single Fe, Co, or Mn magnetic impurity adsorbed on SC Pb, using first-principles simulations in the SC state. With strong SOC in Pb, we find that the YSR states are greatly affected by the rotation of the Fe or Co moment and that even a ZBP with large (normalized) spin polarization can occur at certain directions, although effective models [13, 15, 16] suggest zero normalized spin polarization for trivial ZBPs. Our results clearly show new important features arising from strong SOC when realistic band structure and all 3d orbitals are considered.

Methods

We simulate the normal state of Pb using fully the relativistic screened Korringa-Kohn-Rostoker (SKKR) Green’s function method [26] within density-functional theory (DFT). We employ the embedded cluster method [27] self-consistently within the SKKR formalism to a single Fe/Co/Mn magnetic impurity at the surface of the semi-infinite Pb(110) slab. Assuming a s-wave effective pairing potential, we solve the Dirac-Bogoliubov-de Gennes (DBdG) equations for the self-consistently obtained normal-state heterostructure [38, 39]. We set the SC gap Δ of Pb (magnetic atom) to be the experimental value, 1.36 meV [40] (zero). For method details, refer to Ref. [41] and the Supplemental Material (SM).

Fe impurity on Pb(110)

In the normal state, for an Fe impurity on Pb, the Fe spin-up density of states (DOS) is fully occupied and the Fermi level EF crosses slightly below the spin-down DOS peak [Fig. 1(c)]. Thus, there is large Fe spin-down DOS at EF, while the Fe spin-up states contribute very little at EF. The Fe DOS spectra are broadened due to significant hybridization between the Fe impurity and the Pb substrate. The calculated spin and orbital moments are listed in Table I. The mag-
FIG. 1. (a) Fe electron part of the LDOS (sum of spin-up and spin-down) as a function of $\theta$ (angle of the Fe moment) in the $xz$ plane with SOC in the SC state. Only the bottom plot is obtained without SOC. (b) Fe electron LDOS (sum of spin-up and spin-down) as a function of $\phi$ in the $xy$ plane with SOC in the SC state. In (a) and (b), the plots (zero energy: $E_F$) are vertically shifted for clarity and the QPT angles are shown as red. (c) Normal-state Fe spin-up and spin-down DOS with SOC (dashed line: $E_F$). The $x$ ($y$) axis is along the $[\overline{1}10]$ ([001]) direction. The $z$ axis is normal to the surface. The coordinates for the orbital decomposition shown in (a) and (b) do not change with the moment rotation. (d) Total Fe LDOS from electron and hole parts with and without SOC. (e) Schematic diagram of merging of the deepest spin-down YSR pair at $E_F$ and swapping as the moment rotates, and (f) corresponding orbital characters in each case where electron (solid), hole (dashed), spin-up (blue), spin-down (red). Line thickness and length in (f) are proportional to the LDOS magnitude. In (a), (b), and (f) corresponding $d$ orbitals are indicated.

netic exchange energy is obtained from the difference between the Fe spin-up DOS peak and spin-down DOS peak energies (Table I).

Let us first discuss the local density of states (LDOS) in the SC state without SOC. The calculated total Fe LDOS from electron and hole parts is symmetric with respect to $E_F$ due to particle-hole symmetry, as shown in the bottom panel of Fig. 1(d), where the Fe moment points normal to the surface, i.e., along the $z$ axis. We confirm that without SOC, the LDOS does not depend on the Fe moment direction. We henceforth present only electron part of the impurity LDOS unless specified otherwise. As shown in the bottom plot of Fig. 1(a), we find five pairs of electron Fe LDOS peaks at $E/\Delta = \pm 0.22$, $\pm 0.41$, $\pm 0.69$, $\pm 0.77$, and $\pm 0.94$, where only one of each pair is dominant. The dominant peaks are all spin-down polarized except for the last pair, while the weak peaks are spin-up polarized (Fig. S1 in the SM). (The peak at $-0.94\Delta$ and the weak peaks are visible in Fig. S1.) The YSR peaks at $-0.22\Delta$ and $0.41\Delta$ originate from $d_{xy}$ and $d_{xz}$ orbitals, respectively, while the peaks at $0.69\Delta$ and $0.77\Delta$ arise from $d_{xz}$ and $d_{x^2-y^2}$ orbitals, respectively. The peak at $-0.94\Delta$ originate from $s$, $d_{xz}$, and $d_{x^2-y^2}$ orbitals.

| Material   | Spin moment ($\mu_B$) | Orbital moment ($\mu_B$) | Exchange energy (Ry) | $xz$-plane rotation | $xy$-plane rotation |
|------------|-----------------------|--------------------------|----------------------|---------------------|---------------------|
| Fe/Pb(110) | 3.518                 | 0.906                    | 0.205                | ZBP (1)             | No ZBP |
| Co/Pb(110) | 2.183                 | 1.215                    | 0.145                | ZBP (2)             | No ZBP |
| Mn/Pb(110) | 4.812                 | 0.027                    | 0.275                | No ZBP              | No ZBP |

Now we turn on SOC in the Fe impurity and the SC substrate, and we rotate the Fe moment with angle $\theta$ from the $z$ axis in the $xz$ plane and with angle $\phi$ from the $x$
axis in the $xy$ plane. The $x$ ($y$) axis is along the [110] ([001]) direction of Pb. Here the $x$, $y$, and $z$ axes indicate global coordinates where the $z$ axis is always normal to the surface despite the Fe moment rotation. Figure 1(a) and (b) show the electron part (sum of spin-up and spin-down) of the LDOS spectra as a function of $\theta$ and $\phi$, respectively (see the top panel of Fig. 1(d) for the total LDOS with SOC). For orbital decomposition we use the global coordinates, while for spin polarization, the total electron LDOS is decomposed into parallel (spin-up) and antiparallel (spin-down) components of the rotating Fe moment direction. Due to the two mirror symmetry planes, $1/4$ of the $xz$ plane and $xz$ plane suffices to study the effect of moment rotation. The LDOS spectra with SOC greatly differ from that without SOC. With SOC, the energies and characters of YSR pairs change a lot as the Fe moment rotates. SOC allows mixing of different magnetic quantum numbers, $m_l$, even for the Fe moment normal to the surface. With $\theta = 0$, the deepest YSR pair appears at $-0.5\Delta$ and $+0.5\Delta$ arising from $\{d_{xy}, d_{x^2-y^2}\}$ and $\{d_{yz}, d_{xz}, d_{z^2}\}$, respectively. When the moment points along the $x$ axis, the deepest YSR pair occurs at $-0.01\Delta$ and $+0.01\Delta$ originating from $\{d_{xy}\}$ and $\{d_{yz}, d_{xz}, d_{z^2-y^2}\}$, respectively. As the moment direction becomes closer to the $y$ axis, the deepest YSR pair is not well isolated from the other YSR states and two deep YSR pairs start to hybridize.

Interestingly, with SOC, in most cases, each electron part of the YSR pair within $\pm 0.5\Delta$ has comparable spin-down DOS at both positive and negative energies (Figs. 2(a) and S2). Suppose that without SOC, the $\{e, \downarrow; h, \uparrow\}$ component of a $d$ orbital contributes to the positive-energy YSR state. Strong SOC like Pb allows significant spin mixing, resulting in a significant contribution of the $\{e, \uparrow; h, \downarrow\}$ component to the positive-energy YSR state. Particle-hole symmetry dictates that this component is equivalent to $\{e, \downarrow; h, \uparrow\}$ at the negative-energy YSR state, such that a large (small) spin-down LDOS peak at the positive (negative) energy illustrated in the leftmost scheme of Fig. 1(e) appears.

Importantly, we observe that a deepest YSR pair (with substantial spin-down DOS at positive and negative energies) crosses $E_F$, or equivalently forms a ZBP, as a function of $\theta$ and $\phi$. For the $xz$-plane rotation, as $\theta$ increases, the positive-energy and negative-energy peaks of the pair start to merge near $\theta = 85^\circ$ and then they are swapped [Fig. 1(a)]. The crossing and swapping of the peaks are schematically shown in Fig. 1(e) and (f). For the $xy$-plane rotation, a ZPB is formed near $\phi = 80^\circ$ [Fig. 1(b)]. When the two peaks of the pair share the same $m_l$ values, they are likely to merge at $E_F$. For example, at $\theta = 80^\circ$, $d_{xy}$ orbital at the negative energy and $d_{z^2}$ orbital at the positive energy have $m_l = \pm 2$ components.

This YSR pair crossing $E_F$ is similar to a quantum phase transition (QPT) expected from SOC-free effective models [24, 30, 42–44]. In these models, when an exchange coupling between the impurity spin and conduction electron spin exceeds a critical value (i.e., strong coupling regime), the spin-unpolarized SC state becomes unstable such that the expectation value of the $z$ component of conduction electron spin at the impurity site changes to 1/2. The case that the exchange coupling is less than the critical value is referred to as weak coupling regime. At the critical exchange coupling, the YSR state appears at $E_F$, i.e., ZBP, with equal contributions from electron and hole parts. The QPT was observed for magnetic impurities or molecules [19, 43, 45–47]. Our scenario qualitatively differs from them since the ZBP in our case is induced by the rotation of the impurity moment. The QPT or ZBP induced by the moment rotation in the presence of SOC has not been studied for realistic or experimental systems, although there is an $l = 1$ effective-model study [48]. The conditions for a ZBP from a single magnetic impurity are discussed later.

![Figure 2](image-url)
as well as at both positive and negative energies of the deepest YSR pair except for near φ = 90° (Figs. 2a) and S2). This trend of spin polarization is also found for the hole part of the LDOS (Fig. S3). Note that spin projections can be experimentally measured even in the presence of SOC [15, 16, 49, 50]. We normalize the spin-polarized SC-state LDOS (ρd,ρu) over normal-state spin-polarized LDOS (ρd,N,ρu,N), in order to provide relevance to STM/S experiments and to compare with effective models [13]. The conductance difference between spin-down and spin-up STM tip polarizations is proportional to a difference between the normalized spin-down and spin-up electron LDOS, Δρ (= ρd/N − ρu/N) [13]. At θ = 80° the normalized spin-up (spin-down) deepest YSR state appears at the negative (positive) energy, while at θ = 90° the normalized spin polarization is reversed [Fig. 2b]. With strong SOC like Pb, there is a substantial normalized spin-down contribution even when the normalized spin-up LDOS is dominant, in contrast to the cases of weak SOC and without SOC (Fig. S4). When the ZBP appears at θ = 85°, we find large normalized spin polarization. Overall, Δρ shows complex dependencies on energy and rotation angles (θ, φ) [Figs. 2c, S5].

FIG. 3. (a) Co electron (sum of spin-up and spin-down) LDOS as a function of θ with SOC in the SC state. Only the bottom plot is obtained without SOC. (b) Normal-state Co spin-up and spin-down DOS with SOC (dashed line: EF). (c) Spin-polarized Co electron SC-state LDOS normalized with respect to the normal-state spin-polarized DOS near the QPT.

Co impurity on Pb(110) In the normal state, for a Co impurity on Pb, the Co spin-down DOS at EF is higher than that for the Fe case [Fig. 3b]). As shown at the bottom of Fig. 3a, without SOC, we find five pairs of LDOS peaks from dx2−y2, dxy, {d2-z2-d2-x2}, and dxy orbitals, respectively. (Only five dominant peaks are visible due to the scale.) This shows that different types of magnetic impurities provide very different YSR states even for the same SC substrate. With SOC, the energies of the YSR states change a lot as a function of θ and ϕ. Similarly to the Fe case, for −0.5∆ < E < 0.5∆, the YSR pairs show dominant spin-down peaks at positive and negative energies [Figs. 3c, S6]. However, the angular dependence qualitatively differs from that of the Fe case. The merging of the deepest YSR pair occurs twice, i.e., near θ = 39° and 56°, in the xz-plane rotation [Fig. 3a]. For the xy-plane rotation, however, we do not find a ZBP [Fig. S7b]. The difference between the Co and Fe cases is attributed to the fact that the Co spin (orbital) moment is much smaller (larger) than the Fe spin orbital moment (Table I). Our first-principles simulations show strong correlation among the normal-state LDOS, the impurity spin and orbital moments, and their effects on the YSR states. Despite the different LDOS features, the spin polarization of the ZBPs near θ = 39° and 56° is large whether it is normalized by the normal-state LDOS or not [Figs. 3c, S7a]. The split peaks of the deepest YSR pair are now spin-down at both negative and positive energies near the QPT angles.

Mn impurity on Pb(110) In the normal state, for a Mn impurity on Pb, the Mn spin-down DOS is barely occupied since EF crosses the tail of the Mn spin-down DOS [Fig. 4a]. In the SC state, even with SOC, the electron LDOS peaks appear only near the gap edges and they do not change much with the moment rotation in the xz and xy planes [bottom panel in Fig. 4b]. This is due to the low-normal-state Mn DOS at EF, although the Mn spin moment is the largest among Fe, Co, Mn impurities (Table I). In order to show importance of large normal-state impurity DOS, we calculate the SC-state Mn LDOS as a function of ϕ when the chemical potential is raised to the spin-down LDOS peak marked in Fig. 4a. We find that the YSR states now significantly change with ϕ and that even a ZBP appears near ϕ = 75°.

FIG. 4. (a) Normal-state Mn spin-up and spin-down DOS with SOC (dashed line: EF). (b) Electron Mn SC-state LDOS (sum of spin-up and spin-down) as a function of ϕ with SOC when the chemical potential is EF (bottom panel) and is at the thick dashed arrow denoted in (a) (top panel).
Discussion From our first-principles simulations, we extract the following features common to the ZBP cases. First, the normal-state impurity DOS is high at $E_F$. Second, it is more likely to observe a ZBP for a SC substrate with strong SOC like Pb. Third, the impurity magnetic moment has substantial in-plane components which may be related to Rashba SOC of the SC substrate. Overall, we find strong interplay between the impurity DOS at $E_F$ and the magnetic moment of the impurity, resulting in the intriguing, complex dependence of the YSR states on the impurity moment direction in the presence of SOC.

Since spin polarization is one of the key ingredients to determine the topological nature of ZBPs, we compare our results with effective model studies [13], although we do not expect MZMs from single magnetic impurities. In the single-orbital effective models [13], $\Delta \rho$ is an antisymmetric function of energy relative to $E_F$ due to a sum rule applied for simplicity. Thus, when a YSR pair merge to form a ZBP, the normalized spin polarization of the ZBP vanishes. Now when the band structure of the SC substrate and all five 3d orbitals of the magnetic impurities are taken into account, $\Delta \rho$ is not an antisymmetric function of energy with or without SOC. In the presence of strong SOC, both the height and sign of $\Delta \rho$ for the deep YSR pair strongly depend on the moment direction. Thus, the ZBP in our case has large (normalized) spin polarization.

Conclusion We simulated single magnetic impurities at the surface of SC Pb(110) by solving the DBdG equations using the embedded cluster method within the SKKR formalism. DFT band structures and multiple 3d orbitals of the impurities were included in the normal and SC states. For the Fe and Co impurities, we found a ZBP with large (normalized) spin polarization for the rotation of the impurity moment, whereas for the Mn impurity, a ZBP was not found due to the low impurity DOS at $E_F$. Our results suggest importance of including realistic band structures and multiple orbitals in studies of YSR states of magnetic impurities and they are also relevant to understand effects of canting and noncollinear magnetism on the YSR states including ZBPs in long magnetic atomic chains. Furthermore, they imply our need to search for signatures of topological MZMs beyond spin polarization.

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