

Supplementary Information for “Quantum phase transitions and the role of impurity substrate hybridization in Yu-Shiba-Rusinov states”

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(Dated: September 10, 2020)

SUPPLEMENTARY NOTE 1

Tip and Sample Preparation

The experiments were carried out in a scanning tunneling microscope (STM) operating at a base temperature of 10 mK [1]. The sample was a V(100) single crystal. To obtain a clean surface, the sample was prepared by multiple cycles of Ar sputtering and subsequent annealing to 700°C. The tip material was a polycrystalline V wire, which was cut in air and prepared in ultrahigh vacuum by field emission. The cleaned V(100) always features a (5×1) oxygen reconstruction, which can be seen in Fig. S1(a) and (b), due to migration of oxygen to the surface during annealing procedure [2]. Additional impurities include oxygen vacancies (see Fig. S1(b), which are most abundant and visible in STM topography image and some carbon atoms [3]. Carbon atoms migrate to the surface during slow cool down procedure after annealing, and is invisible in STM topography measurements [4]. Impurities with YSR states can be found on the surface, whose origin is not exactly known. However, from the much smaller abundance compared to oxygen vacancies and the still much higher concentration than remnant transition metal impurities, we conclude that the YSR impurities may originate from combination of the most abundant impurities, such as a carbon-oxygen vacancy complex. The fact that most YSR impurities only show one pair of YSR state in-gap indicates a simple spin structure and supports the simple elements component rather than conventional magnetic transition metal elements.

SUPPLEMENTARY NOTE 2

Deviations from an Exponential Decay of the Conductance

We attribute the deviations from the exponential decay of the conductance as function of tip-sample distance to changes in the impurity-substrate coupling. However, there are other effects that may result in a similar deviation from the exponential behavior of the conductance, such as deformations of the tip. In order to exclude tip deformations, we have performed distance dependent conductance measure-

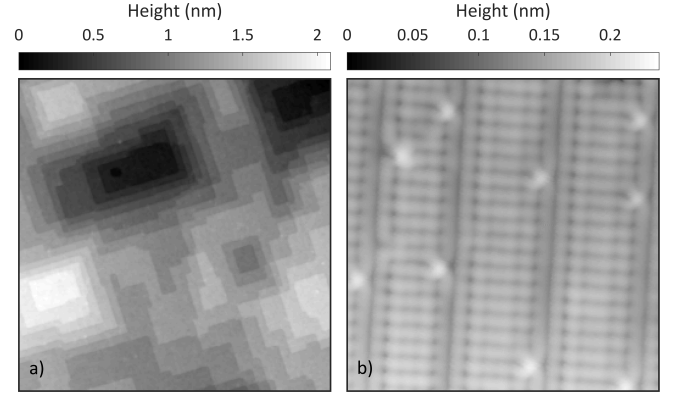


FIG. S1: **Topography of V(100) surface.** (a) An overview topography covering an area of $100 \text{ nm} \times 100 \text{ nm}$. (b) A smaller area ($6 \text{ nm} \times 6 \text{ nm}$) showing the (5×1) oxygen reconstruction with some oxygen defects showing up as bright protrusions.

ments for both a tunnel junction without any YSR state as well as with one YSR state that does not move in energy as function of tip-sample distance. Both curves are plotted logarithmically in Fig. S2(a), which demonstrates their principally exponential evolution. Fitting an exponential to the low conductance regime and dividing the data by this fit, shows a constant behavior across the distance, which is shown in Fig. S2. Therefore, we do not expect tip deformations to contribute as we approach tip and sample. This demonstrates that in the systems presented here, deviations in the exponential behavior can be attributed to changes in the impurity-substrate coupling.

SUPPLEMENTARY NOTE 3

Mean Field Description of the Anderson Impurity Model

In the Anderson impurity model, the Hamiltonian H describes the coupling of an impurity H_i to a substrate H_s by means of an interaction term H_{si} acting like a hopping be-

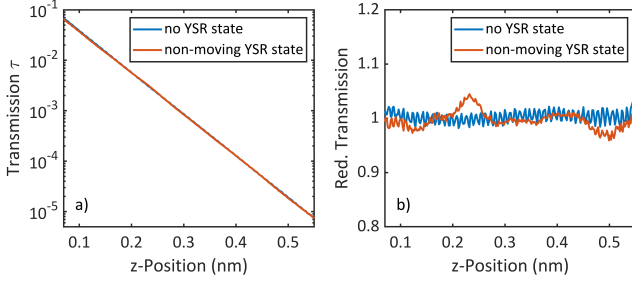


FIG. S2: **z-dependence of conductance of a clean BCS junction without YSR state.** (a) Experimental normal state conductance G_N as function of tip-sample distance z showing the exponential dependence for a tunnel junction without any YSR state as well as with one YSR state that does not move in energy as function of tip-sample distance. (b) The same data as in (a) divided by an exponential fit to demonstrate that no deviations occur in these two instances.

tween impurity and substrate

$$H = H_s + H_i + H_{si}, \quad (S1)$$

$$H_s = \sum_{k\sigma} \varepsilon_k c_{k\sigma}^\dagger c_{k\sigma} - \Delta_s \sum_k \left(c_{k\uparrow}^\dagger c_{k\downarrow}^\dagger + h.c. \right), \quad (S2)$$

$$H_i = \sum_{\sigma} \varepsilon_d n_{d\sigma} + U_d n_{d\uparrow} n_{d\downarrow}, \quad (S3)$$

$$H_{si} = \sum_{k\sigma} t_{kd} \left(c_{k\sigma}^\dagger c_{d\sigma} + h.c. \right), \quad (S4)$$

Here, σ denotes the spin states up ($\uparrow$) and down ($\downarrow$) and $n_{d\sigma} = c_{d\sigma}^\dagger c_{d\sigma}$ is the number operator. The substrate Hamiltonian H_s describes a Bardeen-Cooper-Schrieffer (BCS) superconductor, which is readily solved within mean field theory. The energy-momentum relation is given by ε_k and the superconducting gap is given by Δ_s . Integrating over momentum, we find the Green's function of the substrate in 2×2 Nambu space

$$G_s(\omega) = n_s \frac{(\omega + i\gamma)\sigma_0 - \Delta_s\sigma_1}{\sqrt{\Delta_s^2 - (\omega + i\gamma)^2}}, \quad (S5)$$

with n_s being the density of states of the substrate at the Fermi level in the normal conducting state and γ being a phenomenological broadening parameter [5]. In the impurity Hamiltonian H_i , the four component operator describing the Coulomb repulsion U_d can be reduced to a two component operator by means of a mean field approximation

$$U_d n_{d\uparrow} n_{d\downarrow} = U_d \langle n_{d\downarrow} \rangle n_{d\uparrow} + U_d \langle n_{d\uparrow} \rangle n_{d\downarrow}, \quad (S6)$$

where $\langle n_{d\sigma} \rangle$ denotes the spin down density in the spin up level and vice versa. The spin densities of states $\langle n_{d\sigma} \rangle$ depend on each other, but they can be calculated selfconsistently using the equation

$$\langle n_{d\sigma} \rangle = \int_{-\infty}^{\infty} A_{i\sigma}(\omega) f(\omega) d\omega, \quad (S7)$$

where $A_{i\sigma}(\omega) = \text{Im} G_{i\sigma}(\omega)$ is the spin-resolved spectral function of the impurity Green's function and $f(\omega)$ is the Fermi-Dirac distribution. Within this mean field approximation, we can rewrite the energy levels of the impurity as

$$\begin{aligned} H_i &= (\varepsilon_d + U_d \langle n_{d\downarrow} \rangle) n_{d\uparrow} + (\varepsilon_d + U_d \langle n_{d\uparrow} \rangle) n_{d\downarrow} \\ &= (-E_J + E_U) n_{d\uparrow} + (E_J + E_U) n_{d\downarrow}. \end{aligned} \quad (S8)$$

The second line in Eq. (S8) defines the energy levels in terms of a splitting parameter E_J and an offset parameter E_U , which are used in the main text. The relation to the first line illustrates the connection to the mean field description of the Anderson impurity model. We should point out that the relation of E_J and E_U to ε_d and U_d is likely more complex, when taking into account correlation effects. The impurity Hamiltonian H_i describes an effective Zeeman splitting without introducing a quantization axis as in a magnetic field. The impurity spin is quantized with $s = \frac{1}{2}$ and rotates freely.

With this mean field approximation in mind, we can write down the full Hamiltonian in matrix form

$$H = \begin{pmatrix} H_s & H_{si} \\ H_{si}^\dagger & H_i \end{pmatrix} = \begin{pmatrix} H_s & \hat{t} \\ \hat{t}^\dagger & H_i \end{pmatrix}. \quad (S9)$$

We assume a 2×2 Nambu space for each entry, such that the interaction term becomes $H_{si} = \hat{t} = t\sigma_3$, where $t = t_{kd}$ is a momentum independent hopping term and σ_3 is a Pauli matrix. The corresponding Green's function can be written as

$$G(\omega) = \begin{pmatrix} \omega - H_s & \hat{t} \\ \hat{t}^\dagger & \omega - H_i \end{pmatrix}^{-1} \quad (S10)$$

Focusing on the impurity Green's function $G_i(\omega) = G_{22}(\omega)$, we find the expression

$$G_i(\omega) = (\omega\sigma_0 + E_J\sigma_0 - E_U\sigma_3 - \Gamma_s\sigma_3 g_{sc}(\omega)\sigma_3)^{-1}, \quad (S11)$$

where σ_j are the Pauli matrices, $\Gamma_s = |t|^2 n_s$ is the impurity-substrate coupling parameter, and g_{sc} is the normalized Green's function of the superconducting substrate with $G_s(\omega) = n_0 g_{sc}(\omega)$. Equation (S11) represents the Green's function of the impurity as used in the main text.

While we work in the limit $\Gamma_s \gg \Delta$ in this manuscript, we want to point out that in the regime $\Gamma_s \approx \Delta$ interactions of non-magnetic impurities can lead to Andreev bound states, which are similar to the YSR states, but spin degenerate. This also illustrates the more general character of the Anderson impurity model as it encompasses not just the YSR states, but also the more general Andreev bound states.

Transport through an Impurity

Tunneling involving a YSR state is typically thought of as transport through the YSR state, i. e. transport through the

impurity at the surface. The tunneling current through an impurity not only involves the tunnel coupling between tip and impurity, but also between the impurity and the substrate. This is best modelled within the Anderson impurity model as it naturally involves the impurity-substrate coupling and has been discussed extensively in the literature. The normal state conductance is typically measured at bias voltages V much larger than the superconducting gaps, i. e. $eV \gg \Delta_t + \Delta_s$, where the influence of the superconducting gaps on the normal state conductance can be neglected. In this approximation, the transmission through the YSR state can be written as [6]

$$\tau = \frac{4t_{\text{ti}}^2 n_i n_t}{|1 - t_{\text{ti}}^2 g_i g_t|^2}, \quad (\text{S12})$$

where n_i is the density of states at the impurity, n_t is the density of states in the tip, g_i is the Green's function of the impurity in the normal conducting state, g_t is the density of states in the tip in the normal conducting state, and t_{ti}^2 describes the tunnel hopping between the tip and the impurity. Assuming particle-hole symmetry, i. e. $E_U = 0$, the Green's functions are

$$g_i = \frac{E_J + i\Gamma_s}{\Gamma_s^2 + E_J^2} \quad \text{and} \quad g_t = i n_t, \quad (\text{S13})$$

and the density of states n_i in the impurity is

$$n_i = \text{Im}(g_i) = \frac{\Gamma_s}{\Gamma_s^2 + E_J^2}. \quad (\text{S14})$$

Further defining $\Gamma_t = t_{\text{ti}}^2 n_t$, we can calculate the transmission through the YSR state of the impurity

$$\tau_{\text{YSR}} = \frac{4\Gamma_s \Gamma_t}{(\Gamma_s + \Gamma_t)^2 + E_J^2} = \frac{4\tilde{\Gamma}_s \tilde{\Gamma}_t}{(\tilde{\Gamma}_s + \tilde{\Gamma}_t)^2 + 1}. \quad (\text{S15})$$

In the last expression of Eq. (S15), we relate the impurity-substrate coupling Γ_s to the level splitting E_J , which we assume to be constant, through $\tilde{\Gamma}_s = \frac{\Gamma_s}{E_J}$. Furthermore, we define $\tilde{\Gamma}_t = \frac{\Gamma_t}{E_J}$. This allows us to directly relate the experimentally extracted impurity-substrate coupling in the expression for the YSR state energy with the impurity-substrate coupling in the expression for the channel transmission.

The experimental spectra show pronounced coherence peaks, which are not part of the density of states on the YSR state. We, therefore, assume that a second transport channel going through the impurity, but not through the YSR state, is involved. This means that both transport channels share the

same impurity-substrate transport channel. Assuming a conventional BCS-type superconducting gap based on a constant Green's function $g_i = i/\Gamma_s$ and density of states $n_i = 1/\Gamma_s$, we find for the normal state transmission

$$\tau_{\text{BCS}} = \frac{4\Gamma_s \Gamma_t}{(\Gamma_s + \Gamma_t)^2} = \frac{4\tilde{\Gamma}_s \tilde{\Gamma}_t}{(\tilde{\Gamma}_s + \tilde{\Gamma}_t)^2}. \quad (\text{S16})$$

Further assuming that the two channels are independent, we can add them to find the total transmission τ weighted by the ratio p with which they have been measured

$$\tau = \tau_{\text{YSR}} + \tau_{\text{BCS}} = p \frac{4\tilde{\Gamma}_s \tilde{\Gamma}_t}{(\tilde{\Gamma}_s + \tilde{\Gamma}_t)^2 + 1} + (1 - p) \frac{4\tilde{\Gamma}_s \tilde{\Gamma}_t}{(\tilde{\Gamma}_s + \tilde{\Gamma}_t)^2}, \quad (\text{S17})$$

As can be seen, the transmission does not only carry information about the coupling between the tip and the impurity, but also between the impurity and the substrate. As such, it provides excellent means to confirm the connection between the YSR state energy as well as the impurity-substrate coupling.

SUPPLEMENTARY NOTE 4

Orbital Decay for Different Transport Channels

We use the same decay constants in the calculation of Γ_t for the YSR channel and the BCS channel in the respective systems. While this is *a priori* not necessarily justified, for our specific situation, we argue in the following way. We fit the conductance spectra of Set 1 and 3 at low conductance and find that the contribution from each channel is at least within a factor of three after the conductance has dropped by almost four orders of magnitude. This indicates that the decay constants cannot be very different. In terms of a minimal model that we present here, our assumption of having the same decay constant for both channels is therefore justified. For Set 2, we fitted the spectrum at a higher conductance, but as the three systems are in principle similar, we also make the same assumption for this data set.

SUPPLEMENTARY NOTE 5

Fitting the differential conductance

The differential conductance dI/dV was calculated from the tunneling current $I(V) = e[\tilde{I}(V) - \tilde{I}(V)]$, with the tunneling probability from tip to sample

$$\tilde{I}(V) = \frac{G_N}{2e^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dE dE' (n_t^e(E - eV) n_s^e(E') f(E - eV) [1 - f(E')] - n_t^h(E + eV) n_s^h(E') f(E + eV) [1 - f(E')]) P(E - E'). \quad (\text{S18})$$

Here, G_N is the normal state conductance, $f(E) = 1/(1 + \exp(E/k_B T))$ is the Fermi function, and $n_t^{e,h}$, $n_s^{e,h}$ are the electron (e) and the hole (h) contributions to the DOS in tip and sample, respectively. For the corresponding Green's functions we use the (2×2) Nambu space as in the main text. The $P(E)$ -function describes the exchange of energy with the environment during the tunneling process and is interpreted as the energy resolution function of the STM [7]. The other tunneling direction $\tilde{T}(V)$ from sample to tip can be obtained by exchanging the Fermi functions in Eq. (S18), i. e. $f \leftrightarrow (1-f)$.

The DOS in the sample n_s is modeled by the sum of the DOS of the YSR state n_{YSR} and the DOS of the empty BCS gap n_{BCS} :

$$n_s^{e,h} = p n_{\text{YSR}}^{e,h} + (1-p) n_{\text{BCS}}, \quad (\text{S19})$$

where p is the relative contributions of the two transport channels to the tunneling current.

The DOS of the YSR state is calculated from the Green's function $G(\omega)$ given in Eq. (S23)

$$n_{\text{YSR}}^e(\omega) = \text{Im} G_{11}(\omega) \quad \text{and} \quad n_{\text{YSR}}^h(\omega) = \text{Im} G_{22}(\omega). \quad (\text{S20})$$

The DOS of the empty BCS gap n_{BCS} as well as the DOS of the tip n_t were modeled by the BCS density of states:

$$n_{\text{BCS},t}(\omega) = \text{Re} \left[\frac{\omega + i\gamma_{s,t}}{\sqrt{(\omega + i\gamma_{s,t})^2 - \Delta_{s,t}^2}} \right]. \quad (\text{S21})$$

Here, $\gamma_{s,t}$ is a phenomenological broadening parameter in sample (s) and tip (t). For the vanadium tip, we find $\Delta_s = 760 \mu\text{eV}$, $\gamma_s = \gamma_t = 3 \mu\text{eV}$. In order to account for a slight non-BCS shaped tip gap, we use the Maki model for the tip, which introduces a depairing parameter ζ_t that leads to an energy dependent tip gap parameter Δ_t [8]:

$$\Delta_t = \Delta_t^{\text{BCS}} - \zeta_t \frac{\Delta_t}{\sqrt{\Delta_t^2 - \omega^2}}. \quad (\text{S22})$$

with $\Delta_t^{\text{BCS}} = 780 \mu\text{eV}$ and $\zeta_t = 0.008$. The sharp YSR state in the sample is a direct probe of the coherence peaks in the tip, which can be directly seen in the tunneling current. The asymmetric shape of the coherence peaks and the falling slope away from the gap result in the typical YSR peak shape in the differential conductance with the characteristic negative differential conductance. Hence, a better fit of the YSR state in the sample can be achieved with a modified coherence peak in the tip. Therefore, we phenomenologically adapt the tip gap by employing the Maki model, which can be rationalized by previously observed differences in the vanadium tip gaps compared to the vanadium bulk gap [9–11].

Differential conductance spectra were recorded with a lock-in amplifier having a modulation amplitude of $20 \mu\text{V}$ and a modulation frequency of 793 Hz . The additional broadening in the differential conductance spectra due to the lock-in amplitude is accounted for in the data analysis by means of an additional convolution with a semi-circle shaped resolution function.

Fitting YSR states within the Anderson impurity model

In the strong impurity-substrate coupling limit ($\Gamma_s \gg \Delta$), we find the following Green's function for the YSR states within the Anderson impurity model:

$$G(\omega) = \frac{\Gamma_s \omega \sigma_0 + (E_J \sigma_0 + E_U \sigma_3) \sqrt{\Delta_s^2 - \omega^2} + \Gamma_s \Delta_s \sigma_1}{2E_J \Gamma_s \omega - (\Gamma_s^2 - E_J^2 + E_U^2) \sqrt{\Delta_s^2 - \omega^2}}, \quad (\text{S23})$$

It can be easily seen that there are more variables to be determined than independent fit parameters. Therefore, it is not possible to find an unambiguous value for every variable from the fit. We have to reduce the effective number of variables by introducing the following dimensionless parameters:

$$x = \frac{E_U}{E_J}; \quad y = \frac{\Gamma_s}{E_J}; \quad u = \frac{\omega}{\Delta}. \quad (\text{S24})$$

The resulting Green's function in terms of the parameters x , y , and u is:

$$G(u) = \frac{1}{E_J} \frac{(\sigma_0 + x \sigma_3) \sqrt{1 - u^2} + u y \sigma_0 + y \sigma_1}{2u y + \sqrt{1 - u^2} (1 - x^2 - y^2)}. \quad (\text{S25})$$

The energy position of the YSR state in this notation is

$$u_{\pm} = \frac{\varepsilon_{\pm}}{\Delta} = \pm \frac{1 - x^2 - y^2}{\sqrt{(y^2 + (1 - x^2)^2)(y^2 + (1 + x^2)^2)}}. \quad (\text{S26})$$

The extracted fit parameters for the data sets presented in the main text are summarized in Table SI. We can see that neglecting the particle-hole asymmetry parameter E_U will not cause a significant error in the analysis of the main text as x is smaller than one.

SUPPLEMENTARY NOTE 6

Conductance Measurements as Function of Tip-Sample Distance

For completeness, we show the normal state conductance curves as function of tip-sample distance in Fig. S3 for the data sets in Figs. 4 and 5 of the main text. The exponential dependence of the tunnel coupling dominates the overall

TABLE SI: Fit parameters for the data sets presented in the main text. The parameters x and y are defined in Eq. (S24), p is the contribution of the YSR state to the total normal state conductance, and τ is the total normal state conductance in units of the quantum of conductance G_0 .

Set	Figure	x	y	p	τ
1	2,3	0.42 ± 0.01	1.36 ± 0.01	22%	1.6×10^{-4}
2	4	0.03 ± 0.006	0.86 ± 0.005	39%	2.5×10^{-2}
3	5	0.029 ± 0.005	0.39 ± 0.005	35%	1.6×10^{-4}

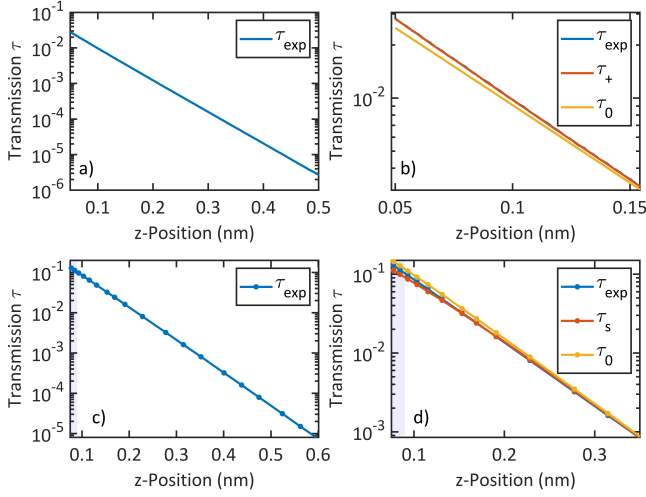


FIG. S3: **z-dependence of conductance of a YSR junction.** (a) Experimental normal state conductance G_N as function of tip-sample distance z showing the exponential dependence for the data set presented in Fig. 4 of the main text. (b) Zoom-in to the high conductance regime, where the strongest deviations are expected between the experimental data and the theoretical model with a constant impurity-substrate coupling. The calculated transmission based on the extracted impurity-substrate coupling provides a much better agreement even in the logarithmic plot. (c) and (d) is the same as (a) and (b) for the data in Fig. 5 of the main text.

behavior, which does not illustrate the comparatively small, but important changes in the impurity-substrate coupling. Therefore, we only show the reduced transmission $\tau/\tilde{\Gamma}_t$ in the main text.

The uncertainty of the data points presented in the raw experimental data, including bias spectra (for example Fig. 2 (d) in the main text) and z -dependence of conductance (for example Fig. S3) is usually too small to show in the graph. On the other hand, the uncertainty of the fit can be qualitatively visualized from the deviation between the fit and the experiment.

SUPPLEMENTARY NOTE 7

Experimentally deciding the scattering regime

If the YSR states are changing their energy $\varepsilon_{\pm}$, when the tip approaches, the scattering regime can be determined. Both $\varepsilon_{\pm}$ and the normal state conductance G_N have to be measured as function of tip-sample distance z . If the conductance G_N increases more than exponentially as the tip approaches, the impurity-substrate coupling Γ_s decreases. If G_N increases less than exponentially, Γ_s . Whether the scattering regime is weak or strong can be found in Table SII.

TABLE SII: Table to decide, if the system is in the weak or strong scattering regime. Both the YSR state energy $\varepsilon_{\pm}$ and the normal state conductance G_N have to be evaluated as function of tip-sample distance z .

tip-sample distance decreases	Γ_s increases	Γ_s decreases
$\varepsilon_{\pm}$ moves towards 0	weak	strong
$\varepsilon_{\pm}$ moves away from 0	strong	weak

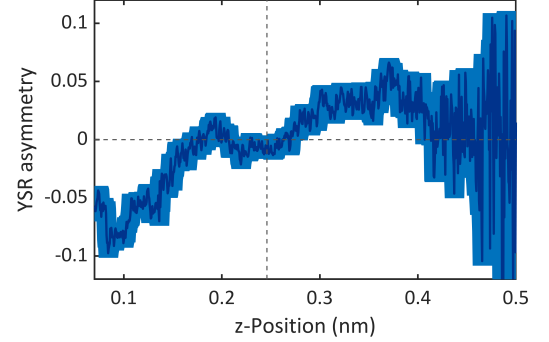


FIG. S4: **The evolution of the asymmetry of a YSR state crossing the quantum phase transition.** Asymmetry of the YSR state intensity shown in Fig. 4 of the main text. The vertical dashed line indicates the position, where the system moves across the quantum phase transition.

YSR State Asymmetry

The asymmetry of the YSR state

$$A = \frac{I_R - I_L}{I_R + I_L}, \quad (\text{S27})$$

where $I_{L,R}$ is the intensity of the left (L) and the right (R) YSR peak, respectively, is particularly interesting when the YSR state moves across the quantum phase transition. In the experiment, it then looks like the asymmetry switches sign. It should be noted that in the model the energies of the electron and hole parts of the YSR state change sign, when moving across the transition, but the asymmetry does not change its sign. In the experimental analysis, the sign change arises when calculating the asymmetry from the left and the right peak irrespective of their electron/hole character.

We plot the asymmetry of the YSR state shown in Fig. 4 of the main text in Fig. S4. The shaded region around the data points indicates an uncertainty of ± 0.004 . The strong scattering of the data points for $z > 0.4$ nm is due to the small lock-in signal at large tip-sample distances. We note that the asymmetry is intrinsically small and moves through zero rather smoothly, such that a discontinuity is not directly visible. The vertical dashed line indicates where the YSR energies cross zero. Still, the overall change in sign of the asymmetry to the left and to the right of the vertical line indicates the quantum phase transition. In addition, the rather small asymmetry throughout the measurement justifies the approximation $E_U = 0$.

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