Tunnelling dynamics between superconducting bound states at the atomic limit

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There is a limit to the miniaturization of every process, and for charge transport this is realized by the coupling of two single discrete energy levels at the atomic scale. In superconductors, Yu–Shiba–Rusinov (YSR) states are such levels. Here, we place a magnetic impurity on the apex of a scanning tunnelling microscope (YSR-STM) and use it to demonstrate sequential tunnelling of electrons between parity-protected YSR states on the tip and in the sample. Using this Shiba–Shiba tunnelling technique we probe the YSR lifetime, which we can enhance by reducing the relaxation of the excited YSR state to the intrinsic channel. Our work offers a way to characterize and manipulate coupled superconducting bound states, such as Andreev levels, YSR states or Majorana bound states at the atomic limit.

In conventional superconductivity, Cooper pairs, formed from pairs of electrons with opposite spin and momentum, condense to a macroscopic quantum state. Excitations from this ground state are Bogoliubov quasiparticles, coherent superpositions of an electron and a hole. In a uniform superconductor, these excitations occupy delocalized states in a continuum separated from the condensate by an energy gap $\Delta$. Localized Bogoliubov states1–3, however, can be coupled to engineer quantum systems predicted to show parity protection (even/odd particle number conservation) as well as topological protection4–5, with applications in quantum information processing6–8.

Inside the gap and thus separated from the continuum, Bogoliubov quasiparticles can be localized at the atomic scale in Yu–Shiba–Rusinov (YSR) states by perturbing the superconductor with a magnetic impurity9–11. YSR states have been observed on a variety of magnetic atoms—intrinsically present or deliberately placed on the surface—on various superconducting substrates using scanning tunnelling microscopy (STM)12–15. Nevertheless, charge transfer between two YSR states remains elusive, despite this being an ideally suited model system for realizing fundamental tunnelling processes between single in-gap energy levels. Since the resulting spectral feature will be isolated in the measurement, this allows for direct characterization of the states, including their energy, their relaxation lifetime, the tunnel coupling from a sequential to an emergent coherent regime, and their coupling to residual quasiparticles16–19. Tunnelling between YSR states can thus provide direct insight into the dynamic properties of coupled superconducting bound states, including their protection and relaxation processes. Due to its abilities to resolve and manipulate single atoms20–23, STM is ideally suited to realize a tunable coupling between one YSR state at the tip apex (YSR-STM) and another on the sample surface. However, reliably producing YSR states in the tip has hitherto been an unsolved challenge.

Here, we use STM at a base temperature of 10 mK (ref. 24) to realize tunnelling between a YSR state on the apex of a superconducting vanadium tip and a YSR state from an intrinsic impurity on the superconducting V(100) sample. We thus demonstrate charge transfer between two individual superconducting bound states, which presents a minimal configuration to produce a tunnelling current. The corresponding spectral feature manifests itself in the current measurement as distinct, sharp peaks. We introduce the peak area, that is the intensity, as a precisely measurable quantity, which is independent of the resolution function of the STM25. We observe a transition from a weakly coupled sequential tunnelling regime to an emergent coherent regime, where the tunnel coupling overcomes the intrinsic relaxation of the YSR states. At the transition point, the peak area itself provides a direct measurement of this intrinsic relaxation rate.

Tunnelling between superconducting bound states

A schematic of the measurement set-up and a topographic map of the V(100) surface are shown in Fig. 1a,h. A sparse distribution of intrinsic magnetic impurities can be observed on the V(100) surface (Fig. 1c), which produce a single well defined YSR state inside the gap. Below, we refer to the spots without YSR states as clean spots. The YSR states appear at a wide range of energies, indicating a varying local exchange coupling. With controlled indentation of the tip on the sample surface, we can reproducibly introduce a YSR state on the apex of the tip at defined energies inside the gap. For more details, see Supplementary Section A. With the YSR state being a single energy level, the YSR tip can be used to separately detect individual states on the sample in a measurement with extremely high energy resolution, which goes beyond the use of the sharp coherence peaks in a superconducting tip.

Typical differential conductance (dI/dV) spectra at a low conductance setpoint $G_0$ are shown in Fig. 1d for a YSR state in the sample (blue), in the tip (red) and in both tip and sample (yellow), as well as an empty gap (grey) without any YSR state. The grey curve represents tunnelling between a clean superconducting tip and sample. We observe the two typical coherence peaks, separated by twice the sum of tip (t) and sample (s) gaps $2(\Delta_t+\Delta_s)$. In the red and blue spectra, we observe a single pair of YSR peaks located at...
Fig. 1 | Tunnelling between YSR states. 

(a) Schematic of the voltage-biased tunnel junction showing a YSR state at the tip apex over an intrinsic YSR state at the V(100) surface. (b) Topographic image of the V(100) surface. (c) Current map of the same area as in (b) at a bias voltage just below $2(\Delta_t + \Delta_s)$. YSR states show up as bright spots. (d) Differential conductance spectra at low conductance at 10 mK. Blue: YSR state on the sample and clean (that is no YSR state) superconducting tip. The peaks inside the superconducting gap at $\pm (\varepsilon_s + \varepsilon_t)$ are due to conventional YSR tunnelling. Red: YSR state on the tip and clean sample. Yellow: YSR state on the tip and another YSR state on the sample. The two sharp peaks inside the shaded region at $eV = \pm (\varepsilon_s + \varepsilon_t)$ are Shiba–Shiba tunnelling peaks. Grey: clean tip and clean sample, where coherence peaks at $eV = \pm (\Delta_t + \Delta_s)$ and a clean gap in between can be seen. SC, superconductor; au, arbitrary units.

$\pm (\varepsilon_s + \Delta_t)$, where $\varepsilon_s$ is the energy of the YSR state inside the sample gap or tip gap shifted by $\Delta_t = 750 \pm 10 \text{ eV}$, respectively. This process describes tunnelling from the YSR state into the continuum and vice versa, which we refer to as conventional YSR tunnelling. The involvement of the gapped continuum generally results in a forbidden region for bias voltages $|eV| \leq \Delta_{sc}$ shown as the shaded area in Fig. 1d, where no tunnelling is expected at low temperature and low conductance.

If, however, we position a tip functionalized with a YSR state over a YSR state in the sample, the spectrum changes considerably (yellow line in Fig. 1d). In addition to the conventional YSR tunnelling processes at $\pm (\varepsilon_s + \Delta_t)$, there is a feature at $\pm (\varepsilon_s + \varepsilon_t)$ inside the shaded area with substantial negative differential conductance. This additional feature can be directly associated with tunnelling between the isolated YSR state in the tip and that in the sample without any contribution from the quasiparticle continuum. The energy of this feature $|e_t + \varepsilon_t|$ is always smaller than the energy needed to access the quasiparticle continuum ($\Delta_s + \varepsilon_s$). In the following, we will refer to this new tunnelling process between two YSR states as Shiba–Shiba tunnelling. In the corresponding current spectrum, an isolated peak can be observed at this energy, which is shown in Fig. 2a (blue arrows). Having zero current on either side of this peak is a clear signature of tunnelling between single levels protected by a gap [27,28]. These observations are robust across many Shiba–Shiba systems and do not rely on a specific value of the parameters $\Delta_s$ or $\varepsilon_s$.

Fig. 2 | Direct versus thermal Shiba–Shiba tunnelling. 

(a) $I(V)$ spectrum of Shiba–Shiba tunnelling measured at 10 mK. The blue arrows mark the peaks for direct Shiba–Shiba tunnelling at $eV = \pm (\varepsilon_s + \varepsilon_t)$, (b) $I(V)$ spectrum of Shiba–Shiba tunnelling measured at 1 K. The red arrows mark the peaks for thermal Shiba–Shiba tunnelling at $eV = \pm (\varepsilon_s - \varepsilon_t)$ (blue arrows: direct Shiba–Shiba peaks). (c) Direct Shiba–Shiba tunnelling process. The spectral functions in tip and sample are shifted by $eV = \varepsilon_t - \varepsilon_s$. The system starts in the ground state ($|00\rangle$). Tunnelling of an electron leaves both tip and sample in an excited state ($|11\rangle$). This is illustrated in the energy diagrams (insets). (d) Thermal Shiba–Shiba tunnelling process. The spectral functions in tip and sample are shifted by $eV = \varepsilon_s - \varepsilon_t$. The system starts in a thermally excited state ($|10\rangle$). Thermally activated tunnelling effectively transfers a quasiparticle across the junction ($|01\rangle$). The grey dashed line denotes zero energy (Fermi level).

Direct and thermal Shiba–Shiba processes

At low temperature (10 mK), the $I(V)$ curve in Fig. 2a shows one pair of Shiba–Shiba peaks located at $eV = \pm (\varepsilon_t + \varepsilon_s)$ (blue arrows), which we refer to as direct Shiba–Shiba tunnelling. The process is explained schematically in Fig. 2c, where the spectral functions of tip and sample are shifted by $V$, such that direct Shiba–Shiba tunnelling occurs when the filled level (solid line) of the sample YSR state is aligned with the unfilled level (dashed line) of the tip YSR state [29]. At high temperature (1 K), the $I(V)$ curve in Fig. 2b features another pair of peaks located at $eV = \pm (\varepsilon_s - \varepsilon_t)$ (red arrows), clearly distinct from the direct Shiba–Shiba process (blue arrows). Looking at the aligned spectral functions in Fig. 2d, the YSR level above the Fermi level (grey dashed line) will be thermally occupied, such that tunnelling to the empty YSR level (dashed line) on the other side is possible. Therefore, in the following we refer to this thermally activated process as thermal Shiba–Shiba tunnelling.

Looking beyond the tunnelling process at what happens inside the superconductor, the simple picture of direct Shiba–Shiba...
Minimizing relaxation channels

Our experimental data clearly confirm tunnelling between two individual quasiparticle levels. We therefore demonstrate the absolute limit of transport both in space and in energy. The reduction of the constituents for tunnelling to a bare minimum turns the tunnelling dynamics into a purely sequential process governed by the lifetime of the excited YSR states. Depending on the energy of the YSR states in the tip and the sample, different channels may be available for relaxing into the ground state. If the energies of the YSR states are close to zero energy as in Fig. 2c, only intrinsic relaxation channels are available (excess quasiparticles). If the energies of the YSR states are close to the gap edge, additional relaxation channels open up at higher conductance through tunnelling to and from the continuum of the other electrode, which are indicated as processes 1 and 2 in Fig. 3a. The intrinsic relaxation channels are indicated by the lifetime broadening parameter $\Gamma_{\text{tr}}$. A diagram indicating the occurrence of the different relaxation processes as a function of the YSR state energies is shown in Fig. 3b. In conventional YSR tunnelling, processes 1 and 2 always occur, which has been discussed in the context of resonant Andreev tunnelling before. The unique aspect of Shiba–Shiba tunnelling is that these relaxation channels can be eliminated so that the possible relaxation channels are reduced to a bare minimum in the blue region in Fig. 3b. In the following, we will focus on Shiba–Shiba tunnelling in this blue region.

Extracting the intrinsic lifetime

The tunnelling dynamics in the blue region is governed by $\Gamma_{\text{tr}}$, as well as the tunnel coupling $t_{s,t}$, which is schematically shown in Fig. 4a. Due to the sequential nature of the tunnelling process, the system needs time to relax before the next tunnelling event is possible. This condition holds as long as the tunnel coupling is small, that is $\gamma_{s,s,t} \ll t_{s,t}$. For strong tunnel coupling, that is $\gamma_{s,s,t} \gg t_{s,t}$, chances increase for higher-order multiple tunnelling (back and forth) between the YSR states without transferring additional charge during the process, which blocks the junction and reduces the current. The tunnel coupling is experimentally accessible through the setpoint conductance $G_{\text{tr}} \propto \gamma_{s,s,t}$ (Supplementary Section C). With the unique possibility to tune the tunnel coupling by varying the tip–sample distance, we can directly access the crossover between these two regimes.

The tunnelling dynamics is reflected in the Shiba–Shiba current peak area, which presents an important quantity that only becomes well defined due to discrete quasiparticle level tunnelling (see Fig. 2a). The Shiba–Shiba peak area does not change during the tunnelling process, that is after the convolution with the environmental interaction, since $P(E)$ is a probability function with normalized area $a,b,c,d$. Therefore, the peak area retains its information during tunnelling and is a precise measure of the tunnelling dynamics (see Supplementary Sections C and D). Figure 4b shows the Shiba–Shiba peak area as a function of $G_{\text{tr}}$. The area first scales linearly (enough time to relax) followed by a sublinear regime with a square-root dependence (not enough time to relax) as a function of $G_{\text{tr}}$. The transition into the sublinear regime describes an emergent coherent interaction between the excited YSR states within their lifetime. This could provide a path towards entanglement of the two Bogoliubov quasiparticles filling the excited YSR levels, which are separated in real space by the tip–sample distance. The extremely low-lying transition point is indicative of a comparatively long lifetime.

This linear-to-sublinear transition can also be seen directly in the raw data of the Shiba–Shiba peak shown in Fig. 4c. In the lower two panels (at extremely high tunnelling resistances in the teraohm regime) the current peak scales linearly with the tunnelling resistance. In the upper two panels, the scaling is sublinear. Despite the small current values, Shiba–Shiba tunnelling is actually quite efficient. Using an ohmic junction at the same conductance, we would need a roughly hundred times higher bias voltage (about 30 mV) to achieve the same current as in the Shiba–Shiba peak (bottom panel...
of Fig. 4c). We rationalize this by the YSR spectral function being effectively a singularity in the limit of infinite lifetime as opposed to a conventional ohmic contact.

Going beyond the intuitive explanation above, we provide a full theory describing Shiba–Shiba tunnelling, the details of which can be found in Supplementary Section B. The central result of this theory is the derivation of the Shiba–Shiba current

\[ I_0(v) = \frac{e}{\hbar} \frac{\Gamma'v^2}{4v^2 + \Gamma^2 + (ev)^2} \]

which has Lorentzian shape. For simplicity, we assume equal \( \Gamma \) for the YSR states in tip and sample (\( \Gamma = \Gamma_c = \Gamma_s \)). The full expression for \( \Gamma_c \neq \Gamma_s \) can be found in Supplementary Section B.4. The voltage \( v \) is the detuning of the bias voltage \( V \) from the level alignment \( \epsilon_\text{s} + \epsilon_\text{t} \), that is \( eV = \epsilon_\text{s} + \epsilon_\text{t} + ev \). The area under the Shiba–Shiba peak is

\[ A = \frac{\pi\Gamma}{\hbar} \frac{\gamma^2_e}{\sqrt{4v^2 + \Gamma^2}}. \]

The evolution of the Shiba–Shiba peak area in equation (2) agrees well with the experiment (see Fig. 4b); in the linear regime \( A \propto \gamma^2_e \propto G_0 \) (dashed–dotted line) and in the sublinear regime \( A \propto \gamma^2_e \propto \sqrt{G_N} \) (dashed line). At the linear-to-sublinear transition where \( 2\gamma_e = \Gamma \), the peak area is given by \( A_{\text{trans}} = \frac{\pi\Gamma^2}{4\sqrt{2}h} \), which gives direct experimental access to \( \Gamma \). For the data in Fig. 4b, the peak area of about \( A_{\text{trans}} = 1 \times 10^{-19} \text{V A} \) translates to a combined \( \Gamma = 86 \text{meV} \), corresponding to a lifetime of \( \tau = \hbar/\Gamma = 48 \text{ns} \). As we have minimized the relaxation channels in this system (cf. blue region in Fig. 3b), we conclude that the extracted lifetime is the intrinsic lifetime of the YSR states due to excess quasiparticles. If the superconducting substrate were further optimized for the reduction of residual quasiparticles, the lifetime would even be longer. In such a situation, lifetimes in excess of 100 \( \mu \text{s} \) have been reported.

### Residual relaxation mechanisms

Looking at the intrinsic lifetime limiting mechanisms in more detail, phonons are excluded due to their exponential suppression at very low temperatures (\( T \ll 1 \text{K} \)) (Supplementary Section E and ref. \(^{30}\)). The only feasible relaxation channel is through quasiparticles, which recombine with the excited Bogoliubov quasiparticles \(^{32,33,35}\). This is schematically shown in Fig. 3c, where we model the effect of excess quasiparticles by adding a phenomenological broadening parameter \( \eta \) (ref. \(^{30}\)). Interestingly, this parameter introduces a finite parity lifetime translating directly into a finite YSR state broadening, even in the simplest YSR model\(^{37-39}\). Excess quasiparticles can occur even at lowest temperatures due to, for example, a paramagnetic background of defects or imperfect crystallinity\(^{40}\). We can directly observe this phenomenon in the current spectrum measured with a clean vanadium tip on a clean spot on the sample (Fig. 3d), and fit this spectrum with \( \eta = \eta_0 = 0.3 \text{meV} \) (yellow line). To demonstrate the sensitivity of the model we have plotted the same spectra with half and double the broadening (yellow dotted and dashed lines), which show substantial deviations. On the basis of this analysis, the lifetime broadening of the excited YSR state translates to \( \Gamma = 0.3 \text{meV} \) (Supplementary Section E), which is of the same order of magnitude as we measured from Shiba–Shiba tunnelling experimentally. Although this phenomenological approach cannot provide a detailed explanation of the relaxation mechanism, we conclude that excess quasiparticles could be a viable intrinsic relaxation channel for the YSR states at low temperatures (10 mK).

### Conclusion and outlook

Introducing a YSR state to the tip provides a versatile atomic probe featuring a single level and high energy resolution. This new tip...
Functionalization opens many new possibilities in tunnelling between single-quasiparticle levels at the atomic scale. It constitutes the ultimate limit in energy and space for the transport current through a tunnel junction. It can be used to reveal the relaxation mechanism and its relation to the in-gap quasiparticle background, which opens prospects to further develop long-lived single-quasiparticle states. In the next step, signatures of the relative spin orientation between the two YSR states can be addressed through the Shiba–Shiba peak area.

Going beyond this proof of principle, this minimal configuration can be exploited for time-dependent manipulation of a YSR state through parity-conserving excitation during a tunnelling event for both even (|100⟩−|111⟩) and odd (|110⟩−|101⟩) parity (at different bias voltages). Parity-breaking mechanisms, such as excess quasiparticles, can be reduced to increase lifetime or deliberately introduced to operate on the YSR states, for example through microwaves. As such, we have demonstrated a tunnelling process at the atomic scale that provides great potential for a deeper understanding of engineering and manipulating superconducting bound states. Furthermore, by extension, this provides a potential path towards detection and manipulation of Majorana bound states by tunnelling from YSR states.

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Methods

Tip and sample preparation. The experiments were carried out in a scanning tunnelling microscope operating at a base temperature of 10 mK (ref. 24). The sample was a V(100) single crystal with >99.99% purity. To obtain a clean surface, the sample was prepared by multiple cycles of argon ion sputtering at 10⁻⁷–10⁻⁶ mbar argon pressure with about 1 keV acceleration energy and annealing at around 700°C. The sample was heated and cooled slowly to reduce strain in the crystal. The tip material was a polycrystalline vanadium wire of 99.8% purity, which was cut in air and prepared in ultrahigh vacuum by sputtering and field emission. The thus-obtained V(100) crystal exhibits a sparse concentration of intrinsic impurities at the surface, giving rise to YSR states. The origin of these magnetic impurities is probably a complex involving an oxygen vacancy. YSR states on the tip were created by controlled tip indentation implemented in a LabVIEW program, enabling automated and reliable fabrication of desired YSR state properties. See Supplementary Section A for more details.

Current measurement. For measurements detecting currents above around 20 fA, a Femto DLPCA-200 was used. For smaller currents down to 1 fA, we used a Keysight B2983A instead. Within the overlap range between the two devices, the measurements on the same Shiba–Shiba area showed consistency. The bias voltage was supplied by one output channel of a Nanonis scanning probe microscopy controller, attenuated by a 1:100 passive voltage divider before being applied to the sample. The dI/dV curves shown in Fig. 1d were measured using standard lock-in techniques with a modulation between 10μV and 20μV at 392.348 Hz. Scanning tunnelling microscopy/ spectroscopy data were analysed and plotted using self-written MATLAB code.

Theory. The dynamics between YSR levels is described by a coupled two-level system. The resulting Shiba–Shiba current (equation (2)) is calculated with a quantum master equation of the density matrix. For more details see Supplementary Section B.

Data availability

Source data are provided with this paper. All other data that support the plots within this paper and other findings of this study are available from the corresponding author upon reasonable request.

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Author contributions

H.H. did the experiments with support from J.S., R.D., K.K. and C.R.A. C.P., A.L.Y., J.C.C., B.K. and J.A. provided theory support. H.H., C.P. and C.R.A. modelled and analysed the data with support from all authors. All authors discussed the results. H.H. and C.R.A. wrote the manuscript with input from all authors.

Competing interests

The authors declare no competing interests.

Additional information

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