Coherent long-range magnetic bound states in a superconductor

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In this supplementary information we first discuss the classical nature of the magnetic defects in terms of absence of Kondo resonance in the normal state. We then give a summary of the model and methods employed to compute the LDOS of the 2H-NbSe2 substrate with magnetic impurities. We also detail the tight-binding model which reproduces the exact band structure of 2H-NbSe2 and solve the Shiba equation with this band structure. Finally we show how to analytically extract the asymptotic behavior of the Shiba wave function.

S1: CLASSICAL NATURE OF THE IMPURITY

Magnetic elements present in our sample, Fe, Cr and Mn are known to be magnetic elements with classical spin since their magnetic moment is of the order of 2µBohr. We checked that indeed no Kondo signature was present. In the hypothesis of quantum impurities we would expect to observe a Kondo peak that might eventually split at high enough field. For this purpose a magnetic field of 5T perpendicular to the sample surface was applied to the sample to destroy the superconducting condensate and thus measure an eventual Kondo signature around the magnetic impurities. Figure 1 shows that no sign of a resonance around the impurity can be seen in the normal state at 5T which strongly advocates for the case of a classical impurity as expected for Fe, Cr and Mn.

FIG. 1: a: Spectroscopic map (21 nm×21 nm) of the area around the magnetic impurity discussed in the main text in Fig. 3.A at a magnetic field of 5T at the Fermi level. The white circle indicates the position of the magnetic impurity. b: In blue, the spectrum taken over the impurity at 5 T. The green spectrum is the reference spectrum of NbSe2 at zero magnetic field.
S2: LESS COMMON OBSERVATION OF MAGNETIC DEFECTS

The chemical analysis of the Nb used for our sample synthesis showed that the main magnetic contaminant was Fe (175 ppm). Other impurities were also measured as Cr and Mn but in smaller proportions (respectively 54 and 22 ppm). These impurities are expected to behave differently regarding their interaction with the superconducting 2H-NbSe₂. While the more prominent type of impurities behaves as the one presented in the main text, we observed around some defects different spectroscopic signatures as it is presented on figure 2. The Shiba states are in every case close to the Fermi level, however the amplitude asymmetry between hole and electron-like states is strongly modified. While in the case of the iron atom presented in Fig.3 of the main text, the amplitude of the hole-like peak is much larger than the one of the electron-like peak they are of comparable amplitude in the figure 2. As a consequence the conductance maps show that the arms of the star-shaped structures surrounding magnetic impurities are thicker than what is presented in the main text. We interpret these differences in terms of different diffusion potentials. These potentials are strongly dependent on the impurity type and are expected to strongly affect the spatial structure of the LDOS (see figure 4 of section S4). In all these cases the position of the Shiba energies is only slightly modified indicating similar magnetic and non-magnetic potentials for all these cases.

![Spectroscopic maps integrated over the width of the overlapping Shiba peaks.](image)

FIG. 2: Spectroscopic maps integrated over the width of the overlapping Shiba peaks. The respective lateral size of the spectroscopic pictures are 17 nm, 21 nm, 14 nm and 17 nm. In the lowest row, the green spectra refer to the superconducting spectra of NbSe₂ taken far from the impurity and the blue ones to the spectra taken on top of the magnetic impurities. In each case the impurity and reference spectra are taken from the same data set.

S3: MODEL AND METHOD

To describe the substrate 2H-NbSe₂ in presence of one magnetic impurity, we assume the impurity spin to behave classically and use for the superconducting part the following Bogoliubov de Gennes Hamiltonian

\[
H_{BdG} = \sum_k \xi_k (c^\dagger_{k\uparrow} c_{k\uparrow} + c^\dagger_{k\downarrow} c_{k\downarrow}) + \Delta (c^\dagger_{k\uparrow} c^\dagger_{-k\downarrow} + c_{-k\downarrow} c_{k\uparrow}),
\]

(1)
where $c_{k\sigma}^\dagger$ and $c_{k\sigma}$ denote the creation and annihilation operators of electron with momentum $k$ and spin $\sigma$. We add a scattering potential at the position of the impurity

$$H_{Imp} = -\frac{JS}{2}(c_{0\uparrow}^\dagger c_{0\uparrow} - c_{0\downarrow}^\dagger c_{0\downarrow}) + K(c_{0\uparrow}^\dagger c_{0\downarrow} + c_{0\downarrow}^\dagger c_{0\uparrow}),$$

where $c_{0\sigma}^\dagger$ denotes the creation operator of an electron at the impurity site. The system can be described by a tight binding model on a triangular lattice [1]. Because of the BdG part we can solve the Hamiltonian in the Nambu space using spinors of the form $\psi(r_{jl}) = (\phi_\uparrow(r_{jl}), \phi_\downarrow^\dagger(r_{jl}))$ where $r_{jl} = jae_x + la(\frac{\sqrt{3}}{2}ae_y + \frac{1}{2}ae_z)$ denote site position in space with $a = 3.444\text{Å}$ the inter site distance. We also consider periodic boundary conditions and Fourier transform the Hamiltonian. We define the spinor in momentum space as:

$$\psi(k_{nm}) = \frac{1}{NM} \sum_{jl} e^{i2\pi jn/M + i2\pi lm/N} \psi(r_{jl}),$$

where $k_{nm} = \frac{2}{\sqrt{3}} \xi_{x} + \frac{\sqrt{3}}{3}(\eta_{y} - \xi_{y})$, $N$ and $M$ denote the number of atomic sites of lattice in x and y directions. If we apply this spinor to the Hamiltonian, we find:

$$[E - \xi_{nm} \tau_z - \Delta_{0} \tau_x] \psi_{nm} = \frac{1}{NM} (-\frac{JS}{2} + K\tau_z) \psi(r_{imp}).$$

We can then infer this equation:

$$\psi(r_{jl}) = \sum_{nm} \frac{1}{NM} \frac{e^{i2\pi (nj/N + ml/M)}}{E_0^2 - c_{nm}^2 - \Delta^2} \psi(r_{jm})$$

From this equation by taking $r_{jl} = r_{imp}$, we can compute the Shiba energy and the amplitude of $\psi(r_{imp})$, and then we can compute the full spatial dependence of the Shiba wave function. The only two adjustable parameters are $JS/2$ and $K$ when considering a fixed band structure.

### S4: NUMERICAL CALCULATION

In order to perform the numerical calculation, we project our tight binding model on a triangular lattice. We have considered hopping terms up to the fifth nearest neighbour. The hopping amplitudes have been chosen in order to reproduce the band structure obtained from ab initio calculations. We refer to Refs [1-5] for the NbSe$_2$ band structure. The diagonalization of the tight-binding model results in the following 2-band dispersion relation (see Fig. 3):

$$\xi(k) = \xi_0 + t_1(2 \cos \xi \cos \eta + \cos 2\xi) + t_2(2 \cos 3\xi \cos \eta + \cos 2\eta) + t_3(2 \cos 5\xi \cos \eta + \cos 4\xi) + t_4(2 \cos 2\xi \cos 2\eta + \cos 4\xi) + t_5(2 \cos 3\eta \cos 3\xi + \cos 6\xi),$$

with $\xi = \frac{1}{2}k_x a$ and $\eta = \frac{\sqrt{3}}{2}k_y a$ and $a$ is the lattice spacing. The hopping parameters take the following values (in meV):

<table>
<thead>
<tr>
<th></th>
<th>$\xi_0$</th>
<th>$t_1$</th>
<th>$t_2$</th>
<th>$t_3$</th>
<th>$t_4$</th>
<th>$t_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>band 1</strong></td>
<td>10.9</td>
<td>86.8</td>
<td>139.9</td>
<td>29.6</td>
<td>3.5</td>
<td>3.3</td>
</tr>
<tr>
<td><strong>band 2</strong></td>
<td>203.0</td>
<td>46.0</td>
<td>257.5</td>
<td>4.4</td>
<td>-15.0</td>
<td>6.0</td>
</tr>
</tbody>
</table>

A magnetic impurity embedded in NbSe$_2$ hybridizes with both bands and can potentially give rise to two Shiba in-gap states. Let us consider both bands separately. For most values of parameters characterizing the magnetic impurity, we find that **band 1** gives a more isotropic Shiba state with a much smaller spatial extension. This is due to the fact that both bands are quite different. Indeed, band 1 has a deeper saddle point than band 2 and is therefore more isotropic around the Fermi surface. As shown in Eq. (5), the contributions to the Shiba wave function come mainly from regions where the energy is near the superconducting gap. Therefore, band 2 will provide more states near the gap edge to the Shiba wave function. These states shall be responsible of the longer spatial extension of the Shiba state associated with band 2 and also of its spatial anisotropy. Since we are interested in long-ranged Shiba states to reproduce the experimental data, we thus focus on **band 2**. Fig. 4 presents the results obtained on a lattice of size $N \times M = 500 \times 500$ with a superconducting gap $\Delta = 1\text{meV}$ for different values of $JS/2$ and $K$ using band 2. Fig. 5 shows the same calculation but using band 1.
**S5: ANALYTICAL SOLUTION**

In the continuum limit, eq. 5 transforms into

\[
\psi(r) = \int \frac{d\mathbf{k}}{(2\pi)^d} e^{i\mathbf{k}\cdot r} \left[ e^{-\frac{JS}{2} \mathbf{1}_{\mathbf{1}} + K \tau_z} \right] \left[ E + \xi_k \tau_z + \Delta \tau_z \right] \psi(r_{\text{imp}}),
\]

(7)
where \( d \) is the dimensionality of the system. Assuming a constant density of states on the range of the superconducting gap, we can solve \([6, 8]\) Eq. (7) with \( r = r_{\text{imp}} \) as:

\[
\{ \mathbb{1} - \frac{\alpha + \beta \tau_z}{\sqrt{\Delta^2 - E^2}} [E + \Delta \tau_z] \} \psi(r_{\text{imp}}) = 0
\]

(8)

where \( \alpha = \frac{\pi \nu_0 \beta S}{2} \) and \( \beta = \pi \nu_0 K \) and \( \nu_0 \) is the density of states at the Fermi energy. The Shiba energy and the amplitude ratio of the wavefunctions on the impurity site therefore read as:

\[
E = \frac{\Delta - \frac{1 - \alpha^2 + \beta^2}{4\alpha^2 + (1 - \alpha^2 + \beta^2)^2}} \quad \frac{\psi_+(0)}{\psi_-(0)} = \frac{1 + (\alpha - \beta)^2}{\sqrt{4\alpha^2 + (1 - \alpha^2 + \beta^2)^2}}
\]

(9)

To solve completely Eq. (7) we follow Ref. \([6, 8]\). We need to compute these two integrals:

\[
f_0(r) = \int \frac{d k^d}{(2\pi)^d} \frac{e^{i k \cdot r}}{E^2 - \xi_k^2 - \Delta^2},
\]

(10)

and

\[
f_1(r) = \int \frac{d k^d}{(2\pi)^d} \frac{\xi_k e^{i k \cdot r}}{E^2 - \xi_k^2 - \Delta^2}.
\]

(11)

In order to obtain an analytical expression for the spatial evolution of the Shiba states, we make the assumption of an isotropic energy dispersion \( \xi_k = k^2/2m + \mu \) where \( \mu \) is the chemical potential. The result depends of the dimensionality \( d \). Let us detail both the 3D and 2D cases for completeness.

**Shiba state in a 3D system**

We change the integration variable to \( \xi_k \) and \( x = \cos \theta_k \) with the polar angle \( \theta \) measured relative to \( r \).

\[
f_0(r) = \frac{\nu_0}{2} \int d \xi_k \int_{-1}^{1} dx \frac{e^{i k r x}}{E^2 - \xi_k^2 - \Delta^2},
\]

(12)
We first perform the integral on $\xi_k$ by linearizing $k$ with $k(\xi) = k_F + \xi / \hbar v_F$,

$$f_0(r) = -\frac{\nu_0 \pi}{2\sqrt{\Delta^2 - E^2}} \int_{-1}^{1} dx e^{ik_F r x} e^{-kSr|x|},$$

(13)

where $k_S = \sqrt{\Delta^2 - E^2 / \hbar v_F}$. This gives

$$f_0(r) = -\frac{\nu_0 \pi}{\sqrt{\Delta^2 - E^2}} e^{-kSr} \frac{k_F \sin k_F r - k_S r \cos k_S r - kSr}{(k_F)^2 + (k_S)^2}. $$

(14)

Finally by the assumption $k_F >> k_S$ we find:

$$f_0(r) = -\frac{\nu_0 \pi}{\sqrt{\Delta^2 - E^2}} e^{-kSr} \frac{k_F r \sin k_F r}{k_F r}. $$

(15)

The second integral reads:

$$f_1(r) = \frac{\nu_0}{2} \int d\xi_k \int_{-1}^{1} dx \frac{\xi_k e^{ikr x}}{E^2 - \xi_k^2 - \Delta^2 \omega_D^2 + \xi_k^2}. $$

(16)

We have incorporated the Debye frequency $\omega_D$ as a UV cut-off, to ensure the convergence of the integral [6]. In the same way we first perform the integral on $\xi_k$,

$$f_1(r) = \frac{i\nu_0 \pi}{2 \Delta^2 - E^2 - \omega_D^2} \int_{-1}^{1} dx \frac{x}{|x|} e^{ikr x} (e^{-kSr|0|} - e^{r|x|/\omega_D / \hbar v_F})$$

(17)

and then on $x$

$$f_1(r) = \pi \nu_0 \mathbb{R}\left[\frac{e^{ikF r e^{-kSr}}(-ikF r + i\frac{\omega_D r}{\hbar v_F}) + ie^{ikF r e^{-\omega_D r / \hbar v_F}}(kF r + ikSr) + (k_S - \frac{\omega_D r}{\hbar v_F})}{(-ikF r + kSr)}\right]. $$

(18)

Now we compute the asymptotic limit and suppose $k_F >> \frac{\omega_D r}{\hbar v_F} >> 1$ and $k_F >> k_S$. This gives:

$$f_1(r) \approx \pi \nu_0 e^{-kSr} \frac{\cos k_F r}{k_F r}. $$

(19)

**Integral in 2D system**

We proceed in the same way for the 2D case:

$$f_0(r) = \frac{\nu_0}{2\pi} \int d\xi_k \int_{0}^{2\pi} d\theta \frac{e^{ikr \cos \theta}}{E^2 - \xi_k^2 - \Delta^2}, $$

(20)

$$f_1(r) = \frac{\nu_0}{2\pi} \int d\xi_k \int_{0}^{2\pi} d\theta \frac{\xi_k e^{ikr \cos \theta}}{E^2 - \xi_k^2 - \Delta^2}. $$

(21)

We first perform the integral on $\xi_k$ and then on $\theta$:

$$f_0(r) = -\frac{\pi \nu_0}{\sqrt{\Delta^2 - E^2}} \mathbb{R}[J_0(kF r + i kSr) + iH_0(kF r + i kSr)], $$

(22)

$$f_1(r) = \pi \nu_0 \mathbb{R}[J_0(kF r + i kSr) + iH_0(kF r + i kSr)], $$

(23)

where $J_0(r)$ and $H_0(r)$ are the Bessel and the Struve function of order 0. These results are in agreement with [7]. Here again we compute the asymptotic limit assuming $k_F >> k_S$, which provides

$$f_0(r) \approx -\frac{\pi \nu_0}{\sqrt{\Delta^2 - E^2}} \sqrt{\frac{2}{\pi k_F r}} \cos(k_F r - \pi / 4)e^{-kSr}, $$

(24)

$$f_1(r) \approx \pi \nu_0 \sqrt{\frac{2}{\pi k_F r}} \sin(k_F r - \pi / 4)e^{-kSr} + \frac{2\nu_0}{k_F r}. $$

(25)

In the regime where we can neglect the last term of $f_1(r)$, $f_1(r) \approx \sqrt{\frac{2}{\pi k_F r}} \sin(k_F r - \pi / 4)e^{-kSr}$. 
Eigenstates

By introducing the angle $\delta$ defined by $\tan \delta^\pm = (K\nu_0 \pm \nu_0 JS/2)$, the equations become simpler and more compact. The Shiba energy is then given by $E = \Delta \cos(\delta^+ - \delta^-)$. We can show easily with the relation $\frac{\psi_+(0) \cos(\delta^-)}{\psi_-(0) \cos(\delta^+)} = 1$ that the asymptotic forms of the eigenstates are given by

$$\psi_\pm(r) = \frac{1}{\sqrt{N}} \sin(k_F r + \delta^\pm) e^{-\Delta \sin(\delta^+ - \delta^-) r/\hbar v_F}, \quad (26)$$

for the 3D case as found by Rusinov [8], and

$$\psi_\pm(r) = \frac{1}{\sqrt{N} \pi k_F r} \sin(k_F r - \frac{\pi}{4} + \delta^\pm) e^{-\Delta \sin(\delta^+ - \delta^-) r/\hbar v_F}, \quad (27)$$

for the 2D case. $N$ is a normalization factor defined by $1 = \int \frac{dk}{(2\pi)r} |\psi_+(k)|^2 + |\psi_-(k)|^2$. The comparison between the 2D case and 3D case is presented on Figs. 6

**FIG. 6: A. (B.) Asymptotic behavior of the Shiba bound states for the 2D (3D) case for electron like (red) and hole like (green) states. C. (D.) Spatial and energy evolution of the Shiba bound states with a thermal broadening corresponding to the experimental temperature of the sample for the 2D (3D) case. These figures were obtained for Shiba energies $E_{Shiba} = \pm 0.2\Delta$ while $k_F$ was chosen as the best fit to the experimental data.**

**S6: ASYMPTOTIC BEHAVIOR**

The calculation performed in section S5 of the supplementary materials provides an asymptotic law for the angularly integrated density of states. We were able to fit for both positive and negative energy peaks the decrease of the spectral weight with a power law in $1/r$ corresponding to the 2D case (Fig. 7). This behavior justifies a posteriori our 2D approximation of the NbSe$_2$ band structure.
FIG. 7: a. Hole like states spatial dependance angularly integrated. b. Same for electron like states. The black dots are the experimental points and the red dashed lines are the power law fits calculated ignoring the first points directly on top of the magnetic impurities in order to match the asymptotic assumption made in the calculation.

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