Supporting Information: Origin of subgap states in normal-insulator-superconductor van der Waals heterostructures

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I. FABRICATION AND MEASUREMENT

The normal-insulator-superconductor (NIS) type planar tunnel junctions are fabricated by dry stacking of MoS2 (3 – 5 layers) or hBN (3 layers) on NbSe2 crystals (~3 nm –20 nm). Polycarbonate (PC) backed by PDMS and glass is used for the standard pickup method. The stacking is performed in a glovebox in N2 atmosphere with H2O and O2 levels below 1 ppm. PC is dissolved in dichloromethane. While MoS2 or hBN act as the tunnel barrier as well as prevent NbSe2 from oxidation during device processing the exposure to the ambient is minimised during device processing. Moreover we encapsulate thin NbSe2 (~ 3 nm) from both sides to prevent degradation. Nearly all devices also contain a graphite crystal transferred over NbSe2, which acts as an ohmic contact to NbSe2. Normal contact regions are defined by ebeam lithography and Ti/Au (5 nm/50 nm) is deposited by ebeam evaporation to create the tunnel junctions. The area of the tunnel junctions is typically ~ 1 µm² to 3 µm², unless stated otherwise. All details of device parameters can be found in the device table at the end of the Supporting Information (SI).

The measurements were performed in a 3He fridge at a base temperature of ~ 250 mK. The electrical lines are filtered by using pi-filters at the breakout box and tapeworm filters at the cold finger. A small ac voltage (Vac < kB T, where kB is the Boltzmann constant and T is the cryostat temperature) is added to the biasing dc voltage V using a transformer and the lockin amplifier.
records the output current via an external current-voltage amplifier. Due to a cryostat installation error the actual magnetic fields may be smaller by up to 10% than reported here.

II. TUNNEL SPECTRA FITTING

In the main text we presented a fit of the tunnel spectra with simple BCS-type density of states, shown in Figure 1b also reproduced here in Figure SIa. However, the tunnel spectra of NbSe$_2$ is known to exhibit features that deviate from the simple BCS model (an isotropic, single gap). Other models have been employed to fit the tunnel spectra, and two important ones are 1) The two-band model [1, 2], for which a fit is shown in Figure SIb and 2) the anisotropic-gap (single gap) model [3] with a fit in Figure SIc. The temperature for all fits is fixed to the measurement temperature, $T = 255$ mK. In our view the two band model presents the most consistent picture, where the superconductivity in thicker NbSe$_2$ is thought to arise from multiple bands. With the layer number decreasing in NbSe$_2$ the superconducting gap approaches a single gap model and is consistent with bandstructure calculations. In contrast it is hard to justify the change of anisotropy as the NbSe$_2$ becomes thinner.

\[ [E_n, \gamma, \Delta, A] = [E_n, 0.045, 1.143, 0.148] \]

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\[ \Delta = 1.0 \text{ meV}, \Gamma = 0.11 \text{ meV} \]

\[ \Delta = 1.14 \text{ meV}, \Gamma = 0.045 \text{ meV} \text{ and } A = 0.15. \]

\[ \Delta_1 = 1.1 \text{ meV, } \Gamma_1 = 0.08 \text{ meV, } \Delta_2 = 0.9 \text{ meV, } \Gamma_2 = 0.08 \text{ meV} \text{ and } N_1/N_2 = 0.6. \]
III. TEMPERATURE DEPENDENCE OF THE TUNNEL SPECTRA

Here we highlight the role of superconductivity by showing temperature dependent tunnel spectra. The tunnel spectra exhibits broadening with temperature, as shown in the differential conductance map in Figure S2(a). The superconducting gap is no longer visible for $T \geq 4.4$ K and is reasonable for a thin ($\sim 3$ nm) NbSe$_2$. In addition, the subgap excitations visible at a base temperature $T = 270$ mK are no longer visible at $T = 1.5$ K, as shown in Figure S2(b). Similarly, for another device D21, shown in Figure S2(c), the subgap excitations are no longer visible at a larger temperature $T = 4$ K, and the tunnel spectrum exhibits thermal broadening.

FIG. S2: Temperature dependence of the tunnel spectra. (a) Differential conductance for device D10 as a function of voltage bias $V$ and temperature $T$, starting at $T = 1.43$ K. (b) Differential conductance measurements for device D10 show that the thermal broadening at $T = 1.5$ K is large enough that the subgap excitations are not visible when compared to $T = 270$ mK. (c) Differential conductance measurements for device D21 at $T = 270$ mK and $T = 4$ K.

IV. SECOND DERIVATIVE

Figure S3 demonstrates the upper branch of the doublet presented in Figure 2(c) of the main text. For this, the second derivative of the differential conductance with respect to the bias voltage was taken. In the main text we indicate bias voltage as $V$, here, bias voltage is indicated both as $V_b$ and $V$. 
FIG. S3: 2nd derivative of the differential conductance with respect to the bias voltage. Here $G$ is normalized conductance. Besides branches of doublets which are possible to see in the main text, the second derivative shows clearer the upper branch of the doublet at the positive bias voltage.

V. ADDITIONAL SUBGAP SPECTRA 1

While measuring in the wide range of magnetic field (Figure S4 and Figure S5), we take care of conductance jumps due to vortices by shifting $dI/dV$. The shift was done such that at all magnetic field values, the conductance at $V_b = 0$ has the same value.
FIG. S4: Magnetic field evolution of the subgap excitations. This is another example of the transition of the ground state from singlet to doublet under in-plane magnetic field measured for the device D21, tunnel junction no.10. (a) Colour map of $\frac{dI}{dV}$ as a function of in-plane magnetic field $B_\parallel$ and bias voltage $V_b$. (b) Shifted differential conductance curves for the same tunnel junction as in (a). The magnetic field step size of the curves is 0.5 T.
VI. ADDITIONAL SUBGAP SPECTRA 2

FIG. S5: Magnetic field evolution of the subgap excitations, device D21, tunnel junction no.13. (a) Colour map of dI/dV as a function of in-plane magnetic field $B_{\parallel}$ and bias voltage $V_b$. (b) Shifted differential conductance curves for the same tunnel junction as in (a). The magnetic field step size of the curves is 0.5 T. At $B_{\parallel} = 9$ T, the full width at half maximum (FWHM) is around 0.5 meV. Such a wide peak hinder us to distinguish if the lines cross as in Figure S4a or if the dI/dV peak sticks to $V_b=0$ above 6 T.

VII. DEVICE DETAILS

The table in this section lists the details of all measured tunnel junctions, particularly geometrical parameters and the suppression factor of the superconducting gap $G_N/G_0$. In the column "Figure", we indicated in what figures the junction was presented. The main focus is on the type of ground state and its evolution under an in-plane magnetic field (g-factor).

The cases of the singlet ground state, a doublet ground state and accidental degeneracy are shown in the main text in Figure 2c, Figure 3a and Figure 3b respectively. The tunnel junctions for which either the magnetic dependence of the subgap excitations was not studied or the ground state is ambiguous, as in Figure S6a have been categorised as 'Unknown' (ground state). The tunnel junctions for which subgap excitations were not visible, as in Figure S6b have been categorised as 'None'.
A count of the ground states shown in Figure S7 summarized our measurements. More than half of tunnel junctions show subgap excitations, however many of them do not show clear behaviour under an in-plane magnetic field or suppress under a small magnetic field. From the behaviour of the rest of the tunnel junctions, we believe six tunnel junctions have singlet ground state, one doublet, and four tunnel junctions show accidental degeneracy of a doublet and a hybridized singlet states.

FIG. S6: Additional definitions for the subgap ground state categories. (a) Tunnel spectra when the subgap ground state cannot be determined are categorised as 'Unknown'. Shown is an example of the subgap features that have a vanishing g-factor for junction 15 device D10. (b) Tunnel spectra where the subgap features are not visible are categorised as 'None' for junction 17 device D10.
FIG. S7: Count of ground states of observed in-gap Andreev bound states

REFERENCES

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[2] Noat, Y., Silva-Guillén, J. A., Cren, T. et al. Quasiparticle spectra of 2H – NbSe$_2$: Two-band superconductivity and the role of tunneling selectivity. Phys. Rev. B 92, 134510 (2015)

[3] Khestanova, E., Birkbeck, J., Zhu, M. et al. Unusual Suppression of the Superconducting Energy Gap and Critical Temperature in Atomically Thin NbSe$_2$. Nano Letters 18, 2623-2629 (2018)
| Device | Junction | NbSe<sub>2</sub> thickness, nm | Tunnel barrier, layers (L) | Area of Tj, um<sup>2</sup> | G<sub>N</sub>/G<sub>0</sub> | Ground state | g-factor | Comments | Figure |
|--------|----------|-----------------------------|-------------------------|-----------------------|----------------|--------------|----------|----------|--------|
| D10    | 10       | 3                           | 3L MoS<sub>2</sub>      | 3.2                   | 11             | Singlet      | 0.70     |          | 2a, 2c, S3 |
|        | 15       | 3                           | 4L MoS<sub>2</sub>      | 1.1                   | 49             | Unknown      | 0.00     | Subgap states at the gap edge | 2a, S6(a) |
|        | 16       | 7                           | 2L MoS<sub>2</sub>      | 2.6                   | 4              | Singlet      | 0.70     | Approximate g factor | 2a |
|        | 17       | 7                           | 4L MoS<sub>2</sub>      | 2.7                   | 400            | None         |          |          | 2a, S6(b) |
| D14    | 1        | 12                          | 4L MoS<sub>2</sub>      | 4                     | 63             | Unknown      |          | on NbSe<sub>2</sub> edge | 3c |
|        | 5        | 12                          | 4L MoS<sub>2</sub>      | 2.4                   | 328            | Singlet      | 0.80     | Anticrossing like feature | 3a |
|        | 7        | 12                          | 4L MoS<sub>2</sub>      | 3.5                   | 100            | Doublet      | 0.64     | Higher excitation has a vanishing g-factor | 3b |
|        | 14       | 5                           | 3L MoS<sub>2</sub>      | 1.3                   | 1              | Unknown      |          | On NbSe<sub>2</sub> edge | 3a |
|        | 15       | 10                          | 3L MoS<sub>2</sub>      | 2.3                   | 24             | Unknown      |          |          | 3a |
|        | 16       | 10                          | 3L MoS<sub>2</sub>      | 2.4                   | 4              | Unknown      |          |          | 3a |
|        | 17       | 10                          | 3L MoS<sub>2</sub>      | 4.1                   | 3              | Accidental degeneracy | 1.70 |          | 3a |
|        | 18       | 10                          | 3L MoS<sub>2</sub>      | 4.2                   | 4              | Unknown      | 0.00     |          | 3a |
|        | 19       | 10                          | 3L MoS<sub>2</sub>      | 1.3                   | 44             | Unknown      |          |          | 2f black |
| D19    | 3        | 7                           | 3L hBN                  | 10                    | 826            | None         |          |          | 2f black |
|        | 5        | 7                           | 3L hBN                  | 9.8                   | 807            | None         |          |          | 2f red |
|        | 7        | 7                           | 3L hBN                  | 10                    | 1563           | None         |          |          | 2f blue |
|        | 10       | 7                           | 3L hBN                  | 10                    | 571            | None         |          |          | 2f green |
|        | 11       | 7                           | 3L hBN                  | 10                    | 760            | None         |          |          | 2f violet |
|        | 16       | 7                           | 3L hBN                  | 12.2                  | 500            | None         |          |          | 2f yellow |
| D20    | 1        | 20                          | 3L MoS<sub>2</sub>      | 2.7                   | 300            | Unknown      |          | NbSe<sub>2</sub> edge isolated by MoS<sub>2</sub> | 2e black |
|        | 2        | 20                          | 3L MoS<sub>2</sub>      | 2.7                   | 150            | Unknown      |          | NbSe<sub>2</sub> edge isolated by MoS<sub>2</sub> | 2e black |
|        | 3        | 20                          | 3L MoS<sub>2</sub>      | 2.3                   | 167            | Unknown      |          | NbSe<sub>2</sub> edge isolated by MoS<sub>2</sub> | 2e black |
|        | 4        | 20                          | 3L MoS<sub>2</sub>      | 2.5                   | 80             | Accidental degeneracy | 0.55 |          | 2e black |

Details of all measured tunnel junctions (53 junctions)
| Device | Junction | NbSe<sub>2</sub> thickness, nm | Tunnel barrier, layers (L) | Area of T<sub>j</sub> um<sup>2</sup> | G<sub>N</sub>/G<sub>0</sub> | Ground state | g-factor | Comments | Figure |
|--------|----------|-----------------------------|-------------------------|----------------|----------------|-------------|---------|----------|--------|
| D20    | 5        | 20                          | 3L MoS<sub>2</sub>      | 2.3            | 10             | None        |         |          |        |
|        | 6        | 20                          | 3L MoS<sub>2</sub>      | 3.1            | 27             | Singlet     | 0.45    | Doublet upper branch not visible |        |
|        | 7        | 20                          | 3L MoS<sub>2</sub>      | 3              | 242            | None        |         |          |        |
|        | 8        | 20                          | 3L MoS<sub>2</sub>      | 2.9            | 80             | None        |         |          |        |
|        | 9        | 10                          | 3L MoS<sub>2</sub>      | 1.8            | 131            | None        |         |          |        |
|        | 10       | 10                          | 3L MoS<sub>2</sub>      | 1.8            | 410            | None        |         |          |        |
|        | 11       | 10                          | 3L MoS<sub>2</sub>      | 3.2            | 141            | None        |         |          |        |
|        | 12       | 10                          | 3L MoS<sub>2</sub>      | 1.8            | 8              | None        |         | V-shaped gap |        |
|        | 13       | 10                          | 3L MoS<sub>2</sub>      | 2.5            | 2              | Unknown     |         | V-shaped gap |        |
|        | 14       | 10                          | 3L MoS<sub>2</sub>      | 2.9            | 104            | None        |         |          |        |
|        | 16       | 10                          | 3L MoS<sub>2</sub>      | 3.5            | 344            | None        |         |          |        |
| D21    | 10       | 8                           | 4L MoS<sub>2</sub>      | 1.52           | 408            | Singlet     | 0.75    | 1d, S4   |        |
|        | 13       | 6                           | 4L MoS<sub>2</sub>      | 1.1            | 425            | Singlet     | 0.67    | S5       |        |
|        | 12       | 8                           | 4L MoS<sub>2</sub>      | 0.71           | 150            | Accidental degeneracy | 0.64 | On NbSe<sub>2</sub> edge | 3b |
|        | 6        | 8                           | 4L MoS<sub>2</sub>      | 1.96           | 554            | Accidental degeneracy |         |          |        |
|        | 7        | 8                           | 4L MoS<sub>2</sub>      | 1.6            | 587            | Unknown     |         |          | S2(c) |
|        | 9        | 8                           | 4L MoS<sub>2</sub>      | 1.96           | 303            | Unknown     |         |          |        |
|        | 16       | 6                           | 4L MoS<sub>2</sub>      | 1.25           | 630            | None        |         |          |        |
|        | 11       | 8                           | 4L MoS<sub>2</sub>      | 1.56           | 650            | Unknown     |         |          |        |
|        | 20       | 6                           | 4L MoS<sub>2</sub>      | 1.4            | 920            | Unknown     |         |          |        |
|        | 14       | 6                           | 4L MoS<sub>2</sub>      | 1.49           | 271            | None        |         |          |        |
| MN1    | 7        | 11                          | 3L MoS<sub>2</sub>      | 1.56           | 826            | Unknown     |         |          | 1b, 1c, S1 |
|        | 17       | 11                          | 3L MoS<sub>2</sub>      | 0.68           | 6              | Unknown     |         | On NbSe<sub>2</sub> edge | 2d blue |
| MN4    | 16       | 8                           | 5L MoS<sub>2</sub>      | 3              | 1013           | Unknown     |         |          |        |
|        | 15       | 8                           | 5L MoS<sub>2</sub>      | 8              | 54             | Unknown     |         | on NbSe<sub>2</sub> crystal step |        |
|        | 14       | 8                           | 4L MoS<sub>2</sub>      | 9.1            | 334            | Unknown     |         | on NbSe<sub>2</sub> crystal step |        |
| Device | Junction | NbSe$_2$ thickness, nm | Tunnel barrier, layers (L) | Area of Tj, um$^2$ | $G_N/G_0$ | Ground state | g-factor | Comments | Figure |
|--------|----------|------------------------|---------------------------|--------------------|-----------|--------------|----------|----------|--------|
| MN4    | 11       | 10                     | 4L MoS$_2$                | 4.6                | 359       | Unknown      |          |          |        |
|        | 3        | 14                     | 5L MoS$_2$                | 3.5                | 327       | Unknown      | on NbSe$_2$ edge |          |        |
|        | 9        | 10                     | 5L MoS$_2$                | 6.2                | 52        | Unknown      | on NbSe$_2$ edge | 2d black and red |        |
|        | 17       | 8                      | 5L MoS$_2$                | 3.64               | 145       | Unknown      | Subgap states at the gap edge |          |        |