Controlling correlations in NbSe$_2$ via quantum confinement

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Transition metal dichalcogenides (TMDC) are a rich family of two-dimensional materials displaying a multitude of different quantum ground states. In particular, d$_3$ TMDCs are paradigmatic materials hosting a variety of symmetry broken states, including charge density waves, superconductivity, and magnetism. Among this family, NbSe$_2$ is one of the best-studied superconducting materials down to the monolayer limit. Despite its superconducting nature, a variety of results point towards strong electronic repulsions in NbSe$_2$. Here, we control the strength of the interactions experimentally via quantum confinement effects and use low-temperature scanning tunneling microscopy (STM) and spectroscopy (STS) to demonstrate that NbSe$_2$ is in strong proximity to a correlated insulating state. This reveals the coexistence of competing interactions in NbSe$_2$, creating a transition from a superconducting to an insulating quantum correlated state by confinement-controlled interactions. Our results demonstrate the dramatic role of interactions in NbSe$_2$, establishing NbSe$_2$ as a correlated superconductor with competing interactions.

Niobium dichalcogenides, and in particular NbSe$_2$ is well-known to be a paradigmatic superconducting two-dimensional material and it realizes Ising superconductivity at the monolayer limit. Due to its superconducting nature, NbSe$_2$ has been considered being a metal where Coulomb repulsions play a marginal role, and its superconducting state arising from conventional electron-phonon coupling. Indeed, the emergence of charge density wave states is usually attributed to soft-phonon modes, so that symmetry broken states are not related with strong Coulomb interactions.

Despite the apparent marginal role of Coulomb repulsion in NbSe$_2$, a related compound in the dichalcogenide family, VSe$_2$, is known to be a strongly correlated material, with competing correlated states including a potential magnetic Mott insulating state. The chemical similarity between NbSe$_2$ and VSe$_2$, contrasted with their dramatically different electronic properties, motivates the question of whether NbSe$_2$ exhibits a strongly correlated superconducting state, in contrast with the originally assumed weakly interacting scenario. In that regard, theoretical calculations have shown that NbSe$_2$ is close to a Mott insulating transition to a ferromagnetic state. These results suggest that competing interactions coexist in NbSe$_2$ system, and in particular suggest the possibility of the superconducting state coexisting with strong Coulomb interactions.

Here, we experimentally demonstrate that NbSe$_2$ is in proximity to a correlated insulating state, by controlling the strength of the electronic interactions by quantum confinement effects. In particular, we show that for NbSe$_2$ of size several times the coherence length, repulsive electronic interactions create a phase transition from a superconducting to a correlated insulating state. This behavior is rationalized from a competing interaction scenario (Fig. 1a), in which attractive electron-phonon interactions compete with strongly repulsive Coulomb interactions. The electron-phonon interactions that give rise to a superconducting ground state do not depend on the system size, and will dominate if the system size is increased sufficiently (Fig. 1b). On the other hand, repulsive Coulomb interactions are strongly dependent on the system size ($U \propto 1/L$) and will drive the system into Coulomb-gapped, correlated state as the system size is decreased. We test this behavior experimentally by tuning the size of the NbSe$_2$ islands and use low-temperature...
FIG. 2. Structure and local density of states of monolayer NbSe$_2$. a, Top and side view schematics of monolayer NbSe$_2$. b, Large-scale STM image of monolayer NbSe$_2$ on HOPG showing a large variation of island sizes. Scale bar, 100 nm. c, Atomic resolution image of monolayer NbSe$_2$ showing 3 × 3 charge density wave modulation. Scale bar, 2 nm. d, Variation of the superconducting gap with island size. e, Variation of the Coulomb gap with island size. f, Evolution of the gap magnitude extracted from the tunneling spectra as a function of the island size showing a transition from Coulomb gap-like to superconducting spectra as the size is increased. The shape of the measured spectrum is indicated by the different symbols: blue triangles and red circles for the spectra exhibiting Coulomb- and SC-type gaps, respectively.

scanning tunneling microscopy (STM) and spectroscopy (STS) to measure the type and magnitude of the resulting energy gap. Our results provide a quantitative experimental bound on the strength of repulsive interactions of NbSe$_2$, highlighting a non-trivial impact of correlations in superconducting dichalcogenides.

We grow a sub-monolayer layer of NbSe$_2$ (Fig. 2a) on a highly-oriented pyrolytic graphite (HOPG) substrate. By adjusting the growth conditions (see Methods for details), we achieve a sample with a wide variety of island sizes and their relative separations. This creates an ideal platform to study the effects of quantum-confinement enhanced correlations. The island sizes vary between a few hundred nm$^2$ to several tens of thousands of nm$^2$ (lateral sizes a few tens of nm to several hundreds of nm). Fig. 2b shows an STM image of a representative area (500 × 500 nm$^2$), where this size variation in individual monolayer islands is apparent. Each individual island has atomically sharp step edges and show the well-known 3 × 3 charge density wave modulation similar to extended monolayer NbSe$_2$ (Fig. 2c). We have characterized the electronic properties of each individual island by carrying out spatially resolved tunneling conductance (dI/dV) measurement (details in the Methods section). Typical examples of the dI/dV spectra are shown in Figs. 2d and e. The spectra can be divided into two groups based qualitative differences. Islands having sizes 4200 nm$^2$ and above shows density of states consistent with BCS-like behaviour having particle-hole symmetric coherence peaks (Fig. 2d) indicating the presence of phase-coherent Cooper pairs. On the other hand, islands having sizes 2700 nm$^2$ and below have distinctive particle-hole asymmetric density of states (Figure 2e) with no coherence peaks. Such asymmetric differential conductance is typical of inelastic steps associated to correlated Coulomb excitations. Furthermore, the magnitude of the energy gap in these islands monotonically increase with decreasing island size (Fig. 2f). This behaviour is consistent with the presence of a Coulomb gap in the small islands, where the repulsive Coulomb interaction dominates over phonon-mediated attractive interactions. On the other hand, the BCS-shaped superconducting gaps in the islands in Fig. 2d are independent of island size (Fig. 2f) as the electron-phonon coupling strength does not depend on the system size.

The previous phenomenology can be easily rationalized with a many-body low energy model. Since the full quantum many-body system for an nm-sized flake cannot
be exactly solved, we will focus on the instability of the
lowest energy $2n$ single-particle eigenstates of the NbSe$_2$
flake $\Psi_{i,s}$, with $i = 1, \ldots, n$ the state number and $s = \uparrow, \downarrow$
the spin quantum number. These states closest to the
Fermi energy will be the ones most impacted by interactions,
and therefore the fundamental physics of the system
can be captured by projecting electronic interactions
in this manifold. For the sake of concreteness, we take
interactions $SU(2)$ symmetric and constant on the Fermi
surface manifold. In particular, we take projected elec-
tronic interactions partitioned into intra-orbital repulsive
ones $U$ (of Coulomb origin) and inter-orbital attractive
ones $V$ (of electron-phonon origin). Furthermore, due
to the existence of nearby large superconducting islands,
the low energy states will feel a superconducting proximity
effect with a value depending on the distance to the
closest big superconducting island. We parametrize this
effect with $\Delta$. The half filling of the low energy manifold
is enforced by $\mu$. The low energy many-body Hamiltonian
takes the form.

$$
\mathcal{H} = \sum_i U \Psi_{i,\uparrow} \Psi_{i,\downarrow} \Psi_{i,\uparrow} \Psi_{i,\downarrow} - \sum_{i,j \neq i,s,s'} V \Psi_{i,s} \Psi_{i,s} \Psi_{j,s'} \Psi_{j,s'} + \mu \sum_{i,s} \Psi_{i,s} \Psi_{i,s} + \Delta \sum_{i} \Psi_{i,\uparrow} \Psi_{i,\downarrow} + \text{H.c.}
$$

(1)

The projected electron-phonon interaction $V$ is taken to be
independent on the system size, whereas the projected
Coulomb repulsive interaction $U$ will get enhanced as the
system size $L$ becomes smaller as $U = U_0 + \frac{C}{L}$
due to the long-range tail of Coulomb interactions. For such
a many-body Hamiltonian single-electron the density of
states can be computed as $A(\omega) = \sum\langle \Omega | \Psi_{i,s} \delta(\mathcal{H} - \omega - E_0) \Psi_{i,s} | \Omega \rangle$, where $E_0$ is the many-body energy and $| \Omega \rangle$
the many-body ground state. In particular, we show in
Fig. 3a the single-electron spectral function $A(\omega)$ as a
function of the system size $L$, where the transition be-
tween a Coulomb dominated gap $\epsilon_L$ to a superconducting
dominated one can be seen. For large system size
$L \to \infty$, the system shows a superconducting gap stem-
ing from the attractive interactions and pinned by the
superconducting proximity $\Delta$. Once the system size goes
below a critical value $L_C$, the nature of the excitation gap
$\epsilon_L$ changes, yet without a gap closing. The different
nature of the two gaps above and below the transition point
$L = L_C$ can be verified by computing the superconduct-
ing expectation value $\Delta = \langle \Psi_{i,\uparrow} \Psi_{i,\downarrow} \rangle$, showing that associa-
ted with the discontinuous jump as the size becomes
smaller, the superconducting order parameter suddenly
disappears (Fig. 3b). It is important to note that in the
absence of competing interactions, the transition between
the two gaped regimes would involve a gap closing in the
spectral function. The absence of such closing in our ex-
perimental data therefore provides a strong signature of
competing interactions. Due to the proximity of NbSe$_2$
to the phase transition point, it is expected that due
to an external perturbation, a critical system can drift
to different regions of the phase diagram. In particular,
increasing a superconducting proximity effect $\Delta$ would
push the system toward the superconducting gapped re-
gion. This can be verified as shown in Fig. 3c where it
can be seen that ramping up the superconducting prox-
imity pushes the system that originally has a correlated
gap towards a superconducting gap. We have verified
that the same behavior remains qualitatively unchanged
upon increasing the number of orbitals considered in the
many-body Hamiltonian.

We now check this proximity-induced phase transition
experimentally by comparing the spectra of different crit-
ical islands with different respective distances to a big
superconducting layer, probing whether the supercon-
ducting proximity effect transforms the correlated gap
into a superconducting one. We start by quantifying the
proximity effect in the NbSe$_2$/HOPG-system as shown in
Figs. 4a-c. Measuring $dI/dV$ spectra close to a SC NbSe$_2$
shows a proximity-induced gap on HOPG and tracking
the spectral evolution allows us to estimate the decay
length. Measuring the zero bias conductance from Fig. 4c
as a function of the distance from the NbSe$_2$ island edge
yields $\xi \approx 7$ nm.

We then proceed to show the effect of proximity in the
non-superconducting islands showing size-dependent

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3}
\caption{Correlated-superconductor transition} Electron spectral function as a function of the system size (a), and
induced superconductivity $\Delta$ as a function of the system size
(b). It is shown that a transition between the superconducting
to the correlated state takes place without gap closing. For
correlated flakes close to the phase transition, increasing the
superconducting proximity effect $\Delta$ can push the system to
the superconducting region as shown in panel (c). We took
$2n = 8$ for a-c, $U_0 = 2$ V and $L_C$ is the critical length for $\Delta_0 = 0.4$ V.
\end{figure}
Coulomb gaps. We selected 2 representative island sizes of 330 nm$^2$ and 650 nm$^2$. Here, the smaller of the islands is well into the Coulomb gapped regime, but the larger one is closer to phase transition determined in Fig. 2f. When each of these islands are not in proximity (∼20 nm) of any superconducting islands (Figs. 4d,e), they show particle-hole asymmetric Coulomb gap (Figs. 4d,e, blue lines). Island having size 650 nm$^2$ in proximity with a larger superconducting island shows a drastically different conductance with gap value comparable to the BCS gap observed in larger islands (Fig. 4e, red line) indicating that the proximity effect is sufficient to push the system into the superconducting phase. Strong particle-hole asymmetric feature indicates significant presence of correlation in this proximity-induced superconducting island. On the other hand, island having size 330 nm$^2$ in proximity with a larger superconducting island shows a complex spectra with no clear gap signature (Fig. 4d, red line) indicating that the proximity-induced Josephson coupling is not sufficient to overcome Coulomb repulsion to induce superconducting order in this island.

To summarize, we have demonstrated that NbSe$_2$ can be pushed to a correlated regime, driving a quantum phase transition from superconducting to a correlated gap. This transition is rationalized form the existence of competing interactions, in which the coexistence of attractive electron-phonon interactions, driving superconductivity, and repulsive Coulomb interactions, driving correlated insulating behavior, allow to dramatically change the nature of the ground state in NbSe$_2$ by slightly enhancing Coulomb interactions. The critical role of Coulomb interactions highlighted in our results suggest a potentially crucial impact of electronic correlations for the emergence of both charge density wave orders and superconductivity besides the typical electron-phonon driven scenarios. We finally showed that for correlated NbSe$_2$ samples close to the phase transition, superconducting proximity effect strongly impacts the ground state, pushing the system through the superconductor-correlated phase boundary. Ultimately, these results suggest that due to the close to critical behavior of NbSe$_2$ correlated states could be promoted in NbSe$_2$ by screening, chemical or twist engineering, putting forward $d^3$ chalcogenides as paradigmatic strongly correlated two-dimensional materials.

**METHODS**

Sub-monolayer NbSe$_2$ was grown by molecular beam epitaxy (MBE) on highly oriented pyrolytic graphite (HOPG) under ultra-high vacuum conditions (UHV, base pressure $\sim 1 \times 10^{-10}$ mbar). HOPG crystal was cleaved
and subsequently out-gassed at \( \sim 400^\circ C \). High-purity Nb and Se were evaporated from an electron-beam evaporator and a dual-filament low temperature Knudsen cell, respectively. The flux ratio of Nb to Se was controlled to be \( \sim 1 : 30 \). During the growth the substrate temperature was kept at \( \sim 330^\circ C \), and after the growth the sample was annealed at the same temperature for 1 hour. The growth speed was determined by checking the coverage of the as-grown samples by scanning tunneling microscopy (STM).

Subsequent to the growth, the sample was transferred to a low-temperature STM (Unisoku USM-1300) housed in the same UHV system. STM imaging and STS experiments were performed at \( T = 350 \) mK. STM imaging was performed in constant current mode. Differential conductance (\( dI/dV \)) spectra were measured using standard lock-in techniques sweeping the sample bias in an open feedback loop with rms bias modulation of 70 \( \mu V \) at a frequency of 873.7 Hz.

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