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Confinement-Engineered Superconductor to Correlated-Insulator Transition in a van der Waals Monolayer

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**ABSTRACT:** Transition metal dichalcogenides (TMDC) are a rich family of two-dimensional materials displaying a multitude of different quantum ground states. In particular, d3 TMDCs are paradigmatic materials hosting a variety of symmetry broken states, including charge density waves, superconductivity, and magnetism. Among this family, NbSe2 is one of the best-studied superconducting materials down to the monolayer limit. Despite its superconducting nature, a variety of results point toward strong electronic repulsions in NbSe2. Here, we control the strength of the interactions experimentally via quantum confinement and use low-temperature scanning tunneling microscopy (STM) and spectroscopy (STS) to demonstrate that NbSe2 is in close proximity to a correlated insulating state. This reveals the coexistence of competing interactions in NbSe2, 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 NbSe2, establishing NbSe2 as a correlated superconductor with competing interactions.

**KEYWORDS:** correlated insulator, superconductor, insulator to superconductor transition, monolayer niobium diselenide, scanning tunneling microscopy and spectroscopy

**Niobium dichalcogenides, and in particular NbSe2, is well-known to be a paradigmatic superconducting two-dimensional material, and it realizes Ising superconductivity at the monolayer (ML) limit.**1−3 Because of its superconducting nature, NbSe2 has been considered to be a metal where Coulomb repulsions play a marginal role and the superconducting state arises from conventional electron–phonon coupling.4 Indeed, the emergence of charge density wave states is usually attributed to soft-phonon modes, 5−10 so that symmetry broken states are not related with strong Coulomb interactions.

Despite the apparent marginal role of the Coulomb repulsion in NbSe2, related compounds in the dichalcogenide family show strong correlations.11−15 In particular, VSe2 is known to be a strongly correlated material16 with competing correlated states including a potential magnetic Mott insulating state.14,17−19 The chemical similarity between NbSe2 and VSe2 contrasted with their dramatically different electronic properties, motivates the question of whether NbSe2 exhibits a strongly correlated superconducting state, in contrast with the originally assumed weakly interacting scenario.20−23 In that regard, theoretical calculations have shown that NbSe2 is close to a Mott insulating transition to a ferromagnetic state.20−23 These results suggest that competing interactions coexist in NbSe2 system, and in particular suggest the possibility of the superconducting state coexisting with strong Coulomb interactions.

In this manuscript, we experimentally demonstrate that ML NbSe2 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 ML NbSe2 islands 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 (Figure 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 (Figure 1b). On the other hand, the repulsive Coulomb interactions are strongly dependent on the system size (U ∝ 1/L24−26) and will drive the system into a Coulomb-gapped, correlated state as the system size is decreased. This picture is complementary to the classical interpretation in terms of Coulomb blockade and completely...
analogous to the approach taken in, for example, interpreting the correlated insulating states in twisted bilayer graphene in terms of local repulsion. We test this behavior experimentally by tuning the size of NbSe$_2$ islands and using low-temperature 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 nontrivial impact of correlations in superconducting dichalcogenides.

**Experimental Superconducting-Correlated Transition.** We grow NbSe$_2$ (Figure 2a) on a highly oriented pyrolytic graphite (HOPG) substrate with a submonolayer coverage. By adjusting the growth conditions (see Supporting Information (SI) 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 hundreds of nm$^2$ to several tens of thousands of nm$^2$ (lateral sizes few tens of nm to several hundreds of nm, see SI for island size determination). Figure 2b shows a STM image of a representative area (500 × 500 nm$^2$), where this size variation of individual ML islands is apparent. Each individual island has atomically sharp edges and show the well-known 3 × 3 charge density wave (CDW) modulation similar to extended ML NbSe$_2$ (Figure 2c). While the data shown in Figure 2c was acquired on a NbSe$_2$ island with a lateral size of ∼92 nm (area 8400 nm$^2$), the CDW modulation persists down to islands sizes of <500 nm$^2$ (see SI). We characterize the electronic properties of each individual island by carrying out spatially resolved tunneling conductance (d$I$/d$V$) measurement (see Methods in SI for details). Typical examples of the d$I$/d$V$ spectra are shown in Figure 2d,e. The spectra can be divided into two groups based on qualitative differences. Islands with sizes 4200 nm$^2$ and above show density of states consistent with BCS-like behavior with particle-hole symmetric coherence peaks (Figure 2d), which indicate a presence of phase-coherent Cooper pairs. On the other hand, islands with sizes 2700 nm$^2$ and below have distinctive particle-hole asymmetric density of states (Figure 2e) with no coherence peaks. This transition occurs at a size range several times larger than the coherence length of NbSe$_2$ (∼7 nm, see below).

Such asymmetric differential conductance is typical of inelastic steps associated with correlated Coulomb excitations. Furthermore, the magnitude of the energy gap in these islands monotonically increases with decreasing island size.
(Figure 2f, the details of extracting the energy gap are given in the SI). This behavior is consistent with the presence of a Coulomb gap in 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 Figure 2d are independent of the island size (Figure 2f) as the electron–phonon coupling strength does not depend on the system size. The Coulomb gap and superconducting gaps can also be distinguished by their respective magnetic field-dependent behavior (see SI).

Disorder driven superconductor–insulator transition (SIT) cannot justify our data, since we observe that the SC gap remains practically constant with reducing island size. The data also suggests that disorder does not have a sizable impact besides a small renormalization of the density of states as given by the Altshuler-Aronov effect. The main source of disorder appears to be on the edges of the islands which show slightly different SC energy gap compared to the center of the island (see SI).

Theoretical Model for Competing Interactions. The previous phenomenology can be rationalized with a many-body low energy model. Many-body interactions are well-known to lead to Coulomb blockade effects in conventional superconductors, promoting intriguing phenomena arising from the interplay of pairing correlations and finite size effects. However, these phenomena have remained unexploited to probe many-body effects in correlated two-dimensional superconductors. Since the full quantum many-body system for a nanometer-sized island cannot be exactly solved, we will focus on the instability of the lowest energy $2n$ single-particle eigenstates of the NbSe$_2$ island $\Psi_n$ with $i = 1, \ldots, n$ as the state number and $s = \uparrow, \downarrow$ as 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 electronic interactions partitioned into orbital-repulsive ones $U$ (of Coulomb origin) and interorbital 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 $\mu$, and computed self-consistently for each $U$ and $V$. The low energy many-body Hamiltonian takes the form

$$H = \sum_i U \Psi_i \Psi_i^\dagger - \sum_{i,j} V \Psi_i \Psi_j \Psi_j \Psi_i^\dagger + \mu \sum \Psi_i \Psi_i^\dagger + H. c.$$  

The projected electron–phonon interaction $V$ is taken to be independent of the system size, whereas the projected Coulomb repulsive interaction $U$ will get enhanced as the system size $L$ becomes smaller as $U = U_0 + \frac{\omega}{L}$ due to the long-range tail of Coulomb interactions. The effective model is solved using exact diagonalization, projecting the electronic repulsion onto the lowest energy states and solving the projected Hamiltonian exactly. This is, of course, an approximate procedure when a finite number of states is considered, and we verified that our results are not qualitatively modified when including a higher number of orbitals. For such a many-body Hamiltonian the single-electron density of states can be computed as $A(\omega) = \sum_{i,n} \langle \Omega \Psi_i \Psi_i^\dagger \delta(\omega - E_0) \Psi_i \Psi_i^\dagger \rangle$, where $E_0$ is the many-body energy and $\Omega$ the many-body ground state.

We show in Figure 3a the single-electron spectral function $A(\omega)$ as a function of the system size $L$, where the transition between a Coulomb dominated gap $\epsilon_L$ to a superconducting dominated one can be seen. For large system size $L \rightarrow \infty$, the system shows a superconducting gap stemming from the attractive interactions and pinned by the superconducting proximity $\Delta$. It is worth noting that, as the system is finite, observing a sharp phase transition from zero to finite superconducting order requires a finite value of the proximity effect $\Delta$. 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 superconducting expectation value $\Delta = \sum \langle \Psi_i \Psi_i^\dagger \rangle$, showing that associated with the discontinuous jump as the size becomes smaller, the superconducting order parameter suddenly disappears (Figure 3b). We note that for small islands the observed spectra featuring a continuum of states above the gap are fundamentally different from the ones expected for systems with confined energy levels. The transition between the correlated gap for small islands and superconducting one for large islands is found to be of first order with a discontinuity on the gap. This is consistent with our experimental data and therefore strongly supports the competing interaction scenario.

Because of the proximity of NbSe$_2$ to the phase transition point, it is expected that an external perturbation can cause a critical system to drift to different regions of the phase diagram. In particular, increasing a superconducting proximity effect $\Delta$
would push the system toward the superconducting gapped region. This can be verified as shown in Figure 3c where it can be seen that ramping up the superconducting proximity pushes the system that originally has a correlated gap toward a superconducting gap. While this is shown for reduced range in Figure 3c, the very same mechanism applies in a broader range of L and \( \Delta \). We have verified that the same behavior remains qualitatively unchanged upon increasing the number of orbitals considered in the many-body Hamiltonian (shown in the SI).

It is well-known that 2H-NbSe\(_2\) exhibits charge-density wave order at low temperatures and the presence of Ising-type spin–orbit coupling might also have an effect on the observed behavior. However, by using a more detailed model incorporating these two effects (see SI), we can demonstrate that the observed phenomenology is a genuine Coulomb effect. Ising spin–orbit coupling leads to momentum dependent spin splitting in the Brillouin zone. As this perturbation respects time-reversal symmetry, it does not have a detrimental impact on the spin-singlet superconducting state. We start by quantifying the proximity effect in the NbSe\(_2\)/HOPG-system as shown in Figure 4a–c. Measuring \( \text{d}I/\text{d}V \) spectra close to a SC NbSe\(_2\) shows a proximity-induced gap on HOPG and tracking the spatial evolution allows us to estimate the decay length. Fitting the spatially dependent \( \text{d}I/\text{d}V \) in Figure 4b to Dynes equation, we extract the gap as a function of the distance from the NbSe\(_2\) island edge (Figure 4c). An exponential fitting of Dynes gap with distance yields \( \xi \approx 7 \) nm (see SI).

We then proceed to show the effect of proximity in the nonsuperconducting islands showing size-dependent Coulomb gaps. We selected two representative island sizes of 330 and 650 nm\(^2\) (Figure 4d,e, additional results on spatially resolved spectroscopy are shown in the SI). Here, the smaller of the islands is well into the Coulomb gapped regime, but the larger one is closer to phase transition determined in Figure 2f. When each of these islands are not in proximity (\( \sim 7 \) nm) to any superconducting islands (Figure 4d,e), they show particle-hole asymmetric Coulomb gap (Figure 4d,e, blue lines). Island with size 650 nm\(^2\) in proximity to a larger superconducting island shows a drastically different conductance with gap value comparable to the BCS gap observed in larger islands (Figure 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 relevant symmetry that could strongly impact the spin-singlet superconducting state.

**Proximity Induced Quantum Phase Transition.** On the basis of the previous results, we check this proximity-induced phase transition experimentally by comparing the spectra of different critical islands with different respective distances to a big superconducting island, probing whether the superconducting 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 Figure 4a–c. Measuring \( \text{d}I/\text{d}V \) spectra close to a SC NbSe\(_2\) shows a proximity-induced gap on HOPG and tracking the spatial evolution allows us to estimate the decay length. Fitting the spatially dependent \( \text{d}I/\text{d}V \) in Figure 4b to Dynes equation, we extract the gap as a function of the distance from the NbSe\(_2\) island edge (Figure 4c). An exponential fitting of Dynes gap with distance yields \( \xi \approx 7 \) nm (see SI).

We then proceed to show the effect of proximity in the nonsuperconducting islands showing size-dependent Coulomb gaps. We selected two representative island sizes of 330 and 650 nm\(^2\) (Figure 4d,e, additional results on spatially resolved spectroscopy are shown in the SI). Here, the smaller of the islands is well into the Coulomb gapped regime, but the larger one is closer to phase transition determined in Figure 2f. When each of these islands are not in proximity (\( \sim 7 \) nm) to any superconducting islands (Figure 4d,e), they show particle-hole asymmetric Coulomb gap (Figure 4d,e, blue lines). Island with size 650 nm\(^2\) in proximity to a larger superconducting island shows a drastically different conductance with gap value comparable to the BCS gap observed in larger islands (Figure 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

![Figure 4.](https://doi.org/10.1021/acs.nanolett.1c03491)
correlation in this proximity-induced superconducting island. The magnetic field-dependent behavior of proximitized island is also indicative of the presence of superconducting order (see SI). On the other hand, an island with a size of 330 nm² in proximity to a larger superconducting island shows a complex spectra with no clear gap signature (Figure 4d, red line), indicating that the proximity-induced Josephson coupling is not sufficient to overcome Coulomb repulsion to induce superconducting order in this island.

■ CONCLUSIONS

We have demonstrated that ML NbSe₂ can be pushed to a correlated regime, driving a quantum phase transition from superconducting to a correlated gap. This transition is rationalized from the existence of competing interactions, in which the coexistence of attractive electron–phonon interactions, driving superconductivity, and repulsive Coulomb interactions, driving correlated insulating behavior, allows to dramatically change the nature of the ground state in NbSe₂ by slightly enhancing the Coulomb interactions. The Coulomb gap observed in our system is inherently different from the single-particle gap observed in small metallic islands. The dI/dV spectra in the smallest NbSe₂ islands (Figure 2e) show a continuum of states above the gap rather than a discrete set of states, indicating many-body nature of the gap in our system. While it is possible to analyze our data using the Coulomb blockade model typically employed for 3D superconductors, it is worthwhile to note that these systems are weakly interacting being far from any Stoner instability and electron induced symmetry breaking, whereas NbSe₂ is in close proximity to correlated state which can be driven by perturbations such as strain. Also, the SIT mechanism observed here veers away from the traditional disorder-driven scenario. In comparison, similar SIT has been observed by controlling electronic interactions in twisted van der Waals multilayers.

The critical role of Coulomb interactions highlighted in our results suggests 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. Recent results show the presence of spin-fluctuations in ML NbSe₂ and nematic superconductivity in few layer NbSe₂ which are indicative of its proximity to correlated regime. We finally show that for correlated NbSe₂ 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 NbSe₂, correlated states could be promoted in NbSe₂ by screening, chemical, or twist engineering, putting forward 2D chalcogenides as paradigmatic strongly correlated two-dimensional materials.

■ ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.1c03491.

Experimental methods, and additional experimental and theoretical results (PDF)

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Author Contributions

S.C.G., S.K., and P.L. conceived and planned the experiment. S.C.G. and S.K. performed the measurements. S.C.G. and V.V. analyzed the STM data. J.L.L. developed the theoretical model. All authors jointly authored, commented, and corrected the manuscript.

Notes

The authors declare no competing financial interest.

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