High-lying valley-polarized trions in 2D semiconductors

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Optoelectronic functionalities of monolayer transition-metal dichalcogenide (TMDC) semiconductors are characterized by the emergence of externally tunable, correlated many-body complexes arising from strong Coulomb interactions. However, the vast majority of such states susceptible to manipulation has been limited to the region in energy around the fundamental bandgap. We report the observation of tightly bound, valley-polarized, UV-emissive trions in monolayer TMDC transistors: quasiparticles composed of an electron from a high-lying conduction band with negative effective mass, a hole from the first valence band, and an additional charge from a band-edge state. These high-lying trions have markedly different optical selection rules compared to band-edge trions and show helicity opposite to that of the excitation. An electrical gate controls both the oscillator strength and the detuning of the excitonic transitions, and therefore the Rabi frequency of the strongly driven three-level system, enabling excitonic quantum interference to be switched on and off in a deterministic fashion.

Transition-metal dichalcogenide (TMDC) monolayers are known to host tightly bound band-edge excitons, as well as a variety of more elaborate many-body species such as exciton complexes in the presence of the Fermi sea of free carriers (known as trions and Fermi polarons) and excitonic molecules. More recently, bound high-lying excitons (HXs), involving electrons from the upper conduction band (in particular, CB+2) and holes from the top-most valence band, have been observed. Even though these high-lying excitons appear at almost twice the energy of the band-edge exciton (X), they exhibit a particularly narrow linewidth that is comparable to that of band-edge excitons. Intriguingly, GW-BSE calculations show that the HX consists of an electron originating predominantly from a downwards-curved conduction band, i.e. a negative effective mass electron. Although trion formation is well-known for the band-edge excitons in two-dimensional semiconductors, it has so far remained unclear whether such states can also form from these more exotic excitonic species.

Coincidentally, in monolayer WSe₂, these high-lying excitons appear at around twice the band-edge exciton transition energy, giving rise to a degenerate atom-like three-level system that allows for a pronounced quantum interference phenomenon to occur in optical second-harmonic generation (SHG). Combining such quantum interference, which generally occurs in discrete multilevel systems such as atomic vapors, crystal defects, or ions, with electronic device functionality has been a long-standing goal. An exciton-based three-level system promises the advantage of facile integration into electronic devices and potentially offers unique control over quantum interference through electrical gate signals. However, such control remains a major conceptual challenge and has not been developed yet.

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Here, we demonstrate experimentally and theoretically that such high-lying trions with negative-mass electrons can indeed form. We probe these charged HXs in a monolayer WSe₂ transistor, where the charge carrier density can be continuously controlled via the gate voltage. We generalize these observations by demonstrating that similar features exist in a monolayer MoSe₂ transistor. In contrast to the neutral HX, high-lying trions show pronounced helicity following a valley polarization selection rule that is distinct from those of the band-edge transitions. In addition to the bright HX trion, a dark charged p-like HX is identified by the signature of excitonic quantum interference in SHG. Finally, we demonstrate robust control of excitonic quantum interference by the gate voltage.

Results

Electrical tuning of high-lying trions in monolayer WSe₂

Figure 1a illustrates two conceivable configurations of high-lying trions in the vicinity of the K-points in momentum space: the photoexcited electron in the high-energy CB+2 band, and the photoexcited hole in the top valence band (VB) forming a negative (positive) trion with an additional resident electron (hole) at the band edge. To probe these trions, a gate-tunable device is needed to control the charge carrier density, i.e., the doping, in the monolayer. Figure 1b illustrates the monolayer WSe₂ transistor device, a microscope photograph of which is shown in Fig. 1c. The gate-voltage dependence of photoluminescence (PL) from band-edge excitons is first measured to characterize the control of doping in monolayer WSe₂. Figure 1d reproduces the characteristic features of the well-documented band-edge excitonic species, such as the negatively charged A exciton singlet (X⁻) and triplet (X⁻²), the positively charged A exciton (X⁺), the bixciton (XX₀), the intervalley dark exciton (X₀), and the charged dark excitons (X⁻ and X⁻²). With a thin graphite flake (few-layer graphene) as the top gate, such gate-voltage dependent measurements are completely reversible without noticeable hysteresis, as discussed in Supplementary Note 1 and Supplementary Fig. 1. From the appearance of the neutral exciton species such as the neutral dark exciton and biexciton in Fig. 1d, we can identify the charge neutrality point centered around −0.15 V.

Resonant pumping of the A exciton followed by Auger-like excitation of the A exciton selectively promotes electrons to the high-lying conduction band near the ±K-points in momentum space, forming a high-lying exciton HX16,23,24. Supplementary Fig. 2 shows a pump-driven power dependence of UPL supporting the Auger-like process. Figure 1e shows the gate-voltage dependence of upconverted PL (UPL) in the energy range of 3.2 to 3.5 eV under continuous-wave (CW) excitation at 1.724 eV, i.e., at about twice the excitation energy. Figure 1f shows example UPL spectra at gate voltages of +0.2 V (negatively charged), −0.15 V (neutral), and −0.5 V (positively charged). In the neutral regime, the UPL spectrum of the HX (black line) shows a characteristic phonon progression, as reported previously25, along with a sharp spectral feature at 3.448 eV, which arises due to the CW SHG of the incident laser. The zero-phonon line of the HX is marked at HX₀. Strikingly, new peaks emerge under both positive and negative doping (Fig. 1e). In the electron-doping regime, a new peak appears at 43 meV below the HX₀. In the hole-doping regime, a peak emerges at 35 meV below the HX₀. These two peaks have narrow linewidths resembling those of the HX and are therefore assigned to the negatively charged HX and positively charged HX, respectively. As shown in Fig. 1e and Supplementary Fig. 1, gate voltages of +0.2 V and −0.5 V correspond to a low doping regime where the Fermi level is close to the band edges to within 1 meV26. The offsets of the trion transitions observed with respect to HX₀ are therefore attributed to their binding energies. As listed in Table S1, these binding energies are, on average, 1.4 times as large as those of band-edge (A exciton) trions, in line with the fact that the HX binding energies, calculated from ab initio GW-BSE theory, are about 1.3 times as large as the A-exciton binding energy27. The negatively charged HX has larger binding energy than the positively charged HXs as shown in Supplementary Note 1 and Supplementary Fig. 1.

The features attributed to the negatively charged HX and to the positively charged HX are marked as HX⁻ and HX⁺, respectively. Figure 1f shows a series of UPL spectra at gate voltages of 0.2 V (electron doping), −0.15 V (neutral), and −0.5 V (hole doping). All measurements were performed at 5 K.

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**Fig. 1** High-lying trions in monolayer WSe₂. a, Illustration of negatively and positively charged high-lying excitons (HX), composed of an electron from a high-lying conduction band with negative effective mass, a hole from the first valence band, and an additional charge from a band-edge state. The semi-transparent electron and curved lines on the left illustrate an alternative structure of the negatively charged HX, where the electrons are in different valleys. b, Schematics and microscope photograph of the transistor device. The WSe₂ monolayer is encapsulated between thin hBN layers and connected to pre-pattern gold electrodes via graphite flakes. The uppermost graphite flake covering monolayer WSe₂ serves as the top gate. d Photoluminescence (PL) of band-edge excitons (X) at 488 nm excitation, measured as a function of gate voltage. e Upconverted PL (UPL) of the HX at 719.2 nm (1.724 eV) excitation, measured as a function of gate voltage. The features attributed to the negatively charged HX and to the positively charged HX are marked as HX⁻ and HX⁺, respectively. f Sample UPL spectra at gate voltages of 0.2 V (electron doping), −0.15 V (neutral), and −0.5 V (hole doping). All measurements were performed at 5 K.
charged one, analogous to the situation for the band-edge trions (Fig. 1d)\(^2\). However, we are not able to resolve singlet and triplet HX\(^-\) species. These species may be masked by the phonon progressions, or are limited in population due to the formation process of the high-lying trions. As we discuss below, the high-lying trions can form through the capture of the resident charge carrier by the HX, which in turn was created in the course of either an Auger-like annihilation of two excitons in the ground state, or via an Auger-like annihilation process between a band-edge trion and a band-edge exciton. It is conceivable that the latter case shows a preference for certain internal structures of negative high-lying trions, as explained in Supplementary Note 2 and Supplementary Figs. 5–7.

The neutral HX PL spectrum is characterized by a distinct phonon progression, as seen in Fig. 1f at a gate voltage of \(-0.15\) V, since the electron in the high-lying conduction band near the \(\pm K\)-points couples strongly to zone-edge longitudinal acoustic (LA) phonons\(^1\). The peak spacing of 31 meV between two bright peaks corresponds to the energy of two LA phonons, scattering the electron between valleys and back again\(^5\). The same spacing is resolved in the trion UPL spectra as marked by the curved black arrows in Fig. 1e. As shown in Supplementary Fig. 3, this phonon progression appears more pronounced after subtracting the UPL spectrum at charge neutrality (\(-0.15\) V), confirming the excitonic origin of these peaks. Nevertheless, the zero-phonon lines for the charged HXs appear much stronger than that for the neutral HX, indicating a weaker electron-phonon coupling for the charged HXs.

**Valley polarization of high-lying trions**

Next, we explore the valley polarization characteristics\(^2\) of these charged HX by examining the degree of circular polarization (CP) in the UPL. Figure 2a, b shows the circular dichroism of the UPL as a function of gate voltage. Polarization resolved UPL spectra at gate voltages of 0.2 V (d), \(-0.15\) V (e), and \(-0.5\) V (f). g Illustration of resonant pumping of the A exciton in the +K valley with a \(\sigma^+\) circularly polarized CW laser. This excitation selectively polarizes resident spin-down electrons in the conduction band, CB. The inset illustrates the Auger-like exciton-exciton annihilation process that promotes the electron to high-lying conduction bands. h Schematic of negatively charged high-lying trion in the \(-K\) valley with \(\sigma^-\) polarized emission and a resident spin-down electron in the \(-K\) valley. i Schematic of the positively charged high-lying trion in the +K valley with \(\sigma^-\) polarized emission.

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**Fig. 2 | Valley polarization and helicity of the high-lying trion in UPL from monolayer WSe\(_2\).** a, b Gate-voltage dependence of co-polarized (a) and cross-polarized (b) UPL under left-hand circularly polarized excitation. c Helicity of the UPL as a function of gate voltage. d–f Polarization resolved UPL spectra at gate voltages of 0.2 V (d), \(-0.15\) V (e), and \(-0.5\) V (f). g Illustration of resonant pumping of the A exciton in the +K valley with a \(\sigma^+\) circularly polarized CW laser. This excitation selectively polarizes resident spin-down electrons in the conduction band, CB. The inset illustrates the Auger-like exciton-exciton annihilation process that promotes the electron to high-lying conduction bands. h Schematic of negatively charged high-lying trion in the \(-K\) valley with \(\sigma^-\) polarized emission and a resident spin-down electron in the \(-K\) valley. i Schematic of the positively charged high-lying trion in the +K valley with \(\sigma^-\) polarized emission.
the electron-doping, neutral, and hole-doping regimes. The highest-energy peak in the spectra again arises from the CW SHG, which, in accordance with the selection rules intrinsic to the \( C_3 \) symmetry\(^{30,31}\), always retains a CP opposite to that of the incident laser and therefore serves as a reference. Remarkably, the UPL from both HX trions is circularly polarized by up to 50\%, whereas the UPL of the neutral HX appears unpolarized. This stark difference in the valley polarization of neutral and charged HXs could be due to the efficient electron-hole exchange interaction\(^{32-34}\), the underlying formation mechanism as illustrated in Supplementary Fig. 5, or differences in their lifetime. Given that spin-valley locking is only effective in a limited region of momentum space around the \( K \)-points for the high-lying conduction band\(^{35}\), the observed valley polarization of high-lying trions also corroborates our earlier finding that stable high-lying excitons must originate from the \( \pm K \)-points\(^{36}\).

Surprisingly, HX\(^+\) and HX\(^-\) exhibit opposite valley polarizations, and the CP UPL hence shows opposite helicity, in stark contrast to the band-edge trions, which generally exhibit the same helicity\(^{27,29}\). Helicity-resolved two-photon PL of the neutral and charged HX displays identical behavior as shown in Supplementary Fig. 4. The HX\(^-\) shows CP opposite to that of the excitation (Fig. 2g, i). This inversion agrees with the significant difference in selection rules for VB \( \leftrightarrow \) CB and VB \( \leftrightarrow \) CB+2 transitions in the same \( \pm K \) valley\(^{30,36}\), as summarized in Table 1. In contrast, the HX\(^+\) state is co-polarized with the laser, which indicates a localization at the \(-K\) valley according to the selection rule as sketched in Fig. 2h. We note that such an opposite helicity of positive and negative trions has recently been observed for band-edge excitons in monolayer WSe\(_2\) under CW excitation and was rationalized by the resident-carrier polarization effect\(^37\), i.e., the creation of a large polarization of resident electrons at the valley opposite to that of excitation. As illustrated in Fig. 2h and elaborated on in Supplementary Fig. 6, we therefore conclude that the most probable configuration of the HX\(^-\) is intravalley in nature. Because of the large spin–orbit splitting in the top valence band, this polarization process is not expected to be applicable to resident holes.

### High-lying excitons and trions in monolayer MoSe\(_2\)

Since the resident-carrier polarization effect relies on a fast intervalley scattering of the excited electron from the upper spin-split CB to the lower spin-split CB, it is not expected to arise in MoSe\(_2\) monolayers, where photoexcited electrons reside in the lower spin-split CB. We would therefore expect positively and negatively charged high-lying trions in MoSe\(_2\) to both have the same helicity, opposite to the helicity of the band-edge excitation. To test this hypothesis, we investigate the high-lying exciton and trions in a monolayer MoSe\(_2\) transistor device.

Figure 3a presents the PL of band-edge excitons from monolayer MoSe\(_2\) as a function of the gate voltage. We probe the HX by resonantly pumping the A exciton and measuring the high-energy UPL. Figure 3b shows the UPL and CW SHG of monolayer MoSe\(_2\) as a function of the gate voltage. In stark contrast to the broad linewidth of the well-known C exciton\(^{38,39}\), a narrow-band high-energy emission feature indeed appears right below the CW SHG, reminiscent of the HX in monolayer WSe\(_2\). Figure 3c shows a rescaled plot, where the gate voltage dependence of this feature is clearly resolved and closely correlates with the gate voltage dependence of the band-edge excitons in Fig. 3a. We assign this feature to the HX of monolayer MoSe\(_2\) and the associated trions. Following our initial report of the HX in monolayer WSe\(_2\), this observation constitutes the first experimental confirmation of the high-energy and narrow-linewidth state in another type of TMDC monolayer. The fact that HX\(^+\) and HX\(^-\) have the same binding energy in this case, in contrast to the case of WSe\(_2\), matches well with the finding that positively and negatively charged A excitons have the same binding energy as seen in Fig. 3a and previously reported in ref. 5. This observation has been supported by the fact that the band-edge excitons and holes having the same effective mass\(^3\). We further characterize the helicities in the n-doped, neutral, and p-doped regimes. As shown in Fig. 3d–f, HX\(^-\) and HX\(^+\) have the same helicity, opposite to that of the excitation laser, which matches well with what is expected from the selection rules in Table 1 when there is no resident-carrier polarization effect. Supplementary Fig. 8 shows the SHG on the full scale.

### Theoretical considerations of high-lying trions

Next, we consider the high-lying trions with negative-mass electrons from a theoretical perspective. We first analyze the HX binding energies in the parabolic approximation for the bands. We introduce the hole effective mass, \( m_h=0 \), the CB electron effective mass, \( m_e=0 \), and the effective mass of the high-lying electron from the CB+2 band, \( m_e=0 \). Corresponding electron-hole reduced masses are denoted as \( \mu_{1,2}=m_e/(m_e+m_h) \) and \( \mu_{1,2}=m_h/(m_e+m_h) \). Accordingly, \( \mu_{1,2}>0 \) because \( |m_e|\approx m_h \). In the case of HX\(^-\), the calculation of the trion binding energy can be performed following ref. 40 (see also refs. 41,42). This calculation yields the binding energy of the HX\(^-\) of approximately 10\% of the HX binding energy, depending on the screening parameters and the effective masses, in reasonable agreement with experimental observations for monolayer WSe\(_2\) summarized in Table 2 and Supplementary Table 1.

The situation with the HX\(^+\) is more involved. Due to the fact that the trion envelope function should be symmetric with respect to the permutation of identical charge carriers, while the antisymmetry of the total wavefunction results from the Bloch amplitudes, the problem for the HX\(^+\) is mapped, in the parabolic approximation, to the problem of \( -2 \) with an effectively reduced mass \( \mu_{1,2}=m_e/m_e+m_h \) and an effective-mass ratio \( \sigma=2m_e/m_e+m_h \). As detailed in Supplementary Note 3, the calculations show that, neglecting the non-local dielectric screening effects, the trion binding energy can be recast as

\[
\frac{E_{\text{b,HX}}}{\hbar^2} = \frac{2\mu_{1,2}^4}{\mu_{1,2}^2 (1+\chi) - 1}
\]

Here, \( \chi=\chi(\sigma)=0.1-0.5 \) is the ratio of the trion to exciton binding energy in the case of equal effective masses of identical electrons. The analysis shows that for the bound trion to exist, \( E_{\text{b,HX}}>0 \), the effective masses need to satisfy stringent conditions, \( m_e<2m_h \), and \( m_h=m_e/(1+\chi) \). The calculations presented in Supplementary Note 3 demonstrate that for \( m_e<0 \) and a not too small \( B>0 \), bound HX\(^+\) states can exist with binding energies in the range of 0.1–1 of the exciton binding energy. We also confirm these variational calculations with the model of contact interaction of the exciton and free electron, accounting for non-parabolic terms in the dispersion. Consideration of dielectric screening by the Rytova-Keldysh potential\(^1\) does not qualitatively change the results. However, a detailed comparison between the

### Table 1 | The selection rules of the group \( C_{3v} \) at \( \pm K \) and \( -K \) valleys for circularly polarized PL

| Irrep   | \( \pm K \) valley | Irrep   | \( -K \) valley |
|---------|--------------------|---------|----------------|
| VB \( \leftrightarrow \) CB+2 | \( A' \leftrightarrow E_1 \) | \( A' \leftrightarrow E_1 \) |
| VB \( \leftrightarrow \) CB | \( A' \leftrightarrow E_1 \) | \( A' \leftrightarrow E_1 \) |

Irrep: irreducible representation.
experiment and theory, and, fitting of the binding energies, requires accounting for the dielectric screening and the full dispersion of CB+2, including its anisotropy, and goes beyond the current work.

**Electrical control of excitonic quantum interference**

Having presented experimental evidence and a theoretical rationalization of high-lying trions, we now turn to the influence of the electrical tunability of these species on excitonic quantum interference. Optical re-excitation of one and the same electron by a femtosecond laser pulse can drive direct transitions between the band edge and the high-lying conduction band, providing an optical coupling mechanism that interconverts the band-edge A exciton and an HX state\(^{16,17}\). Such a high-energy state is clearly identified in the two-photon excitation spectrum but not in the luminescence\(^{16}\), and is therefore attributed to a dark p-like HX. Because of the lack of an inversion center in monolayer WSe\(_2\), both the s-like and p-like excitons at the band edge are mixed and can be simultaneously one- and two-photon active\(^{44}\). However, the p-states are expected to dominate the two-photon absorption\(^{44}\). The same should be true for the trions. Together with the ground state of the system, i.e. the state where no exciton is present, an excitonic three-level system is formed. Interactions with the light field can then be treated in analogy to the familiar case of atomic multi-level systems in quantum optics\(^{17,45}\). As illustrated in the left panel of Fig. 4b, laser-driven transitions between states can undergo Rabi oscillations. The associated quantum interference between \(|1> \rightarrow |2>\) and \(|1> \rightarrow |2> \rightarrow |3> \rightarrow |2>\) transition pathways is then observed in the SHG spectrum generated by a femtosecond laser pulse\(^{15}\). These interferences appear as dips in the SHG spectrum along with a characteristic spectral anti-crossing feature in the excitation-energy dependence of the SHG spectra, shown in the left panels of Fig. 4a.

In analogy to the neutral excitonic three-level system reported previously\(^{15,16}\), it is conceivable that a band-edge trion and a p-like HX trion can also form a three-level system, which should give rise to an

**Table 2 | Experimental binding energies of the high-lying trions and band-edge trions in hBN encapsulated monolayer WSe\(_2\) and MoSe\(_2\)**

| High-lying trions | WSe\(_2\) | MoSe\(_2\) |
|-------------------|-----------|-----------|
|                   | X\(^{-}\) | X\(^{+}\) | X\(^{-}\) | X\(^{+}\) |
| Binding energy (meV) | 43 | 35 | 21 | 21 |
| Band-edge trions | \(X_0\) | \(X_0\) | \(X_0\) | \(X_0\) |
| Binding energy (meV) | 36 | 29 | 21 | 26 |
the excitons and the trions must be comparable. This conclusion of a
excitonic three-level system, we conclude that the coherence times of
similar spectral features are observed in the neutral and charged
species. The neutral three-level system is formed by the band-
edge A exciton and the p-like HX. A negatively charged three-level system is formed
by the band-edge trion and the charged p-like HX. The coherence times of the trion is supported by the relatively
weak effect of the electron-trion scattering, consistent with previous
work on trions and the Fermi polaron description of the effect.

Finally, we evaluate the potential to control the excitonic quantum
interference electrically. The electrical gate tunes the charge-
carrier density in the monolayer and leads to a change in both the
oscillator strength and the detuning of the excitonic transitions
(Supplementary Fig. 1d). These changes are expected to alter the Rabi
frequency. Figure 4c shows the voltage dependence of the SHG
spectrum measured at an excitation energy of 1.7 eV. SHG spectra at gate
voltages of 0, 0.5, and −2.4 V. With simulations of the density-matrix dynamics it can be shown that each dip in the SHG
spectrum corresponds to one full Rabi cycle of the strongly driven
system. At 0 V, the SHG spectrum does not show any prominent dip:
in this case, no Rabi flopping occurs. At −2.4 V, one clear dip emerges in the spectrum, implying one Rabi cycle. At 0 V, two dips are identified, implying that the driven system must undergo two Rabi cycles. Such an
evolution of the number of Rabi cycles with electrical gate voltage demonstrates an unprecedented control over a quantum-optical
phenomenon in the form of excitonic quantum interference.

Discussion
We have demonstrated the existence of UV-emissive trions in both
WSe2 and MoSe2 monolayer transistor structures. These unusual
excitonic species exhibit a high degree of valley polarization, corroborating our earlier conclusion that high-lying excitons originate from the ±K-points in momentum space and consist of an electron from a high-lying conduction band CB+216. We systematically studied the high-lying trions comprising negative-mass electrons in theory and have uncovered a broad set of conditions under which such trions can be stable. In addition to the bright high-lying trions, we identify a dark high-lying trion that couples with band-edge trions to form a charged excitonic three-level system, which enables laser-driven excitonic quantum interference. We show that excitonic quantum interference

Fig. 4 | Electrical control of excitonic quantum interference involving the p-
like high-lying trion in monolayer WSe2. a Excitation-energy dependence of SHG
spectra at gate voltages of 0, 0.5, 1.5, and 2.5 V, measured under excitation by a
laser of 80 fs pulse length. b Illustration of an excitonic three-level system based on
neutral and charged species. The neutral three-level system is formed by the band-
edge A exciton and the p-like HX. A negatively charged three-level system is formed

Signatures of quantum interference in the SHG spectrum also provide insight into the coherence time of the excitonic species, which is a crucial parameter enabling the quantum-interference phenomenon as shown by simulations in the density-matrix formalism. Since similar spectral features are observed in the neutral and charged excitonic three-level system, we conclude that the coherence times of the excitons and the trions must be comparable. This conclusion of a
significant coherence time of the trion is supported by the relatively
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frequency. Figure 4c shows the voltage dependence of the SHG
spectrum measured at an excitation energy of 1.7 eV. SHG spectra at gate
voltages of 2.4, 0, and −2.4 V. With simulations of the density-matrix dynamics it can be shown that each dip in the SHG
spectrum corresponds to one full Rabi cycle of the strongly driven
system. At 2.4 V, the SHG spectrum does not show any prominent dip:
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from both neutral and charged excitonic three-level systems can be controlled by the gate voltage. The number of Rabi cycles undergone during the laser pulse can be tuned via the gate voltage without changing the laser power. Such electrical control of quantum interference is not conceivable in conventional quantum-optical experiments on dilute atomic gases. Our findings therefore expand the spectral working range of future valleytronic devices to the UV, and open up new possibilities for quantum nonlinear optoelectronics.

Methods

Device fabrication

We fabricate the monolayer WSe₂ and MoSe₂ transistors by a dry-transfer method 10. Monolayer WSe₂, monolayer MoSe₂, few-layer hexagonal boron nitride, and few-layer graphite flakes are exfoliated from bulk crystals (WSe₂ and MoSe₂, HQ Graphene; hBN, NIMS) onto PDMS films (Gel-Pak, Gel-film X4) using Nitto tape. We stack these layers onto a Si/SiO₂ substrate with prepatterned gold electrodes using PDMS hexagonal boron nitride, and few-layer graphite flakes are exfoliated from bulk crystals (WSe₂ and MoSe₂, HQ Graphene; hBN, NIMS) onto PDMS films (Gel-Pak, Gel-film X4) using Nitto tape. We stack these layers onto a Si/SiO₂ substrate with prepatterned gold electrodes using a stamping method. A microscope image of a representative device is shown in Fig. 1c.

Optical spectroscopy

We cool down the sample to 5 K in a helium-flow microscope cryostat (Janis, ST-500). We focus the laser onto the sample with an objective of 0.6 numerical aperture (Olympus, LUCPLFLN, 40×) and measure reflected signals. To measure the PL, we use an argon-ion laser (Spectra Physics, 2045E) at 488 nm for excitation and a 488 nm long-pass edge filter to remove the laser line. For the helicity-resolved measurements, we use a grating of 600 grooves mm⁻¹ to generate p-polarized light and a Berek compensator (Newport) to generate s-polarized light. For both PL and UPL measurements, we use a grating of 1200 grooves mm⁻¹ and measure the UPL through a combination of a superachromatic quarter-wave plate and a grating of 1200 grooves mm⁻¹ to generate s-polarized light and a Berek compensator (Newport) to generate p-polarized light. For both PL and UPL measurements, we use a grating of 1200 grooves mm⁻¹ and measure the UPL through a combination of a superachromatic quarter-wave plate and a grating of 1200 grooves mm⁻¹ to generate s-polarized light and a Berek compensator (Newport) to generate p-polarized light.

Data availability

Source data for figures are provided with the paper. Any additional data are available from the corresponding authors upon reasonable request.

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Author contributions

K.-Q.L. conceived the project and carried out the measurements with the support of S.B.; J.D.Z. and A.C. fabricated the gate-tunable devices; M.M.G., M.A.S., and J.V.M. contributed the theoretical work; K.W. and T.T. provided hBN crystals. K.-Q.L., J.D.Z., M.A.S., J.V.M, S.B., A.C., M.M.G., and J.M.L. discussed the results, analyzed the data, and contributed to the writing of the manuscript.

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