Peer Review File

Manuscript Title: Particle-hole symmetry protects spin-valley blockade in graphene quantum dots

Reviewer Comments & Author Rebuttals

Reviewer Reports on the Initial Version:

Referees' comments:

Referee #1 (Remarks to the Author):

This manuscript reports on measurements of an electron-hole double quantum dot made in bilayer graphene. In particular, the work focuses on electron-hole symmetry that is nearly perfect in graphene systems. The authors demonstrate transport via creation and annihilation of electron-hole pairs.
Finally, the work implies robust mechanisms for spin to charge and valley to charge conversion allowing for spintronics/valleytronics to conventional electronics interfaces.

I find this article to be convincing and well put together. The experiment itself, is rather difficult from a technical point of view. The results I believe a of interest to the physics and quantum information community.

At this point, I don't have comments for improvement, and recommend the manuscript for publication.

Referee #2 (Remarks to the Author):

Manuscript by Banszerus, Moeller et al. describes an experiment on double quantum dot (DQD) system realized in bilayer graphene. Application of an external electric field in this material opens an energy gap and thus, it can be used as a semiconductor rather than a semimetal. The authors leverage symmetric band structure of this system to create a double dot system consisting of n- and p-type quantum dots. Similar DQD realization has been shown before in bilayer graphene , see https://pubs.acs.org/doi/10.1021/acs.nanolett.8b01859 as an example, so this aspect is not really new. The authors demonstrate protected single-particle spin-valley blockade which has not been shown before.

I find overall quality of the data and the presentation to be very high. The manuscript reads very well, figures are clear and visually appealing. Measurements, device fabrication and the data analysis are presented in sufficient detail. I also do not have any comments related to description of transport through this DQD. Before seeing the paper published, I'd like to ask the authors to clarify on the items I list below:

1) Authors mention in the abstract Kane-Mele type spin-orbit coupling as well as quantum spin Hall phase, and write later in the text:

"This careful analysis confirms that the system is very close to perfect particle-hole symmetric, with a rich and well-understood single-particle spectrum, in full agreement with the topologically non-trivial Kane-Mele model of a quantum spin Hall insulator"

How should a reader understand this claim? Is that an indirect way of saying that quantum spin Hall effect has been realized in the DQD studied in this work? As far as my understanding goes, quantum-spin Hall effect concerns two dimensional systems, not confined 0D quantum dots with properties renormalized by the level spacing etc. Can the authors be precise and specific about how presented results relate to the quantum spin Hall phase?

2) The authors discuss possible origin of symmetry breaking in the system. Both explanations for symmetry breaking proposed by the authors rely either on different couplings to the substrate on the barrier, or different valley g-factors. In principle, I do not see a reason why creating an e-h DQD in bilayer graphene would be fundamentally non-reproducible. I am wondering however, how easy it is in practice to observe particle hole symmetry in such devices. Could the authors comment on how many of fabricated devices yield similar characteristics?

3) For a Nature aspiring manuscript, I think the outlook is rather vague. I'm precisely thinking of what an immediate follow-up experiment with the use of this platform would be? The authors invoke readout mechanism of spin qubits realized in Silicon. Realizing similar DQD comprising of electrons and holes seems rather difficult in platforms other than graphene. I think it would make the paper much more appealing, if the authors could identify follow-up experiments.

Referee #3 (Remarks to the Author):

The authors report an experimental study of spin-valley blockade in bilayer graphene double quantum dots (BGDQs) of the p-n type and support their experimental results through theoretical interpretations and calculations with a focus on symmetry. Indeed, graphene has special electronic properties as compared to more common semiconductors in that it offers a Dirac spectrum. Transport blockade through double quantum dots relies on the Pauli principle so that certain configurations of occupied states do not allow for transport. Interestingly, this blockade only appears for current flowing in one direction. The general effect is well known and has been studied in different material systems even recently in BGDQs.

The interpretations are very solid and are supported well by the experimental data with several tunable parameters such as gate voltages and magnetic field. The manuscript is in most parts very clearly presented and the supporting information gives relevant details of the experiment and theory.

I have spent quite some time to think about the impact and novelty of the work. I think that in general the idea to use electrons (conduction band) and holes (valence band) in the BGDQs at the same time in connection with a protected spin-valley blockade is quite intriguing. In addition, as the authors well explain, the combination of precisely (gate-) controllable electron and hole transport is not possible in more ordinary two-dimensional electron gases like in GaAs based heterostructures as the semiconducting band gap is too large. The gate-defined BGDQs became a reality in recent years in laboratories as the one in the group of C. Stampfer (corresponding author) and are currently investigated as prime candidates for spin qubit applications. The current results would e.g. support read-out of such qubits.

My main hesitation to recommend publication in Nature is the potential lack of broad impact of the specific idea to use electrons and holes for spin-valley blockade. Also, there is already a spin-valley blockade experiment in BGDQs published in Physical Review Letters highlighted as "editor suggestion" and "featured in physics" from other authors (Ref. [35] in the current manuscript). There are similar claims and results in that publication although not for an electron-hole BGDQ but in an electron-electron BGDQ. The present authors conclude that their particle-hole symmetry protection is not relevant in such systems (Ref. [35]) which is correct. The workhorse in the usual form of the Pauli-spin blockade is based on singlet-triplet splitting whereas in the present setup single-particle electron and hole states in different orbitals can be created or annihilated. It is not clear to me and it is not discussed in detail in the manuscript if the present setup with a blockade protected by electron-hole symmetry is fundamentally more stable than the more ordinary spin-valley blockade using the singlet-triplet splitting? For me that is an important point for the potential impact this work could have in the field.

My specific comments and questions are listed here and might help to amend the presentation and strengthen the message of the work.

- The particle-hole symmetry protected spin-valley blockade which is central to the interpretation and scope of the work is quite powerful as it survives spin-orbit coupling and magnetic fields. However, it is assumed that the shapes (confining potential) of the electron and hole sides are identical or at least very similar. So, the protection seems to me less stable than e.g. effects protected by time-reversal symmetry (which would be broken in the presence of magnetic fields). When compared to Ref. [35], is the present protection of the blockade using electrons and holes superior or it is mainly a different symmetry protecting the selection rules in transport channels through the BGDQ? Suppose, one has two identical tunnel-coupled electron-based quantum dots (same shape, valley g-factor and spin-orbit couplings). I do not see why in such a case the protection of the spin-valley blockade would be fundamentally less strong as the main effect is in both cases (electron-hole BGDQ , electron-electron BGDQ) the Pauli principle by blocking transitions involving the same quantum numbers. I would like the authors to elaborate/comment on this issue.

- I think it would help to include a table either in the main text or supporting information which shows the different effects (magnetic field, spin-orbit interaction, displacement field etc.) and if they break particle-hole symmetry or not.

- On page 9, it is mentioned that the "… inversion symmetry is broken due to the electric

displacement field …” in connection with effects that can break particle-hole symmetry.
But I think that the displacement field does not break particle-hole symmetry as far as it is included in E_g appearing in H_{BLG} on page 3. I find the quoted statement therefore confusing.

- On page 5, the authors write “This blockade is robust up to very high detuning energies, because it can only be overcome by involving excited states that are separated in energy from the low energy spectrum by the band gap, which is typically 20-60 meV”. I do not understand this statement. The orbitals belonging to a different group (four valley-spin configurations) of states are separated by the confinement energy that depends on the size of the quantum dot and not the band gap. Can the author comment on this? Maybe I just misunderstand the statement.

- In Fig. 4, broadenings are extracted from the data and attributed to the degree of difference of valley g-factors in the two dots (on top of page 11). To me it is not clear why broadenings of resonances are related to broken symmetries (here valley g-factors) and not just to the coupling strengths of the QD states to the leads? Or are these broadenings dominated by the interdot couplings?

Author Rebuttals to Initial Comments:

Reviewer 1:

This manuscript reports on measurements of an electron-hole double quantum dot made in bilayer graphene. In particular, the work focuses on particle-hole symmetry that is nearly perfect in graphene systems. The authors demonstrate transport via creation and annihilation of electron-hole pairs. Finally, the work implies robust mechanisms for spin to charge and valley to charge conversion allowing for spintronics/valleytronics to conventional electronics interfaces.

I find this article to be convincing and well put together. The experiment itself, is rather difficult from a technical point of view. The results I believe of interest to the physics and quantum information community.

At this point, I don't have comments for improvement, and recommend the manuscript for publication.

We would like to thank the reviewer for her/his time and interest to examine our manuscript.

We are pleased to read that the reviewer considers our work as "*convincing and well put together*", and we are delighted to read that she/he believes that our results are of interest to the broad "*physics and quantum information community*" and that she/he recommends our manuscript for publication in *Nature*.

Reviewer 2:

Manuscript by Banszerus, Moeller et al. describes an experiment on double quantum dot (DQD) system realized in bilayer graphene. Application of an external electric field in this material opens an energy gap and thus, it can be used as a semiconductor rather than a semimetal. The authors leverage symmetric band structure of this system to create a double dot system consisting of n- and p-type quantum dots. Similar DQD realization has been shown before in bilayer graphene, see https://pubs.acs.org/doi/10.1021/acs.nanolett.8b01859 as an example, so this aspect is not really new. The authors demonstrate protected single-particle spin-valley blockade which has not been shown before.

I find overall quality of the data and the presentation to be very high. The manuscript reads very well, figures are clear and visually appealing. Measurements, device fabrication and the data analysis are presented in sufficient detail. I also do not have any comments related to description of transport through this DQD. Before seeing the paper published, I'd like to ask the authors to clarify on the items I list below:

We thank reviewer for her/his time and effort reading carefully through the manuscript and appreciate the questions and suggestions raised below. We are pleased to read the reviewer considers the *'quality of the data and the presentation to be very high'* and thinks that the *'manuscript reads very well'*.

We agree with the reviewer that electron-hole DQDs have been shown before (see also Banszerus et al. Nano Lett. 18, 4785 (2018)) but it is only now that (i) we enter the few-electron / few-hole regime and that (ii) we are able to investigate particle-hole symmetry in this system and to demonstrate the single-particle electron-hole blockade. This allows us to go far beyond what can be done in GaAs, Si and SiGe and of what has been shown before in BLG QDs.

1) Authors mention in the abstract Kane-Mele type spin-orbit coupling as well as quantum spin Hall phase, and write later in the text:

"This careful analysis confirms that the system is very close to perfect particle-hole symmetric, with a rich and well-understood single-particle spectrum, in full agreement with the topologically non-trivial Kane-Mele model of a quantum spin Hall insulator"

How should a reader understand this claim? Is that an indirect way of saying that quantum spin Hall effect has been realized in the DQD studied in this work? As far as my understanding goes, quantum-spin Hall effect concerns two dimensional systems, not confined 0D quantum dots with properties renormalized by the level spacing etc. Can the authors be precise and specific about how presented results relate to the quantum spin Hall phase?

We thank the reviewer for raising this concern. We fully agree with the reviewer that quantum spin Hall insulators (QSHIs) are two-dimensional systems and some of their properties (insulating bulk, chiral edge states) are lost when one maps them onto (quasi) zero-dimensional QDs. Other properties, such as the spin and valley texture (i.e. the level ordering of the single particle spectrum) and the electron-hole symmetry are preserved, as they are a direct consequence of the Kane-Mele Hamiltonian, $H_{\mathrm{KM}} = \frac{1}{2}\Delta_{\mathrm{SO}}\Psi^\dagger\sigma_z\tau_z s_z\Psi$, which renders (two dimensional) graphene a QSHI. Our experiment is – to the best of our knowledge – the very first that demonstrates the electron-hole mirror-symmetry of the spin-orbit gap in bilayer graphene, and that demonstrates that this Hamiltonian is indeed imprinted on the single particle spectrum for electrons and holes.

We agree with the reviewer that the statement in the summary "*in full agreement with the topologically non-trivial Kane-Mele model of a quantum spin Hall insulator*" is not well-phrased and may lead to misunderstandings. We therefore have rewritten the sentence in the following way:

This careful analysis confirms that the system is very close to perfect particle-hole symmetric, with a rich and well-understood single-particle spectrum, in full agreement with the Kane-Mele spin-orbit Hamiltonian [7].

2) The authors discuss possible origin of symmetry breaking in the system. Both explanations for symmetry breaking proposed by the authors rely either on different couplings to the substrate on the barrier, or different valley g-factors. In principle, I do not see a reason why creating an e-h DQD in bilayer graphene would be fundamentally non-reproducible. I am wondering however, how easy it is in practice to observe particle hole symmetry in such devices. Could the authors comment on how many of fabricated devices yield similar characteristics?

We thank the reviewer for this question. In short, we agree and we also do not see any reason why the reported observations based on the electron-hole DQD should be fundamentally non-reproducible. In total we have now observed the robust single-particle electron hole blockade in 5 DQD devices.

In the manuscript and the supplementary material, we present two complete data sets demonstrating electron-hole blockade for various in-plane and out-of-plane magnetic fields recorded on two different DQD devices on the same chip (DQD devices #1 and #2). Additionally, a strong single-particle electron-hole blockade is also observed in a third DQD device (#3) shown in Fig. S1 in the supplementary material (see red dashed circle in Fig. S1a,b), which is based the same hole QD as in DQD device #1, but uses a different electron QD on the opposite side of the hole QD (compare Fig. S1c and Fig. S1d). In addition to these three DQD devices reported in the manuscript and the supplementary material, we present below very recent data of two additional DQD devices recently measured on a second chip. In Figs. R1a and R1b we show charge stability diagrams for different source-drain bias voltage directions of DQD device #4, highlighting the single-electron / single-hole regime and the single-particle electron-hole blockade. Close-ups are shown in Fig. R1c and R1d. Figs. R1e and R1f show close-ups of the single-electron / single-hole triple point of the DQD device #5, which is on the same chip as DQD device #4 but instead of finger gates (FG) FG7 and FG9 (DQD #4) we used FG9 and FG11 for defining the individual QDs (device looks similar to the image shown in Fig. 1c in the main text). Interestingly, the absolute values of the voltages on the different finger gates for reaching the first electron and first hole are very similar (compare voltage values in Figs. R1c-f) demonstrating the high homogeneity in our samples. Moreover it should be noted that in the DQD devices #4 and #5, the leads are n-doped in contrast to the p-doped channel in DQD devices #1, #2 and #3 (compare Fig. 1Rg with Fig. 1d in the main manuscript). Note that also for the two more recently studied devices, the α and β resonance can be observed in the forward bias direction (Fig. R1c,e), while a strong electron-hole single-particle blockade of the current for reversed bias can be observed (Fig. R1d,f).

In summary, we have observed the effect in 5 DQDs, and have not observed a single electron-hole DQD, which did not show the single-particle electron-hole blockade. Hence, we are by now very confident that a robust electron-hole blockade can be regularly reproduced in this type of devices. We thus believe that this robustness and good reproducibility are essential for harnessing the electron-hole blockade for further experiments, e.g. spin or valley to charge conversion in qubits.

Furthermore, we would like to point out that perfect particle-hole symmetry is not required for the presence of a protected electron-hole blockade as long as the spin and valley texture, i.e. the level ordering does not become asymmetric. A more detailed discussion of the symmetry-protection of the single-particle blockade and mechanisms that could break the electron-hole symmetric spin and valley texture are discussed in the newly added section F in the supplementary material (see also page 19 in this reply letter).

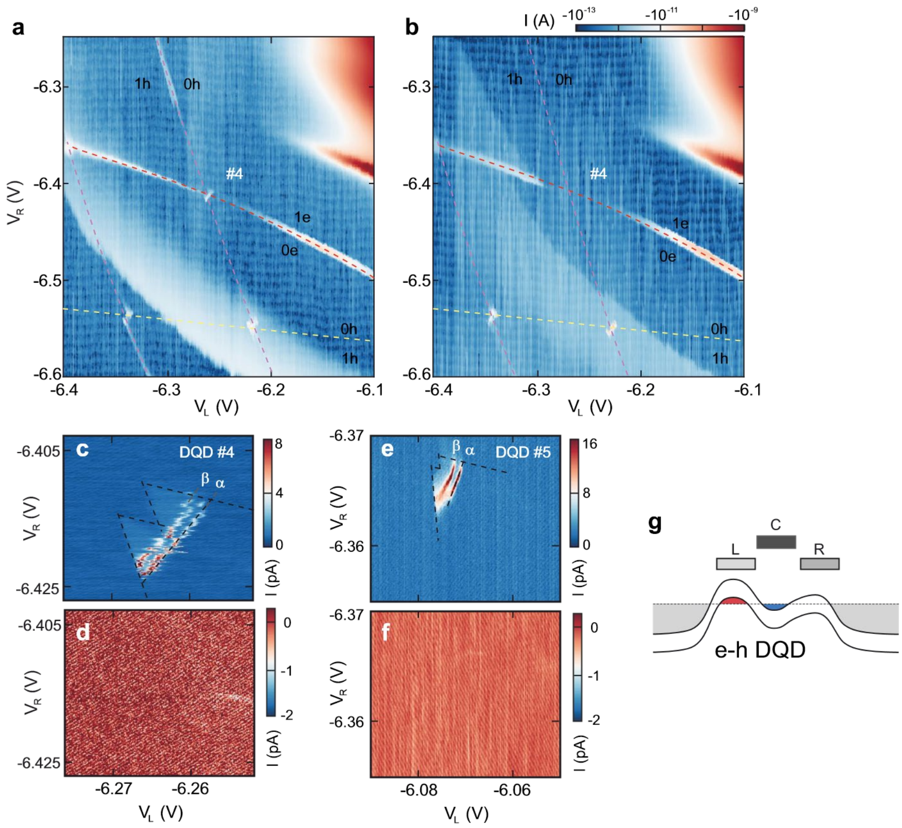

Figure R1: **a** and **b** Overview charge stability diagram for an electron hole DQD realized on a similar DQD device on another chip (DQD #4). Here the channel polarity (and the polarity of all gates) is inverted with respect to the main text (illustrated in panel g). The $(0e, 0h) \Leftrightarrow (1e, 1h)$ triple point is located at the white circle. Measurements were performed at $V_{SD} = 0.7$ mV (panel a) and $V_{SD} = -0.7$mV (panel b) with $V_{SG} = -5.44$ V and $V_{BG} = 5.0$ V. **c** and **d** Zoom-in measurements on the $(0e, 0h) \Leftrightarrow (1e, 1h)$ transition at $V_{SD} = 0.7$ mV (panel c) and $V_{SD} = -0.7$ mV (panel d). For positive bias the α and β resonances are visible, for the reversed bias direction a robust single-particle blockade is observed. **e** and **f** Same measurements as in panels c and d for a second DQD on the same chip (DQD device #5) with $V_{SD} = \pm 0.5$ mV, $V_{SG} = -5.45$ V and $V_{BG} = 5.025$ V. **g** Schematic of the valence and conduction band edge profiles along the n-type channel (please compare to Fig. 1d in the main manuscript) with negative voltages applied to the finger gates (FGs) L, C and R forming an electron-hole (e-h) DQD. In this case, hole QDs reside underneath FGs of the lower layer, while electron QDs reside underneath the FGs of the upper layer.

3) For a Nature aspiring manuscript, I think the outlook is rather vague. I'm precisely thinking of what an immediate follow-up experiment with the use of this platform would be? The authors invoke readout mechanism of spin qubits realized in Silicon. Realizing similar DQD comprising of electrons and holes seems rather difficult in platforms other than graphene. I think it would make the paper much more appealing, if the authors could identify follow-up experiments.

We thank the reviewer for raising this point. We fully agree that a connection to follow-up experiments and the broader field is an important point to put the relevance of our findings in the right perspective.

We now substantially revised the outlook section and added a more detailed and elaborated paragraph mentioning a number of follow up experiments and also highlight better the broader relevance of our work. The revised paragraph reads now (see page 8 ff. in the manuscript):

This careful analysis confirms that the system is very close to perfect particle-hole symmetric, with a rich and well-understood single-particle spectrum, in full agreement with the Kane-Mele spin-orbit Hamiltonian [7]. The electron-hole-symmetric level texture leads to a strong single-particle spin and valley blockade, which is robust up to very high detuning energies and independent of magnetic field, in strong contrast to the conventional two-particle singlet-triplet Pauli blockade [27–29]. This robust single-particle blockade will allow for high fidelity spin-to-charge and valley-to-charge conversion, providing a reliable read-out scheme for spin and valley states [36]. Combined with microwave control, this will enable to study spin and valley coherence times by electron spin resonance [37, 38] or electron dipole spin resonance techniques [39, 40], and open the door for full spin and valley qubit operation. BLG electron-hole QDs are also well suited for implementing long range qubit coupling in extended chains of ambipolar quantum dots [36], a goal that is also explored in other material systems such as silicon [41]. Furthermore, the single-particle blockade presented in this work makes electron-hole symmetric DQDs an highly interesting system for implementing gate-tunable single-photon THz detectors [42, 43], entangled electron-hole pair pumps or highly efficient Cooper pair splitters [44, 45]. When coupling a BLG electron-hole DQD to a superconductor, conventional elastic co-tunneling is forbidden by spin and valley selection rules, enabling for pure Cooper pair splitting and crossed interband Andreev reflection [46]. This makes such electron-hole QDs coupled to a superconductor also an interesting building block for a topological Kitaev chain [47, 48].

Being limited by space, we could not enter in the details of the follow-up experiments in the manuscript, but we give more details below.

1) Towards spin and valley qubits in BLG.

Certainly, using the electron-hole blockade for reading out spin or valley states in BLG QD systems (with an exceptionally high readout fidelity given the strong protection of the blockade) opens up the door towards investigating relaxation and coherence times of spin and valley states. This may lead to the demonstration of a spin (or valley) qubit in a graphene based system – almost 15 years after the theoretical proposal [Trautzettel et al. Nat. Phys. 3, 192 (2007)] and a lot of effort in the field. Along this line there are a number of very concrete follow-up experiments including:

- Manipulation of electron spins in a QD by electron spin resonance. This can be realized by implementing a microwave strip-line on the device to create an in-plane AC magnetic field generated by an AC current running through it (see Fig. R2a). This concept has been widely used in GaAs and silicon spin qubit devices (see e.g. [Koppens et al. Nature 442, 766 (2006), Veldhorst et al. Nature 526, 410 (2015)]). Note, that in contrast to silicon devices, the AC field needs to point in-plane in order to drive the electron spins, which are polarized out-of-plane in BLG due to the small Kane-Mele spin-orbit coupling. In brief, the device could be operated in the following way: An electron-hole pair is created in a BLG DQD, the system is tuned into Coulomb blockade, the electron spin is manipulated via electron spin resonance and finally the spin states is read out making use of the single-particle spin and valley blockade mechanism. It is important to stress that the possibility of constructing a qubit based on the single particle spectrum in combination with using a high-fidelity readout scheme that relies on blockade physics rather than on the Elzerman readout [Elzerman et al. Nature 430, 431 (2004)] can be of great practical advantage for the operation of a qubit in BLG. Often, read-out mechanisms based on blockade physics require two-particle states, which are rather complex in BLG due to the spin and valley degree of freedom [Möller et al. Phys. Rev. Lett. 127, 256802 (2021) and Knothe et al. New J. Phys. 24, 043003 (2022)]. A read-out based on two-particle states in BLG is therefore likely to require delicate fine-tuning of the qubit operation point.

- A similar approach is spin manipulation via electron dipole spin resonance. For that purpose, micromagnets have to be deposited on top of the QDs, as already successfully used in several silicon qubit devices (see e.g. [Yoneda et al. Nat. Nanotechnol. 13, 102 (2017), Mills et al. Science Advances 8, 14 (2022), Philips et al. Nature 609, 919 (2022)]). The implementation of how a micromagnet could be integrated in a BLG qubit device is illustrated in Fig. R2b. The micromagnet generates an in-plane magnetic field gradient. By applying microwave bursts to one of the finger gates, the wave function of the electron in the QD will be slightly shaken in real space, which translates the AC electric filed into an effective AC magnetic field. This field couples to the electron spins and, hence, allows for resonantly driving the spin transitions.

- An interesting future experiment is also to test a long-range coupling mechanism of electron spins in non-neighboring QDs, which has been suggested for single-layer graphene [Trauzettel et al. Nature Physics 3, 192 (2007)]. This concept can potentially be adapted for BLG QDs, considering an electron-hole-electron multi QD system. In this case, the states of the hole QD would act as mediators for the coupling of the adjacent electron QDs. This is a highly interesting scheme for allowing a somewhat "long-distance" coupling, an important ingredient for multi-qubit systems based on spins.

- Another concept for long-distance coupling between spin qubits is based on shuttling charge carriers (with quantum information encoded in their spin (or valley) state) between distant QDs via time-dependent gate-voltages [Vandersypen et al. npj Quantum Information 3, 34 (2017)]. Charge shuttling has been demonstrated recently [Seidler et al. npj Quantum Information 8, 100 (2022)] in a silicon system, but suffers from a small, spatially varying valley splitting, such that the shuttled "quantum information" is easily lost due to transitions to other valley states. We envision to implement the shuttling concept in an electron-hole DQD system in BLG were we are able to valley polarize our states already at small magnetic fields, while having an excellent read-out mechanism due to the single-particle blockade. Together with the expected long spin coherence time in BLG and a very low disorder potential in BLG-based heterostructures [Icking et al. Adv. Electron. Mater. 8, 2200510 (2022)], this promises high shuttling fidelities.

- Finally, we would like to note that the idea to utilize electron and hole QDs has gained attention also in the silicon qubit community. In silicon, spin orbit coupling is present for holes, but absent for electrons. In this case the idea is to combine the readout possibilities of a single electron transistor as a charge detector with the advantages of silicon hole qubits (e.g. spin-orbit coupling for an all-electrical spin manipulation). A proof of concept has been shown in a device where an electron and a hole QD were capacitively coupled allowing mutual charge detection [Mueller et al. Nano Lett. 15, 5336 (2015), Sousa de Almeida et al. Phys. Rev. B 101, 201301 (2020)]. This concept can also be realized by creating electron-hole DQDs in BLG which is proximitized by e.g. WSe_2, strongly enhancing the SOC for one type of charge carrier (on one layer of the BLG) but not the other.

Beyond spin and valley qubits in BLG.

- Beside the use for spin- and valley-qubit applications, a symmetric electron-hole DQD is a very interesting system also for THz detection [Bandurin et al. Nature Communications 9, 5392 (2018), Riccardi et al. Nano Lett. 20, 5408 (2020)], as it can act as a sensitive photon detector when operated in the blocked configuration at finite magnetic field and low bias. The absorption of a photon can lift the blockade by exciting the charge carriers above the band gap and allow their recombination. Then, the DQD is loaded again from the leads and is – thanks to the electron-hole symmetry – immediately blocked, since the magnetic field and the low bias ensures that only two incompatible charge carriers can tunnel into the DQD. This sequence can be monitored using a capacitively coupled charge detector, allowing the detection of individual THz photons. The detectable photon frequency in the THz regime can be adjusted by the detuning energy and the voltage controllable band gap in BLG.

- The electron-hole symmetry is also a very intriguing property for Cooper pair splitters based on BLG QDs are coupled via an s-wave superconductor. In conventional systems the spin of the ground states in the two QDs are identical, forbidding crossed Andreev reflection and Cooper pair splitting, but allowing for elastic (co-)tunneling from one QD to the other. In order to enable crossed Andreev processes, careful tuning of the system by close-by ferromagnets or spin orbit interaction are used [Wang et al. Nature 612, 448 (2022) and Bordoloi et al. Nature 612, 454 (2022)]. In stark contrast to these conventional systems, the ground state to ground state transition between an electron and hole QD in BLG is intrinsically spin forbidden, which gives rise to the electron-hole blockade reported in our work and is identical to the statement that elastic co-tunneling is forbidden. Instead, crossed Andreev reflection (or Cooper pair splitting), which requires two electrons of opposite spin to be involved remains allowed. This renders electron hole QDs in BLG an ideal platform for Cooper pair splitters with very high splitting efficiency. Please note, that the potentially high energy scales in the bilayer DQD system makes such a configuration also very interesting for charge pumps [Connolly et al. Nature Nanotechnology 8, 417(2013)].

- QD systems with a finite intrinsic probability for crossed Andreev reflection are compelling platforms for tuning the system to a balance between crossed Andreev reflection and elastic co-tunneling (e.g. by canting the spin into the BLG plane using a parallel magnetic field), and for realizing 'poor-man's Majorana states' and elemental unit cells of Kitaev chains [Leijnse et al., Phys. Rev. B. 86, 134528 (2012) and Dvir et al. arxiv:2206.08045 (2022)]. A schematic illustration of such a system is shown in Fig. R2c. In particular the low electrostatic disorder and absence of accidental QDs, often observed in InAs, could make BLG an intriguing platform for this direction.

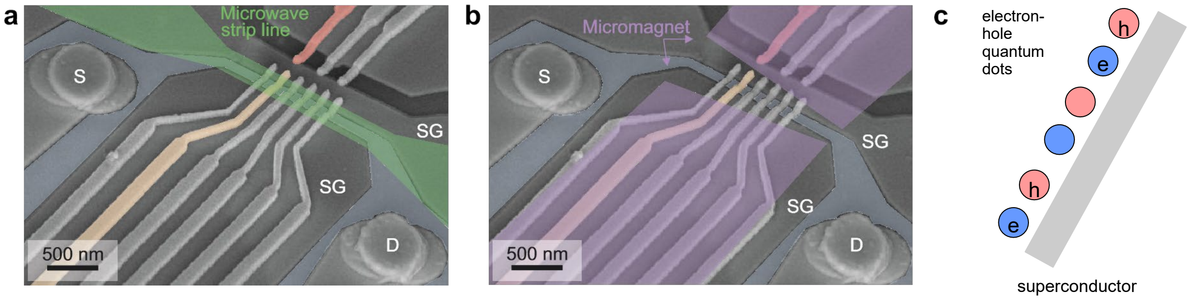

Figure R2: **a** Schematic illustration of a BLG QD device, where a superconducting strip line has been added to create an in-plane AC magnetic field to resonantly drive spin transitions. **b** Schematic illustration of a BLG QD device, where a micromagnet has been added to create an in-plane magnetic field gradient. **c** Schematic illustration of electron-hole quantum dots coupled to a superconductor formin a building block of a potential Kitaev chain.

Reviewer 3:

The authors report an experimental study of spin-valley blockade in bilayer graphene double quantum dots (BGDQs) of the p-n type and support their experimental results through theoretical interpretations and calculations with a focus on symmetry. Indeed, graphene has special electronic properties as compared to more common semiconductors in that it offers a Dirac spectrum. Transport blockade through double quantum dots relies on the Pauli principle so that certain configurations of occupied states do not allow for transport. Interestingly, this blockade only appears for current flowing in one direction. The general effect is well known and has been studied in different material systems even recently in BGDQs.

The interpretations are very solid and are supported well by the experimental data with several tunable parameters such as gate voltages and magnetic field. The manuscript is in most parts very clearly presented and the supporting information gives relevant details of the experiment and theory.

I have spent quite some time to think about the impact and novelty of the work. I think that in general the idea to use electrons (conduction band) and holes (valence band) in the BGDQs at the same time in connection with a protected spin-valley blockade is quite intriguing. In addition, as the authors well explain, the combination of precisely (gate-) controllable electron and hole transport is not possible in more ordinary two-dimensional electron gases like in GaAs based heterostructures as the semiconducting band gap is too large. The gate-defined BGDQs became a reality in recent years in laboratories as the one in the group of C. Stampfer (corresponding author) and are currently investigated as prime candidates for spin qubit applications. The current results would e.g. support read-out of such qubits.

We would like to thank reviewer for spending time and effort to carefully read our manuscript and for making suggestions and raising questions in order to improve important aspects of it. We are pleased to read that the reviewer thinks that our *"interpretations are very solid and are supported well by the experimental data"* and that she/he considers *"a protected spin-valley blockade quite intriguing"*.

My main hesitation to recommend publication in Nature is the potential lack of broad impact of the specific idea to use electrons and holes for spin-valley blockade. Also, there is already a spinvalley blockade experiment in BGDQs published in Physical Review Letters highlighted as "editor suggestion" and "featured in physics" from other authors (Ref. [35] in the current manuscript). There are similar claims and results in that publication although not for an electron-hole BGDQ but in an electron-electron BGDQ. The present authors conclude that their particle-hole symmetry protection is not relevant in such systems (Ref. [35]) which is correct. The workhorse in the usual form of the Pauli-spin blockade is based on singlet-triplet splitting whereas in the present setup single-particle electron and hole states in different orbitals can be created or annihilated. It is not clear to me and it is not discussed in detail in the manuscript if the present setup with a blockade protected by particle-hole symmetry is fundamentally more stable than the more ordinary spin-valley blockade using the singlet-triplet splitting? For me that is an important point for the potential impact this work could have in the field.

We would like to thank the reviewer for raising this important point. We agree that it is essential for our work to discuss and show that the symmetry protected spin and valley blockade is fundamentally different and more stable than the conventional singlet-triplet spin Pauli blockade, which has been studied in GaAs, SiGe, Si-MOS, Ge and more recently also in BLG ([Tong et al. Phys. Rev. Lett. 128, 067702 (2022)], also mentioned by reviewer).

After reviewing the manuscript, we note that important aspects could have been presented more clearly and that some arguments were not made explicit enough, which may have led to misunderstandings. We have adapted the main manuscript to clarify these points, and added two new sections to the Supplementary (Section E, F, see page 16 ff. in this reply letter.) dedicated to an in-depth discussion of the symmetry protection and the comparison to conventional singlet-triplet Pauli blockade. A detailed explanation of the difference between "conventional" and "symmetry protected" Pauli blockade is also given below.

My specific comments and questions are listed here and might help to amend the presentation and strengthen the message of the work.

- The particle-hole symmetry protected spin-valley blockade which is central to the interpretation and scope of the work is quite powerful as it survives spin-orbit coupling and magnetic fields. However, it is assumed that the shapes (confining potential) of the electron and hole sides are identical or at least very similar. So, the protection seems to me less stable than e.g. effects protected by time-reversal symmetry (which would be broken in the presence of magnetic fields). When compared to Ref. [35], is the present protection of the blockade using electrons and holes superior or it is mainly a different symmetry protecting the selection rules in transport channels through the BGDQ? Suppose, one has two identical tunnel-coupled electron-based quantum dots (same shape, valley g-factor and spin-orbit couplings). I do not see why in such a case the protection of the spin-valley blockade would be fundamentally less strong as the main effect is in both cases (electron-hole BGDQ , electron-electron BGDQ) the Pauli principle by blocking transitions involving the same quantum numbers. I would like the authors to elaborate/comment on this issue.

We thank the reviewer for raising this concern, which helps to clarify a central claim of the manuscript. Thanks to the remark, we realize that in the original manuscript we did not formulate clearly the symmetry requirements needed for the single-particle electron-hole blockade. It is very important to note that there is a difference between (I) the perfect electron-hole symmetry and (II) the electron-hole symmetry of the spin and valley texture (i.e., the ordering of the quantum states), which plays the crucial role for the blockade. While for perfect electron-hole symmetry the shapes of the electron- and hole-QDs (confinement potentials) need to be identical (or at least very similar), the requirements for a symmetric electron-hole spin-valley texture are substantially less strict. In particular, asymmetries in QD shapes, valley g-factors and the Kane-Mele spin orbit gap are tolerated to a large extend, while still having a robust symmetry protected single-particle blockade. This aspect is now discussed in detail in the new section F of the supplementary material (see also page 19 of this letter).

It is also important to note that the symmetry protected single-particle electron-hole blockade is fundamentally different with respect to the conventional singlet-triplet spin Pauli blockade. The single-particle electron-hole blockade is a consequence of the *mirror symmetry* (highlighted in Figs. 1a,b in the main manuscript) of the electron and hole Hamiltonian ($H_e = -H_h$), which causes the ground states of the electron and hole QD to have the same spin and valley quantum numbers. However, for an electron-hole interdot transition the quantum numbers need to be opposite and therefore the ground-state to ground-state transition is both spin and valley blocked.

The situation is different in the more conventional situation of a unipolar DQD made of two single-electron (or two single-hole) QDs: Here, every state in the left QD has a matching state in the right QD and the system does not show Pauli blockade, i.e. the transition $(1,0) \leftrightarrow (0,1)$ is always possible. Thus in order to obtain spin Pauli blockade in a unipolar QD, the two-particle spectrum with a sizeable singlet-triplet splitting is utilized.

The differences between the conventional singlet-triplet Pauli blockade (for various materials, incl. BLG) and the single-particle electron-hole blocked is now discussed in detail in the newly added section E of the supplementary material (see also page 16 of this letter). In this context, we would also like to emphasize the new schematics in Fig. R5 (new supplementary Fig. S7), which shows the direct comparison of the single-particle electron-hole blocked and the conventional singlet triplet spin Pauli blockade for different detuning.

While the reviewer is correct in stating that the blockade in both cases relies on Pauli's principle, the symmetry protected single-particle blockade is significantly more robust because of the following reasons:

(i) Excitations or detuning energies larger than the singlet-triplet splitting, which e.g. in silicon are limited by the valley splitting, lift the conventional singlet-triplet Pauli blockade. This restricts the allowed detuning to approx. 50-300 μeV in SiGe [Borselli et al. Appl. Phys. Lett. 99, 063109 (2011), Philips et al. Nature 609, 919 (2022)], 300-800 μeV in Si-MOS [Yang et al. Nat. Commun. 4, 2069 (2013)], and 850 μeV for holes in germanium [Hendrickx et al. Nat. Commun. 11, 3478 (2020)] and to around 1.7 meV in a unipolar BLG DQD device [Tong et al. Phys. Rev. Lett. 128, 067702 (2022)]. In contrast, the next available (spin and valley matching) state in case of the electron-hole blockade requires an interband transition and is protected against excitations by the size of the band gap, which is typically on the order of 20-120 meV [Icking et al. Adv. Electron. Mater. 8, 2200510 (2022)] (see Fig. R4 and Fig. R5 and detailed response below), which makes the electron-hole blockade robust beyond the experimentally accessible detuning values.

(ii) In case of the symmetry-protected blockade, the ground state transition is protected by both, spin and valley selection rules, for all magnetic fields, and there is no weakly blocked regime as the valley blockade in [Tong et al. Phys. Rev. Lett. 128, 067702 (2022)], dominating at zero and low magnetic fields. Importantly, the doubly blocked ground-state to ground state-transition makes the single-particle electron-hole blockade robust to relaxation into the ground state. Conveniently, the DQD does not need to be tuned to the spin-valley blockade, because the electron-hole symmetric spin and valley texture is independent on the magnetic field.

Importantly, these protection mechanisms remain robust also when the electron and hole QD spectra are not perfectly symmetric, as long as the spin and valley texture, i.e. the ordering of states is not altered. Altering the electron-hole symmetric spin-valley texture is very unlikely, because it is either protected by large energy scales (the large band gap, or the displacement field direction, i.e. the potential applied to the top and back gate) or by the intrinsic electron hole symmetry of the Hamiltonian (H_{BLG}, H_{SO}) and so far no conditions have been reported which could lift this blockade. By now, we have investigated 5 different electron-hole DQD devices, and all of them presented a robust single-particle spin-valley blockade (see also very recent data shown in Fig. R1).

To clarify this point, we have added a detailed discussion on potential symmetry breaking mechanisms (asymmetric valley g-factors, asymmetric spin orbit interaction, and extrinsic spin orbit coupling) and their required strength in order to lift the electron-hole blockade in the new supplementary section F (see also page 19 in this reply letter) and adapted the main text and supplementary material, stating more clearly that perfect electron-hole symmetry is not required for the blockade. Moreover we extended Fig. S8 in the supplementary material (see also Fig. R3 to highlight that asymmetries in the valley g-factor ($g_v^e \neq g_v^h$) indeed cannot lift the blockade.

For being more precise we also modified the second last sentence of the abstract to:

Moreover, we show that the particle-hole symmetric spin and valley textures lead to a protected single-particle spin-valley blockade.

In the main manuscript we modified the following paragraph (see page 7 in the manuscript):

The robustness is a direct consequence of (i) the separation of higher orbital states by the band gap (see lower panel in Fig. 2e) and (ii) the spin and valley texture of our system (i.e. the ordering of the states) imposed by particle-hole symmetry, which forbids ground-state to ground-state transitions, by both spin and valley selection rules, independent of the applied magnetic field. This is in stark contrast to the conventional singlet-triplet Pauli-blockade [27,28], which only exists in a limited range of detuning and magnetic field, and which is only protected by spin selection rules that can be lifted by relaxation mechanisms [27] (see Suppl. Sec. E).
It should be noted that perfect particle-hole symmetry is not necessary for achieving a robust blockade, but only the ordering of the electron and hole states needs to be symmetric. The symmetric state ordering is strongly protected as it is intrinsic to the BLG band structure and no conditions have been observed which allow to lift the blockade (see Suppl. Sec. F). The robustness of the single-particle blockade also indicates the absence of spin- or valley-flipping processes and that mixing between the states within a Kramers' pair is negligible.
In the following, we demonstrate that we not only have a symmetric state texture, but observe indeed near perfect symmetry of the particle-hole states in our system. This is not a priori granted, since electrons and holes are physically separated into two different QDs on different layers of the BLG (see Fig. 4a), giving rise to two mechanisms that can potentially break the perfect symmetry of the system.

- I think it would help to include a table either in the main text or supporting information which shows the different effects (magnetic field, spin-orbit interaction, displacement field etc.) and if they break particle-hole symmetry or not.

We thank the reviewer for this very helpful suggestion. We now added a new section in the supplementary material (Section F), in which we discuss in detail potential symmetry breaking mechanisms and elaborate on the requirements to lift the single-particle electron-hole blockade. In the supplementary section F (see also page 19 of this reply letter) we also included the following table.

Mechanism breaking the symmetry of the level texture	Requirement for symmetry breaking
Carrier-type dependent valley g-factors	$\mathrm{sgn}(g_\mathrm{v}^\mathrm{e}) \neq \mathrm{sgn}(g_\mathrm{v}^\mathrm{h})$
Layer dependent Kane-Mele term	$\mathrm{sgn}(\Delta_\mathrm{SO}^\mathrm{t}) \neq \mathrm{sgn}(\Delta_\mathrm{SO}^\mathrm{b})$
Bychkov-Rashba SO coupling	$\lambda_\mathrm{ex} \gtrsim E_\mathrm{g}$

Table 1: Summary of the potential mechanisms that might break the symmetric spin and valley texture for particles and holes. g_v^e and g_v^h are the valley g-factors of the electrons (e) and the holes (h). Δ_{SO}^t and Δ_{SO}^b are the coupling constants of the Kane-Mele SO coupling for the top (t), bottom (b) layer of BLG. λ_{ex} is the coupling constant of extrinsic SO coupling, scaling linearly with applied displacement field. E_g is the band gap energy.

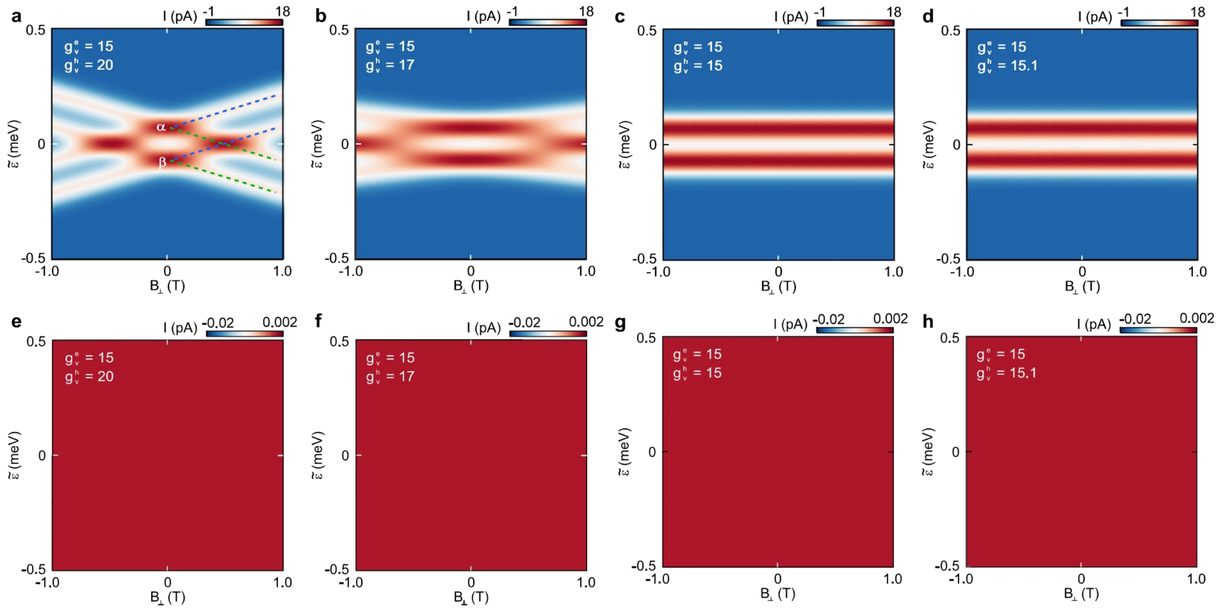

Figure R3: [Revised supplementary Fig. S8] Calculation of the current through the device as a function of the detuning energy ε (see arrow in Fig. 2c of the main text) and perpendicular magnetic field at a finite bias of $V_{\mathrm{SD}} = 2$ mV (a-d) and $V_{\mathrm{SD}} = -2$ mV (e-h). In **a**, the valley g-factors of the two QDs are chosen asymmetrically ($g_v^e =$ 15 for the electron QD and $g_v^h = 20$ for the hole QD), resulting in a splitting of both, the α and β transition, which scales with the difference in the valley g-factors. In **b**, the valley g-factors of the two QDs are chosen less asymmetrically ($g_v^e =$ 15 for the electron QD and $g_v^h =$ 17 for the hole QD), resulting in a smaller splitting of both, the α and β transition, which scales with the difference in the valley g-factors. In **c** the valley g-factors are chosen symmetrically (g_v = 15), and no dependence on $B_\perp$ is observed. In **d**, the experimentally observed g-factor difference of g_v^e = 15 and g_v^h = 15.1 is used for the simulation. **e-h** For reverse bias, the Pauli blockade remains robust and the current is zero, independent of the chosen g-factor asymmetry, as the spin and valley texture, i.e. the level ordering remains symmetrical.

- On page 9, it is mentioned that the "... inversion symmetry is broken due to the electric displacement field ... " in connection with effects that can break particle-hole symmetry. But I think that the displacement field does not break particle-hole symmetry as far as it is included in E_g appearing in H_{BLG} on page 3. I find the quoted statement therefore confusing.

We thank the reviewer for mentioning this point of confusion. The reviewer is absolutely correct in stating that neither H_{BLG} nor H_{SO} describe the breaking of the particle-hole symmetry by the displacement field. The argument here is a bit more subtle since it is implicit: Inversion symmetry in BLG forbids a Bychkov-Rashba spin-orbit term, which would break particle-hole symmetry (Kane and Mele, Phys. Rev. Lett. 95, 226801 (2005), see also Refs. [8] and [10]). This term becomes allowed in the presence of a displacement field that breaks inversion symmetry, but it is strongly suppressed close to the K and K' points, which is consistent with the absence of an asymmetry between the electron and hole spectrum in our data. A detailed discussion is now presented in the new section F (see subsection "3. Particle-hole symmetry breaking due to Bychkov-Rashba spin-orbit coupling" of the supplementary material (see page 20 of this reply letter).

In the main manuscript we refer to it in the following way (see page 7 in the manuscript):

It should be noted that perfect particle-hole symmetry is not necessary for achieving a robust blockade, but only the ordering of the electron and hole states needs to be symmetric. The symmetric state *ordering is strongly protected as it is intrinsic to the BLG band structure (see Suppl. Sec. F). The robustness of the single-particle blockade also indicates the absence of spin- or valley-flipping processes and that mixing between the states within a Kramers' pair is negligible.*

- On page 5, the authors write "This blockade is robust up to very high detuning energies, because it can only be overcome by involving excited states that are separated in energy from the low energy spectrum by the band gap, which is typically 20-60 meV". I do not understand this statement. The orbitals belonging to a different group (four valley-spin configurations) of states are separated by the confinement energy that depends on the size of the quantum dot and not the band gap. Can the author comment on this? Maybe I just misunderstand the statement.

We thank the reviewer for asking this question, which shows that this unique aspect of electron-hole DQDs needs a bit more explanation: In order for an electron from the electron QD to tunnel into the hole QD via an interdot tunneling process, it needs to access a free state in the adjacent hole QD. All states of the hole QD in the blockade regime are occupied with electrons up to the valence band edge (see black dots in the lower panel of Fig. R4) except for the (single) 'hole' state of interest depicted in the schematic (see white dot), which is a missing electron. If the electron cannot occupy this state due to spin or valley selection rules (which is the symmetry protected single-particle electron-hole blockade), the next free state requires an interband transition and lies above the conduction band edge, and is hence separated not only via the confinement energy, but via the confinement energy plus the band gap ($< E_g$). This is also true for the hole state, where the next free state for a hole (which is one not occupied by an electron) lies in the valence band of the electron QD (see Fig. R4).

For making this more clear we adapted the main manuscript and added a new schematics in Fig. 2 (see new lower panel in Fig. 2e corresponding to the lower panel shown in Fig. R4).

At this point we also would like to mention that in the revised manuscript we modified the typical BLG band gap range from 20-60 meV to 20-120 meV motivated by recent work (see Fig. 6 in [Icking et al. Adv. Electron. Mater. 8, 2200510 (2022)]).

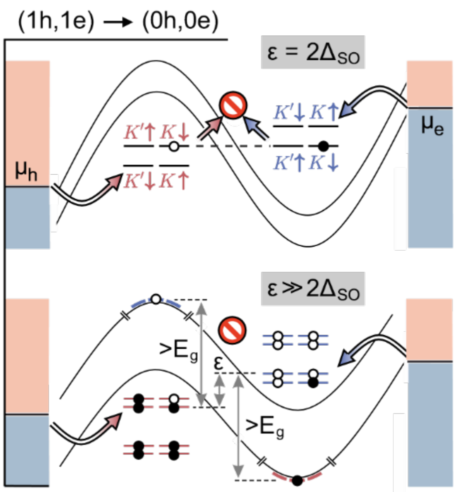

Figure R4: [Revised Fig. 2e in the main manuscript] Schematic of the alignment of energy levels in the shells around the Fermi energy of an electron-hole DQD for negative bias. The blockade can only be lifted via an excitation into the next available orbital state, which in contrast to unipolar quantum dots corresponds to an interband-excitation over the band gap (see lower panel).

- In Fig. 4, broadenings are extracted from the data and attributed to the degree of difference of valley g-factors in the two dots (on top of page 11). To me it is not clear why broadenings of resonances are related to broken symmetries (here valley g-factors) and not just to the coupling strengths of the QD states to the leads? Or are these broadenings dominated by the interdot couplings?

We thank the reviewer for raising this point. The reviewer is perfectly correct in stating that the broadening most likely originates from magnetic field dependent coupling strengths of the QD states to the leads. However, apart for this there could also be other mechanisms leading to peak broadening. Attributing the peak broadening entirely to a splitting of α and β transitions due to different valley g-factors in the two QDs (i.e. the electron and hole QD), corresponds to the "worst case scenario" in terms of breaking the particle-hole symmetry. This allows us to estimate an upper bound for the asymmetry in the valley g-factor between the two QDs. Here, the origin of the splitting of the α and β resonances results from a lifting of the degeneracy of the two processes contributing (e.g. $|K'\uparrow\rangle_e \leftrightarrow |K\downarrow\rangle_h$ and $|K\downarrow\rangle_e \leftrightarrow |K'\uparrow\rangle_h$ for α) (see also Fig. S7 for details).

We have changed the phrasing slightly in the revised manuscript which now reads (see page 8):

To quantify an upper bound for these effects, we extract the full width at half maximum (Γ) of the resonances α, β, and γ by fitting Gaussian line shapes and assuming a constant background and an equal width of the α and β peaks (see Fig. 4c,d). For increasing $B_\perp$, we observe a slight broadening of the α and β resonance, as shown in Fig. 4e. Attributing this broadening entirely to a difference of valley g-factors between the electron and hole QD (rather than e.g. to variations in the the tunnel coupling) we get an upper limit for the valley g-factor mismatch below 1% of g_v, which is consistent with the high symmetry of our gate design.

Copy of the new sections E and F in the supplementary material[1]

E. Comparison of singlet-triplet Pauli blockade and the single particle electron-hole blockade

In this section, we compare the robustness of the single-particle electron-hole blockade to the conventional singlet-triplet spin Pauli blockade in different material systems, which is summarized in Table 2.

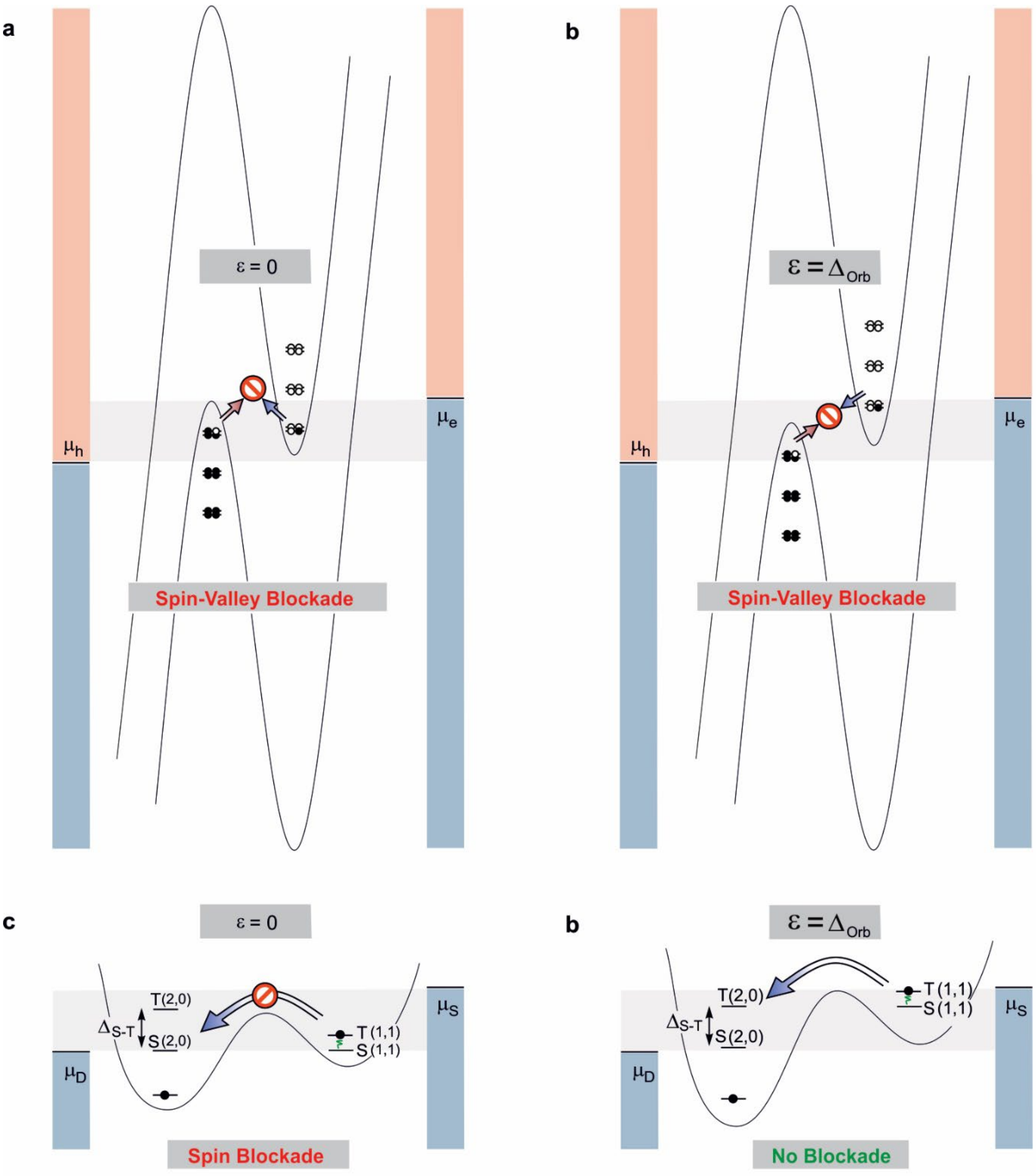

Figure R5: Schematic of the chemical potentials in an electron-hole DQD for **a** $\epsilon = 0$ and **b** $\epsilon = \Delta_{SO}$. For clarity the energy axis of the schematic is drawn to scale, such that $E_g = 10\,\Delta_{orb} = 100\Delta_{SO}$. It can be seen that the band gap energy protects the blockade to be lifted by detuning. **c, d** show the same configurations in a unipolar DQD in (1,1) → (2,0) configuration. The singlet-triplet splitting Δ_{S-T} is chosen to be equal to the orbital splitting Δ_{orb} in a,b. Is can be seen that the blockade is lifted as soon as $\epsilon = \Delta_{S-T}$. Additionally, it can be lifted by relaxation of the triplet (1,1) state into the singlet (1,1) state.

[1] References can be found in the supplementary material.

For the conventional singlet-triplet spin Pauli blockade in unipolar DQDs (i.e. electron-electron or hole-hole DQDs), a finite tunneling probability into higher orbital states (or valley states in silicon) lifts the blockade and sets a limit to the detuning window (typically in the order of $0.05-1.7$ meV depending on the material system and QD size), in which the DQD remains Pauli blocked, as illustrated by Fig. R5c,d. In a unipolar BLG DQD, spin blockade has been observed with a detuning range limited by the B-field dependent excited state splitting and by the orbital splitting to a maximum of 1.7 meV, but only for magnetic fields larger than 0.6 T [3]. In the single-particle electron-hole regime however, the blockade is robust over the entire experimentally available detuning window instead of merely a small region, which is illustrated in Fig. R5a,b. This is due to the fact that the next higher accessible states for increasing detuning are not only separated by the confinement energy of the QDs but by the sum of the confinement energy and the size of the band gap, which is typically on the order of $20 - 120$ meV [4].

Additionally, due to particle-hole symmetry, electron and hole states have a symmetric spin and valley texture. This means that a ground state $|\mathrm{K}' \uparrow\rangle$ for the electron QD demands that the ground state in the hole QD is $|\mathrm{K}' \uparrow\rangle$. Because of this, ground state to ground state transitions are twofold blocked, both by spin and valley selection rules. Crucially, the ground state to ground state transition remains blocked independent of the applied perpendicular or parallel magnetic fields, allowing to tune the system without losing the single-particle blockade. This is in contrast to the conventional singlet-triplet spin Pauli blockade, which is only blocked by spin selection rules and where the blockade is lifted as soon as the Zeeman splitting of the triplet state equals the singlet-triplet splitting, $\Delta_{\mathrm{S-T}}$. For qubit operations in most systems, this is not a large obstacle, as the involved states only weakly tune with magnetic field and one usually stays at low B-fields in order to have the longest spin (and/or valley) lifetimes. What makes our system stand out however, is the fact that it is strongly tunable by magnetic fields (due to the high valley g-factors (10 - 70), while still maintaining the blockade across the whole tuning range (making it robust for electron or hole shuttling or other long-range coupling mechanisms [5]). Moreover, it is noteworthy that while relaxation processes that bring the QD to its ground state do not lift the blockade in our electron-hole system, they do lift the blockade in singlet-triplet Pauli blockade systems [6].

When considering material systems that possess a valley degree of freedom, using an electron-hole single particle blockade has additional advantages. Together, spin and valley degree of freedom give rise to many possible states for few-particle QD systems. For example, a two-electron single QD with 2 spin and 2 valley degrees of freedom already has 16 possible states [7], which results in a total of 256 transitions for two electrons ((1,1) → (0,2)) in a unipolar DQD. Even though this number is reduced by spin and (much weaker) valley selection rules [3], the large number of transitions (which depend on the device geometry and the applied magnetic field), strongly reduce the parameter window and require the fine-tuning of a device into spin or valley blockade [3], which becomes a disadvantage when scaling the system to many DQDs, i.e., for quantum computing applications. Hence, being able to operate the blockade in the single particle regime is very convenient, as the number of possible transitions is significantly reduced. Also, in the case of unipolar BLG DQDs, spin blockade is even absent for magnetic fields smaller than 0.6 T. These high magnetic fields result in large spin splittings ($\Delta E = \sqrt{\Delta_{\mathrm{SO}}^2 + (\mu_{\mathrm{B}} g_{\mathrm{s}} B_{\perp})^2}$), which correspond to experimentally challenging qubit frequencies in excess of 25 GHz.

It is very important to note that perfect particle-hole symmetry is not necessary for the single particle blockade to be present, only the texture of the states need to have the same ordering for particles and holes. All mechanisms changing this texture are strongly suppressed, as discussed in the next section.

	This work	Singlet-triplet spin Pauli blockade in				
Blockade lifting mechanism	single particle electron-hole blockade	GaAs [6,8]	SiGe [9-11]	Si-MOS [12]	Ge (holes) [10,13]	unipolar BLG [3]
Detuning (meV)	20 - 120 [4]	0.5	0.05 - 0.3	0.3 - 0.8	0.85	≤ 1.7
Magnetic field B (T)	no lifting	< 2	$< 0.5 - 2.6$	$< 2.6 - 6.9$	< 40	spin blockade only for $B > 0.6$ T
Relaxation	no lifting	yes	yes	yes	yes	no lifting for $B > 0.6$ T
Spin g-factor	~ 2	0.1 - 0.5	~ 2	~ 2	0.9 - 2	~ 2
Valley g-factor	10 - 70 [14]	-	0	0	-	10 - 70 [14]

Table 2: Comparison of the conventional singlet-triplet spin Pauli blockade in other material systems with the single particle electron-hole blockade. In the two upper rows "detuning" and "magnetic field" we show in which corresponding parameter range the blockade is present in each system, while the row "relaxation" states whether the blockade can be overcome by ground-state relaxation. The last two rows show the g-factors (spin and in case valley) of each system to put the magnetic field range into perspective.

F. Breaking the symmetry of the spin and valley texture in BLG

The invariance of the Hamiltonian of BLG, H_{BLG}, under the particle hole transformation K (see main text) results in a mirror symmetric spectrum for electrons and holes, where the electron and hole ground states have the same spin and valley quantum number. Thus, the ground state to ground state transition is forbidden both by spin and valley selection rules. This transition remains forbidden, independent of the applied magnetic field.

In this section, we will discuss possible mechanisms that break the symmetry of the spin and valley texture, i.e. the ordering of the electron and hole states. Such mechanisms have therefore the potential to lift the single-particle blockade. Table 3 at the end of this section (see subsection 4) summarizes the potential mechanisms and the requirements to break the symmetry of the spin or valley texture.

The single particle Hamiltonian describing the states in the electron (H_{e} with $\sigma_z = +1$) and hole (H_{h} with $\sigma_z = -1$) QD under the influence of an external magnetic field is given by

$$\begin{aligned}\mathrm{H_e} &= +\tfrac{1}{2}\Delta_{\mathsf{SO}}\tau_z s_z + \tfrac{1}{2}g_{\mathsf{s}}\mu_{\mathsf{B}}\mathbf{B}\cdot\mathbf{s} + \tfrac{1}{2}g_{\mathsf{v}}^{\mathsf{e}}\mu_{\mathsf{B}}\mathrm{B}_z\tau_z,\\ \mathrm{H_h} &= -\tfrac{1}{2}\Delta_{\mathsf{SO}}\tau_z s_z - \tfrac{1}{2}g_{\mathsf{s}}\mu_{\mathsf{B}}\mathbf{B}\cdot\mathbf{s} - \tfrac{1}{2}g_{\mathsf{v}}^{\mathsf{h}}\mu_{\mathsf{B}}\mathrm{B}_z\tau_z.\end{aligned}$$

Breaking of the symmetric spin and valley texture in our electron-hole DQD system could arise from (i) strong asymmetries – in the end sign flips – of the individual terms (i.e. Δ_{SO}, g_s or g_v) in the single particle Hamiltonian, H_{e} and H_{h} , describing the states in the two QDs or by (ii) introducing extrinsic Bychkov-Rashba type SO coupling with different strength to both QDs.

1. Spin and valley g-factors

In order to allow the spin-Zeeman term and the valley-Zeeman term to break the symmetric ordering of the electron and hole states in the two QDs, variations in the spin or valley g-factor are not sufficient, but a sign change of the g-factor in the two QDs would be required. As the spin g-factor of electrons and holes in BLG has been found – in agreement with graphene and carbon nanotubes [15,16] – to be in good agreement with the Landé g-factor of free electrons, $\mathrm{g}_s \approx 2$ [17,18] there is no reason to expect an asymmetry or even a sign change here. Therefore, the spin Zeeman term cannot break the symmetry of level texture and this term will not be discussed further.

Although the precise value of the valley g-factor depends on the QD confinement potential and the applied electric displacement field (see e.g. [2,14,19]), the sign of the valley g-factor for a confined electron in BLG depends only on the sign of the Berry curvature. This is a robust property of the BLG band structure, only dependent on the valley and band indices. Hence, a sign reversal of the spin- and valley-Zeeman terms between the two QDs can be excluded.

2. Layer-dependent Kane-Mele spin orbit term

The intrinsic Kane-Mele spin-orbit Hamiltonian, which acts on the states of the four-band Hamiltonian (see H_{BLG} in the main manuscript) is given by [20], $H_{\mathsf{SO}} = \frac{1}{2}\Delta_{\mathsf{SO}}\sigma_z\tau_z s_z$. It is symmetric under particle-hole transformation, but may be subject to (small) corrections, due to a substrate-dependent proximity induced enhancement or potential partial cancellations (not yet observed) of Δ_{SO}. Such a correction to Δ_{SO} only affects the particle-hole symmetry if the electron and hole QDs experience a different effective SO gap, either due to layer dependent variations of Δ_{SO}, or due to a strong spatial variation of Δ_{SO}. In the more general setting, the spin-orbit Hamiltonian can be described by the form

$$H_{\mathrm{SO}} = \frac{1}{4}\Psi^\dagger[(\Delta^{\mathsf{t}}_{\mathrm{SO}} + \Delta^{\mathsf{b}}_{\mathrm{SO}})\sigma_z - (\Delta^{\mathsf{t}}_{\mathrm{SO}} - \Delta^{\mathsf{b}}_{\mathrm{SO}})\sigma_0]\tau_z s_z \Psi,$$

with different spin-orbit coupling energy gaps Δ^{t}_{SO} and Δ^{b}_{SO} for the top (t) and bottom (b) layer of the BLG[i] [22]. In order to allow these mechanisms to alter the spin and valley texture, they must be large enough to flip the sign of Δ_{SO} in one of the QDs: $\mathrm{sgn}(\Delta^{\mathsf{t}}_{\mathrm{SO}}) \neq \mathrm{sgn}(\Delta^{\mathsf{b}}_{\mathrm{SO}})$. In Figs. 1b, 3a (in the main manuscript) or Fig. S5a it can be seen that a sign change in Δ_{SO} for either electrons or holes is required in order to change the ordering of the states. Please note that a decrease of, or even a sign change of the SO gap have not been observed experimentally so far. Measurable differences between Δ^{t}_{SO} and Δ^{b}_{SO} are only likely to occur if the BLG is encapsulated between two different materials with very different SO coupling [1], [2]. In previous publications, it has been shown that the SO gap in similar devices is always very close to 70 μeV [3], [4], with deviations from this value only on the order of 10%, which is close to the measurement uncertainties.

Interesting side note: A strong asymmetry between Δ^{t}_{SO} and Δ^{b}_{SO} leads not only to different spin-orbit gaps at zero magnetic field, but also to a finite non-collinearity between the spin states in the electron and hole QD for intermediate in-plane magnetic fields. This is because a tilting of the spin states into the plane with increasing $B_{\parallel}$ occurs at higher magnetic field with increasing Δ_{SO}. This effect, however, is suppressed, when the spin quantization axis is along the in-plane or out-of plane direction, i.e. either $\frac{1}{2}g_{\mathsf{s}}\mu_{\mathsf{B}}B_{\parallel} \ll \Delta_{\mathrm{SO}} + \frac{1}{2}g_{\mathsf{s}}\mu_{\mathsf{B}}B_{\perp}$ or $\frac{1}{2}g_{\mathsf{s}}\mu_{\mathsf{B}}B_{\parallel} \gg \Delta_{\mathrm{SO}} + \frac{1}{2}g_{\mathsf{s}}\mu_{\mathsf{B}}B_{\perp}$.

3. Particle-hole symmetry breaking due to Bychkov-Rashba spin-orbit coupling

Since the inversion symmetry of BLG is explicitly broken in our case by applying a perpendicular electric displacement field, extrinsic (Bychkov-Rashba) spin-orbit coupling poses an additional mechanism to break the particle-hole symmetry in our electron-hole DQD system. The corresponding term in the Hamiltonian is given by [22]

$$H_{\mathrm{BR}} = \frac{1}{2}\lambda_{\mathrm{ex}}\Psi^\dagger\Big(\sigma_y s_x + i\tau_z\sigma_x s_y\Big)\Psi.$$

The extrinsic (Bychkov-Rashba) SO coupling, λ_{ex}, scales linearly with the applied electric displacement field[ii]. For understanding the influence of the extrinsic (Bychkov-Rashba) term, we note that for Fermi energies close to the band edge, the sublattice space is equivalent to the layer space and therefore to the conduction and valence band. This is caused by the fact that excess charge is strongly layer polarized, only leading to a small admixture of the sublattices [27,28]. The extrinsic SO term H_{BR} couples the two sublattices via $\sigma_{x,y}$ and therefore to the two layers, which experience a potential difference due to the electric displacement field. As a consequence, the extrinsic spin-orbit term is suppressed proportional to $\sim \lambda_{\mathrm{ex}}^2/E_{\mathrm{g}}^2$. Theoretical predictions of λ_{ex} are at least three orders of magnitude smaller than the band gap (E_{g}), rendering extrinsic spin-orbit coupling irrelevant for our system [1,22].

4 Summary Table

Mechanism breaking the symmetry of the level texture	**Requirement for symmetry breaking**
Carrier-type dependent valley g-factors	$\mathrm{sgn}(g_{\mathrm{v}}^{\mathrm{e}}) \neq \mathrm{sgn}(g_{\mathrm{v}}^{\mathrm{h}})$
Layer dependent Kane-Mele term	$\mathrm{sgn}(\Delta_{\mathrm{SO}}^{\mathrm{t}}) \neq \mathrm{sgn}(\Delta_{\mathrm{SO}}^{\mathrm{b}})$
Bychkov-Rashba SO coupling	$\lambda_{\mathrm{ex}} \gtrsim E_{\mathrm{g}}$

Table 3: Summary of the potential mechanisms that might break the symmetric spin and valley texture for particles and holes. g_v^e and g_v^h are the valley g-factors of the electrons (e) and the holes (h). Δ_{SO}^t and Δ_{SO}^b are the coupling constants of the Kane-Mele SO coupling for the top (t), bottom (b) layer of BLG. λ_{ex} is the coupling constant of extrinsic SO coupling, scaling linearly with applied displacement field. E_g is the band gap energy.

[i] Δ_{SO}^t and Δ_{SO}^b correspond to λ_{I1} and λ'_{I1} in Ref. [22]

[ii] λ_{ex} corresponds to λ_3 in Ref. [22]

Reviewer Reports on the First Revision:

Referees' comments:

Referee #2 (Remarks to the Author):

I'm satisfied with the replies received by the authors. I do not have further technical comments regarding the paper. I'd like to thank the authors for the very clear and exhaustive replies.

Referee #3 (Remarks to the Author):

This is my second report on this manuscript. I think the authors have convincingly addressed my questions from the first report and I think in particular they made clearer the distinction between the ordinary case of a spin-blockade in unipolar double dots and the specific case of a gapped bilayer graphene double quantum dot operated in a bipolar configuration considered in this work. I think that in the revised manuscript it is now clearer what is the advantage of an enhanced protection of the spin-valley blockade by particle-hole symmetry as well as the role of the band gap as a relevant energy scale for lifting the blockade that indeed is potentially much larger than the singlet-triplet splitting employed in the conventional way of the spin blockade. Having a stable spin-valley blockade is potentially interesting for read-out of qubits (valley or spin). The additions made to the manuscript and in particular to the supporting information clarifies further the role of particle-hole symmetry and its robustness against various
perturbations. I think that the manuscript is now suitable for publication in Nature as it brings up a new mechanism (a spin-valley blockade protected by particle-hole symmetry) explained theoretically and shown convincingly experimentally. The paper has impact for quantum manipulations of qubits using the spin or/and the valley index in bilayer graphene quantum dots.

I have one remark for the authors. It seems that the large voltage induced bandgap mentioned E_g ~ 20-120 meV seems very promising to protect the blockade as explained by the authors in their reply and also in the revised manuscript, and I agree with the argument. However, I think at some point also the charging energy (which most likely is smaller than 120 meV) becomes the limiting energy scale as charge fluctuations could also lift the blockade. Did the authors thought about this point?

Author Rebuttals to First Revision:

Reviewer 2:

I'm satisfied with the replies received by the authors. I do not have further technical comments regarding the paper. I'd like to thank the authors for the very clear and exhaustive replies.

We are pleased to read that Reviewer #2 is satisfied with our reply to her/his comments, and we would like to express our gratitude for her/his useful comments and the effort invested in reviewing our manuscript, which has clearly helped to improve the manuscript.

Reviewer 3:

This is my second report on this manuscript. I think the authors have convincingly addressed my questions from the first report and I think in particular they made clearer the distinction between the ordinary case of a spin-blockade in unipolar double dots and the specific case of a gapped bilayer graphene double quantum dot operated in a bipolar configuration considered in this work. I think that in the revised manuscript it is now clearer what is the advantage of an enhanced protection of the spin-valley blockade by particle-hole symmetry as well as the role of the band gap as a relevant energy scale for lifting the blockade that indeed is potentially much larger than the singlet-triplet splitting employed in the conventional way of the spin blockade. Having a stable spin-valley blockade is potentially interesting for read-out of qubits (valley or spin). The additions made to the manuscript and in particular to the supporting information clarifies further the role of particle-hole symmetry and its robustness against various perturbations. I think that the manuscript is now suitable for publication in Nature as it brings up a new mechanism (a spin-valley blockade protected by particle-hole symmetry) explained theoretically and shown convincingly experimentally. The paper has impact for quantum manipulations of qubits using the spin or/and the valley index in bilayer graphene quantum dots.

We are pleased to read that we have been able to convincingly address the comments of Referee #3. We would like to thank her/him for her/his useful questions and the effort in reviewing our work, which has clearly helped to improve our manuscript.

I have one remark for the authors. It seems that the large voltage induced bandgap mentioned $E_g \sim 20-120$ meV seems very promising to protect the blockade as explained by the authors in their reply and also in the revised manuscript, and I agree with the argument. However, I think at some point also the charging energy (which most likely is smaller than 120 meV) becomes the limiting energy scale, as charge fluctuations could also lift the blockade. Did the authors thought about this point?

We thank the reviewer for raising this point. Indeed, charge fluctuations (incl. "intrinsic" charge noise, gate noise and effective temperature broadening of the source/drain Fermi functions) can lift the blockade if their magnitude is sufficiently large to induce a charge transition between the DQD and the reservoirs. The electron-hole spin-valley blockade is most resilient against charge fluctuations if the DQD is tuned to the center of the $(1h,1e)$ occupation, i.e. the configuration with the maximum distance in gate voltage space to neighboring charge transitions. In this case, the blockade is robust against charge noise with a magnitude on the order of the charging energy, E_C. In typical BLG QDs, the charging energy is on the order of 2-6 meV [1, 2, 3, 4]. However, it has already been shown experimentally that by design optimization (i.e. changing the gate layout), it is possible to reduce the size of the QD in order to increase the charging energy E_C to above 10 meV [5]. Further miniaturization of the graphene QD dimensions has the potential to increase the charging energy even more and values around 20 meV are absolutely realistic. For this estimation we considered a BLG QD with a lateral extent of 40 x 40 nm^2 and a 20 nm thick hBN crystal as the dielectric, the parallel plate capacitor model yields an estimate of $E_\mathrm{C} \approx 19$ meV (we think that hBN dielectric layers down to 5-10 nm are also feasible).
To estimate the magnitude of charge noise, we have determined the (effective) electron temperature from the width of a Coulomb peak of a BLG single QD, $T_\mathrm{el} \approx 60$ mK [6] (see Fig. R1) corresponding to an energy broadening of around 5 μeV. Hence, the charging energy E_C exceeds the charge noise by about three orders of magnitude and is thus in practice not limiting the blockade.

Note that in case of the singlet-triplet Pauli blockade, the singlet triplet splitting is the relevant energy scale limiting the maximum amount of charge noise that can be tolerated. This energy scale lies below 1 meV for conventional semiconductors (see Extended Data Table 1).

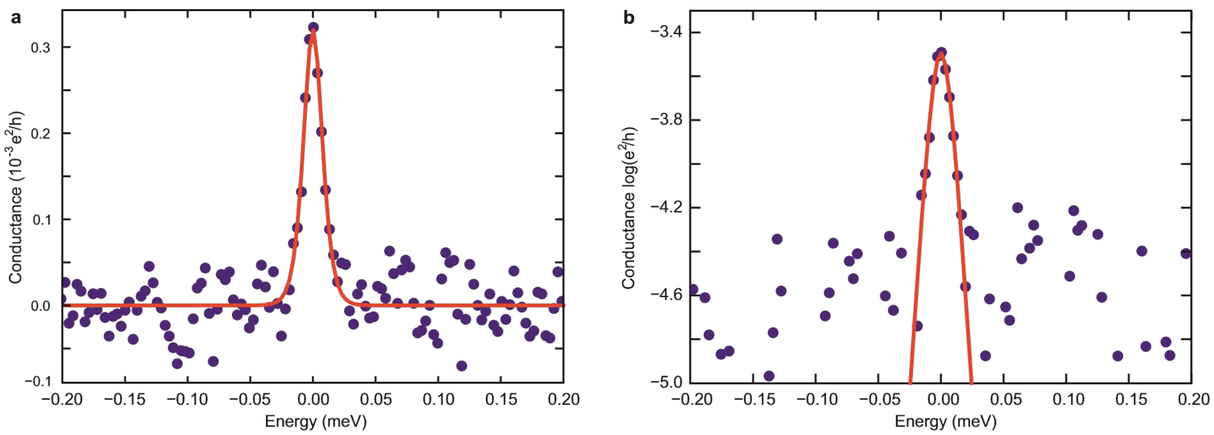

Figure R1: **Determination of the electron temperature.** Conductance G through a BLG quantum dot (plotted in linear (panel a) and logarithmic scale (panel b)) as a function of the relative energy $\alpha\Delta V_{G}$. To determine the electron temperature T_{el}, the Coulomb peak has been fitted according to $G = G_0 \cosh^{-2}(\alpha\Delta V_G/(2k_B T_{el}))$. Here, α is the gate lever arm and ΔV_G is the applied gate finger voltage. For more details on this device, see Ref. [1].

We have added the following paragraph to the discussion of possible lifting mechanisms in the Methods section (former Supplementary Material; see blue text):

Finally, we note that the electron-hole blockade is robust against charge noise up to a magnitude on the order of the charging energy, E_C, in case the e-h DQD is tuned to the most noise resilient configuration, the center of the $(1h,1e)$ charge occupation. Typical charging energies in BLG QDs measure 2-10 meV [1, 2, 3, 4, 5]. These values are typically around three orders of magnitude larger than the effective charge noise, which can be estimated from the effective electron-temperature broadening of the Coulomb peaks of a quantum dot. In our setup, the effective electron temperature is around 60 mK [6]. This corresponds to an energy scale of around 5 μeV, which is indeed three order of magnitudes smaller than the charging energy of our DQD #1 device, $E_C = 6$ meV.

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