Reviewers' comments:

Reviewer #1 (Remarks to the Author):

This manuscript describes a theoretical study of the spectrum of a rhombohedrally stacked multilayer graphene in the presence of a magnetic field. In particular, the authors study the effects of top-bottom asymmetry breaking the valley symmetry of the Landau level spectrum, and the effects of the Berry curvature of the bands. In addition, they predict the presence of transverse photoconductivity for circularly polarized light.

The predicted effects are rather interesting, but they are somewhat confusingly presented, and the cited literature is rather narrow (see below). Therefore I cannot recommend publishing this manuscript in Nature Communications at least in its present form.

My main cricitism concerns the following:
(i) Confusing: The authors start the text by presenting the spectrum calculated with a tight-binding model with several parameters (gamma_1 to gamma_4, delta, Delta) etc., without telling what the relevance of the different parameters is. They point out that they take into account more parameters than some previous works, but essentially the same set of parameters has been studied before. For example, Kopnin, et al., PRB 87, 140503 (2013) and arXiv:1210.7075 shows a similar type of spectrum and also indicates the relevance of the different terms. The PRB shows also a DFT simulation of the surface spectra, i.e., without having to resort to some particular values of the parameters. In this work it was also noticed that the exact values of the tight binding parameters depend on how many of the other parameters are included.

Without this insight to the properties of the model, the focus in the present manuscript seems to be too much on looking into some features of numerical curves (like the Landau level pictures showing many tens of curves), rather than qualitative insight.

One of the most interesting aspects of the presented results relates to the Berry phase, but again it is difficult to estimate just from the curves why for example the magnetic moment is so large. Apparently the magnetic moment is zero for Delta=0, because nothing breaks the valley symmetry. How can this be seen from the expression of the magnetic moment? Does the finite magnetic moment depend on the presence of the coupling terms gamma_2, gamma_3, gamma_4?

(ii) Literature: Three-dimensional rhombohedral graphite is a nodal line semimetal, as discussed for example Ref. 16 based on an approximate Hamiltonian, and in Hyart, et al., JLTP 191, 35 (2018), based on the structural inversion symmetry and hierarchy of hopping constants. This means that there is a band-crossing line extending the whole 3D Brillouin zone. A multilayer graphene spectrum describes this line at discrete longitudinal momenta. This should be better acknowledged, because it also reveals the reason for the electron and hole pockets at different doping levels.

Moreover, the Landau level spectrum of rhombohedral graphite was considered already before by Ho, et al., New J. Phys. 15, 053032 (2013). The results presented in this manuscript should also be compared to that work.

I also would like to point out a few other confusing statements or possible sources of error:

(iii) The authors state in the beginning that "The interlayer hybridization... leads to a gapped electronics spectrum in the middle of a thin film." It is not gapped, because it is a semimetal! However, one can view (some) topological semimetals as systems where there is a transition between a topological insulator to a trivial insulator state as a function of momentum. The transition here is marked by the presence of the nodal line. Is this what the authors meant?

(iv) Authors should tell how they define the "2D semi-metal, 2D metal and a 3D metal". For example, is graphene semimetal only when the charge density is exactly zero, or can it be viewed as a semimetal because of the band crossing point? How can a 2D multilayer become a 3D metal?

(v) "Vertical displacement field" is discussed in the beginning of the text without proper definition. One understands it only a couple of pages later.

(vii) A spectral gap could be opened not only via magnetism, but also via superconductivity, as studied in RHG for example in the above-mentioned PRB by Kopnin (see also Kopnin, et al., Phys Rev B 83, 220503 (2011)). However, this is in fact not so clear because a surface order parameter cannot gap the bulk, and the resulting gap in the spectrum of the multilayer tends to be much smaller than the size of the order parameter. The same should happen in the magnetic state.

(viii) Parameter delta appearing in the text after Eq. (1) is not defined before Methods.

(ix) The authors should indicate how they get the precise form for beta_1 (or alternatively the precise forms for kappa_{n,n} and kappa_{n,n+1} in the Methods section).

(x) I think X(p) appearing in Eq. (1) should be multiplied by a factor (1-p^2/pc^2), to correctly describe the fact that the surface states merge with the continuum when p=p_c. This is explained in the above papers by Kopnin, et al. This might not affect the actual spectra very much, though.

(xi) For Fig. 3b the authors have taken some precise value for the scattering time. Some justification should be given for that value.

(xii) Omega_K^- appearing in Eq. (3) has strictly speaking not been defined, because the un-numbered equation defining Omega^\pm does not contain the valley index. If it does, why K and not K' in this formula?

(xiii) The authors state that to calculate the Landau level energies, they introduce a cutoff at N_0=250. Sometimes the energies depend on how this cutoff procedure is carried out (i.e., is it assumed that phi_N+1=0, or that it is some constant). Could the authors detail how they did the cutoff and check if the results depend on it.

This is the first time I sign a referee report.

Tero Heikkilä

Reviewer #2 (Remarks to the Author):

The manuscript “Films of rhombohedral graphite as two-dimensional topological semimetals” by Sergey Slizovskiy et al. reports on the theoretical studies on the topological properties of 2D rhombohedral graphite. The authors claim tens layer of rhombohedral graphite exhibit 2D properties with a large Berry curvature and a giant intrinsic magnetic moment. They also demonstrate that the size of Berry curvature and magnetic moment can be controlled by electrostatic gating, inducing a tunable anomalous Hall effect. The manuscript is well organized, and the conclusions are scientifically sound and backed by the calculated results. However, there are still some points should be addressed:

1. Authors claim in the abstract that “thin films of rhombohedral graphite, which appear to retain truly two-dimensional properties up to tens of layers of thickness and host two-dimensional electron states…” However, in the main text, they did not give us a clear standard to judge what is 2D electronic properties. The method mentioned in Nature 569, 537 (2019) may be helpful to this point.
2. The calculated results of the energy band, berry phase, and gate-tunable berry curvature in rhombohedral graphite are similar to Phys. Rev. B 80, 165409 (2009), and the topological surface state was also demonstrated in Phys. Rev. B 84, 165404 (2011). Do authors have breakthrough or further comprehensions beyond previous references?
3. Since the author claim that thin films of rhombohedral graphite exhibits 2D electronic properties, why there exist a 3DM phase? How do authors define the 3DM phase?
4. In the middle of Page 4, authors claim that “A spectral gap can also be induced by spontaneous symmetry breaking into a magnetic state, making Δ spin dependent”. What’s the relationship

between “gap” and “spin”? For example, Ref. Nat. Phys. 8, 550 (2012) illustrates that the spontaneous symmetry breaking induced gap (half filling of 0LL) under magnetic fields is valley dependent.

5. Why a nonzero Δ can enhance some of the avoided crossings in the LL spectrum, as illustrated in Fig. 1(d) and (e)? Authors should give out the corresponding physical picture to this point.

Reviewer #1 (Remarks to the Author):

We thank the referee for their useful comments. We have followed their suggestions by adding text to improve the clarity of the paper, particularly with respect to the relationship between the band structure of rhombohedral graphite with an infinite number of layers and with a finite number, the latter being the focus of our manuscript. Also we have included additional references to broaden the cited literature. Detailed replies to the referee's comments are given below.

This manuscript describes a theoretical study of the spectrum of a rhombohedrally stacked multilayer graphene in the presence of a magnetic field. In particular, the authors study the effects of top-bottom asymmetry breaking the valley symmetry of the Landau level spectrum, and the effects of the Berry curvature of the bands. In addition, they predict the presence of transverse photoconductivity for circularly polarized light.

The predicted effects are rather interesting, but they are somewhat confusingly presented, and the cited literature is rather narrow (see below). Therefore I cannot recommend publishing this manuscript in Nature Communications at least in its present form.

My main cricitism concerns the following:
(i) Confusing: The authors start the text by presenting the spectrum calculated with a tight-binding model with several parameters (gamma_1 to gamma_4, delta, Delta) etc., without telling what the relevance of the different parameters is.

The relevance of the different parameters is now described in detail in the Methods section.

They point out that they take into account more parameters than some previous works, but essentially the same set of parameters has been studied before. For example, Kopnin, et al., PRB 87, 140503 (2013) and arXiv:1210.7075 shows a similar type of spectrum and also indicates the relevance of the different terms. The PRB shows also a DFT simulation of the surface spectra, i.e., without having to resort to some particular values of the parameters. In this work it was also noticed that the exact values of the tight binding parameters depend on how many of the other parameters are included.

Yes, the zero magnetic field spectrum shown in Fig.1a has been studied previously, e.g. in Refs[15,23,24]. We thank the referee for pointing out that this was also done in Kopnin et al 2013, we have added a reference to this (Ref[18]).

Without this insight to the properties of the model, the focus in the present manuscript seems to be too much on looking into some features of numerical curves (like the Landau level pictures showing many tens of curves), rather than qualitative insight. One of the most interesting aspects of the presented results relates to the Berry phase, but again it is difficult to estimate just from the curves why for example the magnetic moment is so large. Apparently the magnetic moment is zero for Delta=0, because nothing breaks the valley symmetry. How can this be seen from the expression of the magnetic moment? Does the finite magnetic moment depend on the presence of the coupling terms gamma_2, gamma_3, gamma_4?

We have added analytical formulae (Eqs 2 and 3) for the Berry curvature and magnetic moment, obtained by neglecting trigonal warping. They demonstrate the dependence on Delta (the Berry curvature and magnetic moment are zero in a gapless system) and on layer number N. The numerical plot (Fig 2) takes into account trigonal warping. The smaller parameters (gamma_2, gamma_3, gamma_4) are not needed to produce non-zero magnetic moment.

(ii) Literature: Three-dimensional rhombohedral graphite is a nodal line semimetal, as discussed for example Ref. 16 based on an approximate Hamiltonian, and in Hyart, et al., JLTP 191, 35 (2018), based on the structural inversion symmetry and hierarchy of hopping constants. This means that there is a band-crossing line extending the whole 3D Brillouin zone. A multilayer graphene spectrum describes this line at discrete longitudinal momenta. This should be better acknowledged, because it also reveals the reason for the electron and hole pockets at different doping levels.

Yes, it is possible to obtain the bulk bands of a finite N system by quantizing the spectrum of the 3D material. In fact, the closing of the gap between the bulk bands at p=p_c for large N (the bulk gap scales like gamma_1/N) is related to the 3D nodal line. The bulk bands with the surface bands are shown explicitly in Fig.5b for N = 10. When discussing the bulk gap for finite N, we have added a comment about those papers describing the nodal line in 3D rhombohedral graphite [Refs 16, 20 plus we have added Ho et al NJP (2013), Ho et al Solid State Communications (2014), Hyart et al JLTP (2018)]. However, the surface bands – which lie within the bulk gap for p < p_c and are the focus of our manuscript Fig.1a,1c – cannot be obtained by quantizing the spectrum of the 3D material. As in the SSH model (Ref[6]), the low-energy edge states can't be obtained from the bulk band structure, although bulk-edge correspondence can be used to infer their existence.

Moreover, the Landau level spectrum of rhombohedral graphite was considered already before by Ho, et al., New J. Phys. 15, 053032 (2013). The results presented in this manuscript should also be compared to that work.

Our plotted Landau level spectra (e.g. Fig1d) are consistent with previous studies using the minimal model (e.g. Refs[15,21]). A comparison with Ho et al (2013) is not helpful because they considered a different situation: Landau subbands as a continuous function of k_z (i.e. for the 3D material and not including the surface states) using semiclassical quantization and a very large magnetic field value (30T). Nevertheless, we have added a reference to Ho et al (2013) because of its relevance to 3D rhombohedral graphite.

I also would like to point out a few other confusing statements or possible sources of error:

(iii) The authors state in the beginning that "The interlayer hybridization... leads to a gapped electronics spectrum in the middle of a thin film." It is not gapped, because it is a semimetal! However, one can view (some) topological semimetals as systems where there is a transition between a topological insulator to a trivial insulator state as a function of momentum. The transition here is marked by the presence of the nodal line. Is this what the authors meant?

The central region of a finite thin film is gapped; the semimetallic behavior is due to the surface states; only the surface states are shown in Fig1a (bulk and surface bands are shown in Fig5b). To clarify this point, we have added an analytical approximation of the bulk gap size which shows how it depends on layer number (bulk gap ~ gamma1/N). In the Methods, we have added a description of how this estimate of the bulk gap is obtained. Of course, in an infinitely thick bulk sample, the bulk gap is closed at p = p_c, this is related to the nodal line.

(iv) Authors should tell how they define the "2D semi-metal, 2D metal and a 3D metal". For example, is graphene semimetal only when the charge density is exactly zero, or can it be viewed as a semimetal because of the band crossing point? How can a 2D multilayer become a 3D metal?

This is a question of whether (only) the surface bands or the bulk bands are occupied. For a finite number of layers N, the bulk bands are gapped by an amount ~ gamma1/N where gamma1 is the vertical interlayer hopping parameter. The surface states give bands, Fig 1a, within this bulk gap (the bulk bands with the surface bands are shown explicitly in Fig.5b for N = 10). The 2D semimetal corresponds to densities for which the Fermi level intersects both the surface conduction and valence bands; 2D metal means the Fermi level intersects only one of these bands; 3D metal means the Fermi level lies in the region of the bulk bands. We have clarified this point at the beginning of the fourth paragraph.

(v) "Vertical displacement field" is discussed in the beginning of the text without proper definition. One understands it only a couple of pages later.

To clarify, we have written "… of a vertical electric displacement field (perpendicular to the thin film), the bands …"

(vii) A spectral gap could be opened not only via magnetism, but also via superconductivity, as studied in RHG for example in the above-mentioned PRB by Kopnin (see also Kopnin, et al., Phys Rev B 83, 220503 (2011)). However, this is in fact not so clear because a surface order parameter cannot gap the bulk, and the resulting gap in the spectrum of the multilayer tends to be much smaller than the size of the order parameter. The same should happen in the magnetic state.

We thank the referee for noting that this paper discussed the possibility of a superconducting gap, we have added this to our manuscript. As mentioned above, in a finite film with N layers, the bulk is gapped as ~ gamma1/N in the non-interacting picture. A magnetic state, say, only needs to gap the two surface states. Note that the gap of ~80meV observed experimentally at charge neutrality in N=4 rhombohedral graphite appears to be consistent with a layer antiferromagnetic state (K Myhro et al 2018 2D Mater. 5 045013).

(viii) Parameter delta appearing in the text after Eq. (1) is not defined before Methods.

This is now defined in the text where it first appears.

(ix) The authors should indicate how they get the precise form for beta_1 (or alternatively the precise forms for kappa_{n,n} and kappa_{n,n+1} in the Methods section).

We have added a note of explanation in the Methods and added a reference to a paper in bilayer graphene where an analogous term was derived.

(x) I think X(p) appearing in Eq. (1) should be multiplied by a factor (1-p^2/pc^2), to correctly describe the fact that the surface states merge with the continuum when p=p_c. This is explained in the above papers by Kopnin, et al. This might not affect the actual spectra very much, though.

In principle, yes, it is possible to include further small corrections such as this. However, they don't provide any new qualitative information and they only have a tiny quantitative effect in the regime of validity p << p_c. Note that Fig. 5 shows a comparison of the full HkpTB model with the effective two-band model, showing that the latter provides a good qualitative description without these additional corrections.

(xi) For Fig. 3b the authors have taken some precise value for the scattering time. Some justification should be given for that value.

The value of the scattering time for which we plot the result is near the maximal possible time, where the effect in question will be observable (anomalous contribution is comparable to conventional one). If the sample is of higher quality, we expect the classical contribution will overshadow the anomalous one. We have added this clarification in the text and added the plots with different scattering times.

(xii) Omega_K^- appearing in Eq. (3) has strictly speaking not been defined, because the un-numbered equation defining Omega^\pm does not contain the valley index. If it does, why K and not K' in this formula?

We have now defined Omega_K^-. Only one K point is needed because the value of Omega in the valleys is related by opposite sign and orientation (see fig2(a) for the magnetic moment).

(xiii) The authors state that to calculate the Landau level energies, they introduce a cutoff at N_0=250. Sometimes the energies depend on how this cutoff procedure is carried out (i.e., is it assumed that phi_N+1=0, or that it is some constant). Could the authors detail how they did the cutoff and check if the results depend on it.

The cutoff we used is described explicitly in the text. The proper cutoff should not let any high-energy states descend to low energies and create the artefact states. A naive cutoff of \phi_N+1 = 0 would create such fake states even for a monolayer graphene. We have tried to use such a naive cut-off, but had to remove the fake states by looking at the wave-functions. The proper cutoff we use is designed not to disturb the main in-plane A to B sublattice raising operators and the main gamma_1 inter-plane hopping. It is given by \phi_A_(N-n) = 0 and \phi_B_(N-n+1) = 0 (where n is the layer number and N is a large cutoff) does the job. N=250 is sufficient to get excellent convergence for B >0.5 T.

Reviewer #2 (Remarks to the Author):

We thank the referee for their useful comments. We have followed their suggestions by adding text to improve the clarity of the paper particularly with respect what is meant by 2D properties and the possible nature of a gap on taking into account electronic interactions. We have also added a qualitative explanation of the valley dependence of avoided crossings in the Landau level spectra. Detailed replies to the referee's comments are given below.

The manuscript "Films of rhombohedral graphite as two-dimensional topological semimetals" by Sergey Slizovskiy et al. reports on the theoretical studies on the topological properties of 2D rhombohedral graphite. The authors claim tens layer of rhombohedral graphite exhibit 2D properties with a large Berry curvature and a giant intrinsic magnetic moment. They also demonstrate that the size of Berry curvature and magnetic moment can be controlled by electrostatic gating, inducing a tunable anomalous Hall effect. The manuscript is well organized, and the conclusions are scientifically sound and backed by the calculated results. However, there are still some points should be addressed:

1. Authors claim in the abstract that "thin films of rhombohedral graphite, which appear to retain truly two-dimensional properties up to tens of layers of thickness and host two-dimensional electron states…" However, in the main text, they did not give us a clear standard to judge what is 2D electronic properties. The method mentioned in Nature 569, 537 (2019) may be helpful to this point.

This is a question of whether (only) the surface bands are occupied or the bulk bands, too. For a finite number of layers N, the bulk bands are gapped by an amount ~ gamma1/N where gamma1 is the vertical interlayer hopping parameter. The surface states give bands, Fig 1a, within this bulk gap. The 2D semimetal corresponds to densities for which the Fermi level intersects both the surface conduction and valence bands; 2D metal means the Fermi level intersects only one of these bands; 3D metal means the Fermi level lies in the region of the bulk bands. We have clarified this point at the beginning of the fourth paragraph.

2. The calculated results of the energy band, berry phase, and gate-tunable berry curvature in rhombohedral graphite are similar to Phys. Rev. B 80, 165409 (2009), and the topological surface state was also demonstrated in Phys. Rev. B 84, 165404 (2011). Do authors have breakthrough or further comprehensions beyond previous references?

The fact there are surface states with flat bands is well known e.g. Refs [16,17]; Ref [14] did show energy bands but only up to N = 7 and gapped bands (due to a gate) only for N = 3. There was no mention of Berry curvature there. The present manuscript focusses on larger layer number: we show that rhombohedral graphite retains truly two-dimensional properties up to tens of layers of thickness (in contrast to other stackings such as Bernal) and that the two dimensional electrons in this system have large Berry curvature accompanied by a giant intrinsic magnetic moment, both strongly-dependent on the number of layers and a gap controlled by asymmetry induced by a vertical displacement field. We then make specific predictions of potential experimental observations of effects induced by the quantum topology.

3. Since the author claim that thin films of rhombohedral graphite exhibits 2D electronic properties, why there exist a 3DM phase? How do authors define the 3DM phase?

Please see the reply to point 1.

4. In the middle of Page 4, authors claim that "A spectral gap can also be induced by spontaneous symmetry breaking into a magnetic state, making Δ spin dependent". What's the relationship between "gap" and "spin"? For example, Ref. Nat. Phys. 8, 550 (2012) illustrates that the spontaneous symmetry breaking induced gap (half filling of 0LL) under magnetic fields is valley dependent.

In principle, one can imagine combining spin and valley degrees of freedom into four species which can appear in different configurations in symmetry broken gapped states. It is likely that these are analogous to those discussed in bilayer graphene (see Min et al PRB 77, 041407 (2008); Jung et al PRB 83, 115408 (2011)), possibilities include layer antiferromagnetic configurations which are charge balanced hence minimising the Hartree energy cost. Experiments observing large gaps in N=3 (Bao et al, Nat. Phys. 7, 948 (2011), Lee et al Nat. Commun. 5, 5656 (2014)) and N=4 (K Myhro et al 2018 2D Mater. 5 045013) rhombohedral films claim to be consistent with these layer antiferromagnetic configurations. We have added references to these papers which may be used for clarification if necessary.

5. Why a nonzero Δ can enhance some of the avoided crossings in the LL spectrum, as illustrated in Fig. 1(d) and (e)? Authors should give out the corresponding physical picture to this point.

We thank the referee for this question. We were puzzled by this ourselves and have developed a qualitative explanation that is now included in the Methods section. In short, the Berry curvature contribution to the equations of motion [see the denominators in the new Eqs.(9,10)] almost stops the valence band carriers in the vicinity of the breakdown region in one of the valleys while it accelerates them in the other valley.