Excitons in Bent Black Phosphorus Nanoribbons: Multiple Excitonic Funnels

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ABSTRACT

Quasi-one-dimensional nanoribbons are promising candidate materials for flexible optoelectronics with high device density. The optical properties of nanomaterials are strongly influenced by excitons, and it is important for flexible devices to explore how excitons behave under strain. In this work, we investigate the electronic and excitonic properties of bent black phosphorus (BP) nanoribbons (NRs) via density-functional theory and many-body Green's function methods. We find that inhomogeneous strain fields affect not only the first excitonic energy and thus the optical gap, but also the spatial distribution of the excitons. In particular, excitonic funnels can occur in bent BPNRs, which drive higher-energy excitons towards lower-energy locations. The funnels can be effectively tuned by the intensity and sign (compressed to tensile) of the strain field. Another critical factor is anisotropy: the funnel effect is much more pronounced in armchair BPNRs than in zigzag BPNRs. In addition, we find that the excitonic funnel effect in 2D monolayer BP differs from that in multi-layer BP films.

1. Introduction

Recent advances in flexible nanotechnology have paved the way for promising applications such as displays, sensors, actuators, photovoltaics, radio-frequency identification and many others [1, 2]. Flexible electronic materials bring many advantages and new functionalities, leading to low-cost devices that are characterized by light weight, thinness and durability, and which can be stretched and bent [3]. In particular, two-dimensional (2D) layered nanosheets are one of the most appealing families of materials for making flexible devices, due to the intrinsic thickness scalability and mechanical flexibility [4, 5]. In addition, many 2D materials such as black phosphorus (BP) and MoS_2 [6, 7, 8, 9] are equipped with excellent electronic and optical properties [10].

Even smaller-size devices can be achieved by tailoring 2D nanosheets into quasi-one-dimensional (1D) nanoribbons, as was demonstrated for graphene early on [11]. Since a nanoribbon can be regarded as a 2D nanosheet with a finite width along a given direction, many favorable properties of the nanosheets are retained in the corresponding 1D nanoribbons [12, 13, 14, 15]. However, quasi-1D nanoribbons offer additional ways of tuning device properties via quantum confinement effects, absorbed edge atoms, or enhanced anisotropy [16, 17, 18, 19]. Atomically thin layered nanoribbons show great potential for high-density flexible optoelectronic device applications.

The optical properties of low-dimensional materials are dominated by excitonic effects, where optically excited electron-hole pairs form strongly bound excitons via screened Coulomb interactions [20, 21, 22, 23]. Besides their obvious influence on optical absorption and emission, excitons also play a crucial role in phenomena such as valley excitonics [24], Hall effect [25], charge transfer [26] and many others [27]. Therefore, in the context of flexible optoelectronics, it is important to understand how the excitonic properties change under a strain field. Previous works have shown that a homogeneous strain field only shifts the energy of excitons, but hardly changes the motion or spatial location of excitons [28, 29]. However, this is no longer the case for inhomogeneous strain fields (ISFs) in flexible devices.

In 2D MoS₂, an ISF was shown to cause excitons to accumulate isotropically around regions of high tensile strain, forming a so-called excitonic funnel [30]. It was proposed that this funnel effect might be harnessed to overcome the Shockley-Queisser limit [31] and open up new opportunities for manipulation and harvesting of light [30]. The excitonic funnel effect was further experimentally investigated in MoS₂ and other transition metal dichalcogenides [32, 33, 34, 35], as well as in different families of 2D materials such as BP [36]. Moreover, the funnel effect in BP is of opposite sign compared to MoS₂, which means that the excitons are pushed away from the highly strained regions; this is known as the *inverse funnel* effect [37]. Thus, MoS₂ and BP are representatives for the rich variety and complexity of excitonic funnel effects among different materials.

While the excitonic funnel effect in 2D nanosheets has been widely studied [38, 39, 40, 41], the behavior of excitons under ISF in nanoribbons has so far not received much attention. A practical reason is the difficulty of producing few-layer nanoribbons with a controlled width; however, significant progress is being made in this direction [42, 43, 44]. Therefore, a theoretical investigation of excitons in nanoribbons under ISF is a timely subject.

In this paper, we present a computational study of excitons in black phosphorus nanoribbons (BPNRs). We treat the BPNRs with atomistic resolution, using various bend-

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ing configurations to simulate the presence of an ISF, see Fig. 1. In addition to calculating optical spectra and exciton binding energies in bent BPNRs, we investigate the spatial distribution of excitons through a detailed analysis of the exciton wave functions. We find that the spatial distribution of excitons in BPNRs is strongly influenced by several factors: the sign of the strain (tensile or compressive), the intensity of the strain, as well as the anisotropy of the ribbons (zigzag or armchair). We also discuss excitonic funnel effects in BP nanoribbons and nanosheets.



Figure 1: (a) Geometrical structure of 2D BP. The blue and red dotted boxes indicate the orientation of aBPNR and zBPNR, respectively. (b) Schematic bending diagram (for the case of zBPNR), where purple and white balls represent P atoms and H atoms, respectively. The bending deformation is defined by two parameters: the vertical distance h from the top P atoms to the edge P atoms and the change of horizontal width Δw of the edge P atoms with respect to the corresponding atoms in the lower sub-layer. The corresponding deformed BPNR is labeled as BPNR($h/\Delta w$) in this work.

2. Computational Details

The details of the first-principles calculations used in this work are as follows. Geometries and ground-state band structures were obtained with density functional theory (DFT) within the generalized gradient approximation of Perdew, Burke, and Ernzerhof (PBE) [45], using the Quantum Espresso code [46]. All geometries were relaxed until an energy convergence of 10^{-9} Ry and a force convergence on individual atoms of 0.01 eV/Å. The plane-wave cutoff was set as 45 Ry with a norm-conserving pseudopotential. A vacuum slab of at least 12 Å was placed perpendicular to the layer surface, in order to avoid interaction between adjacent periodic images of the nanoribbons.

The optical excitation properties were computed using the BerkeleyGW package [47]. First, we obtain the quasiparticle (QP) energies and spectral distributions within the GW approach (using the wave functions and energies calculated with DFT as input), followed by the Bethe-Salpeter equation (BSE) for the optical spectra. In the following, we use the notation I^0 for the first dark exciton, and I^1 and I^2 for the first and second bright exciton, respectively. The associated exciton energies are denoted by E_I^0 , E_I^1 and E_I^2 .

For the DFT and GW calculations, we adopted $1 \times 10 \times 1$ and $14 \times 1 \times 1$ **k**-point grids for armchair and zigzag BP-NRs (aBPNRs and zBPNRs), respectively. The QP energies were obtained from single-shot G_0W_0 calculations, using the standard random phase approximation and generalized plasmon-pole model [48] for the dynamical dielectric matrix; the number of unoccupied bands was set to be at least 10 times the number of occupied bands. For the BSE, we used 12 valence bands and 12 conduction bands, with dense **k**-point grids of $1 \times 40 \times 1$ and $56 \times 1 \times 1$ for aBPNRs and zBPNRs, respectively.

The geometrical structure of 2D BP (phosphorene) is shown in Fig. 1a. The calculated lattice constants (a = 3.3Å and b = 4.6 Å) as well as the optical gap, with the first bright excitonic energy located at $E_I^1 = 1.12$ eV, are in good agreement with previous computational studies [22, 28]. We adopted the aBPNR and zBPNR with fixed width of 16 and 15 pairs of phosphorus atoms, respectively. All the edge P atoms are passivated with H atoms. Compared to 2D phosphorene, the nanoribbons have much larger optical gaps and significantly higher exciton binding energies, thanks to a combination of quantum confinement and reduced Coulomb screening [13]. The calculated E_I^1 of flat aBPNR and zBPNR are 2.13 eV and 2.35 eV, respectively.

As illustrated in Fig. 1b, the bending deformation is defined by just two parameters: the vertical distance h (in Å) from the top P atoms to the edge P atoms in the lower sub-layer, and the change of horizontal width Δw (in Å) of the edge P atoms with respect to the corresponding atoms in the lower sub-layer. The deformed BPNRs are labeled as BPNR($h/\Delta w$). For the armchair ribbons, we considered aBPNR(0/0), (3.7/0), (5.3/4.6) and (6.8/6.8) to simulate the ribbons under no strain, tensile strain only, moderate compressive strain and strong compressive strain, respectively. Similarly, for the zigzag ribbons we considered zBPNR(0/0), (4.7/0) and (9.7/9.3) for no strain, tensile strain only and strong compressive strain, respectively.

3. Results and Discussions

3.1. Armchair Nanoribbons

We first consider the electronic structure and optical properties of aBPNRs. It has been reported in the literature that the band gap decreases and increases when 2D BP is compressed and stretched, respectively [36, 49]. On the other hand, our calculations show that when an aBPNR is subject to compressive or tensile strain, its band gap always becomes larger, in agreement with Ref. 50. We attribute this behavior to quantum confinement effects when going from 2D nanosheets to 1D nanoribbons.

Table 1 presents the calculated QP gap (E_g) , valence



Figure 2: (a) QP bandstructures of aBPNRs, with excitonic optical transitions represented by black arrows. I^1 in aBPNR(3.7/0) has contributions from two different transitions, shown by two black arrows. The points in the valence and conduction bands related to the transitions are labeled in blue. (b) Optical absorption spectra of aBPNRs. (c)-(f) Exciton probability distributions $|\psi(r_e; r_h)|^2$ in real space as a function of electron position r_e for corresponding excitonic states in aBPNRs. The positions r_h of the hole are indicated by the black dots. The isosurface level of all the plotted excitonic wavefunctions is 85% of the maximum probability.

Table 1

QP band gaps E_g , VBM, CBM, the first bright excitonic energies (optical gaps) E_I^1 , binding energy of first bright excitons E_b^1 and the second bright excitonic energies E_I^2 in aBPNRs. All energies are in eV.

	E_{g}	VBM	СВМ	E_I^1	E_b^1	E_I^2			
aBPNR(0/0)	2.13	-4.82	-2.69	1.17	0.96	1.33			
aBPNR(3.7/0)	2.28	-4.94	-2.66	1.33	0.95	1.46			
aBPNR(5.3/4.6)	2.55	-5.13	-2.58	1.49	1.06	1.70			
aBPNR(6.8/6.8)	2.44*	-4.94	-3.01	1.39	1.05	1.42			
*indirect gap of 1.93 eV									

band maximum (VBM), conduction band minimum (CBM), first and second bright excitonic energies $(E_I^1 \text{ and } E_I^2)$ and first exciton binding energy (E_b^1) of three strained aBPNRs compared to aBPNR(0/0). Clearly, the deformation causes an increase of the band gap in each case; this is also seen in Fig. 2a, which shows the detailed QP band structures. As shown in Fig. 2b, which plots the imaginary part ϵ_2 of the frequency-dependent dielectric function, the first optical absorption peaks of strained aBPNRs are all blue shifted up to 0.3 eV compared to aBPNR(0/0). This demonstrates how an ISF affects the optical absorption edge of BPNRs.

3.1.1. Spatial distribution of the excitons

As stated above, the ISF in bent BPNRs causes dramatic changes in the spatial distribution of excitons. This is illustrated in Figs. 2c-f, where we plot the exciton probability densities $|\psi(r_e; r_h)|^2$ in real space [51] as a function of electron position r_e (the hole position r_h is fixed), for several excitonic states of aBPNRs. For I^1 in aBPNR(0/0), the electron is evenly spread around the hole in the center, which is similar to what is found in 2D monolayer BP [22]. By contrast, the exciton wave functions of I^1 in aBPNR(3.7/0) and aBPNR(5.3/4.6) split into two parts, separated by a nodal line (see Figs. 2d and left panel of Figs. 2e). The two parts accumulate predominantly on opposite sides of the ribbons, i.e. the less strained regions. These results indicate that an "inverse funnel" can be realized in aBPNRs, just as predicted in 2D BP [36].

In the right panel of Fig. 2e, we also plot $|\psi(r_e; r_h)|^2$ of I^1 in aBPNR(5.3/4.6), in which the hole sits on the left-hand side. The resulting exciton wave function is almost entirely restricted to the left region. Of course, the center of mass of the exciton can be located on either side of the ribbon, given



Figure 3: Side view of partial charge densities for corresponding states in aBPNR (a) (0/0), (b) (3.7/0), (c) (5.3/4.6) and (d) (6.8/6.8). The isosurface level of all the plotted density distributions is $4 \times 10^{-4} e/Å^2$.

the mirror symmetry of the NR.

However, the inverse funnel scenario is no longer so clear in the strongly compressed case. In aBPNR(6.8/6.8), we find that the distribution of the lowest-energy exciton (I^0) is relatively localized around the middle region, see Fig. 2f. On the other hand, the second-lowest energy exciton, I^1 , is entirely concentrated at the edges of the ribbon, although E_I^1 is only 0.03 eV higher than E_I^0 . The third-lowest exciton, I^2 , again localizes around the midsection of the ribbon. The distinct distributions of these three excitons indicate that the simple inverse funnel picture is dramatically changed by the increase of the ISF (i.e., the curvature of the aBPNR). Is there any funnel in such a strongly bent ribbon? We suggest there are two funnels along opposite directions, which is illustrated in the following.

To better understand the exciton wave functions, we analyze the partial charge density (PCD, Fig. 3) of the dominant conduction band contributions to the excitons. The energy levels related to the transitions are the *i*th states below the highest valence band (VBM-i@k-point) and jth states above the lowest conduction band (CBM+i@k-point) at given kpoints (Fig. 2a). We find that I^1 in aBPNR(0/0) mainly arises from the transition from VBM@ Γ to CBM@ Γ . The PCD of CBM@ Γ shown in Fig. 3a is contiguous, like the distribution of I^1 in aBPNR(0/0). By contrast, the electron of I^1 in aBPNR(5.3/4.6) mostly hops to CBM+1@ Γ instead of CBM; the PCD of CBM+1@ Γ is split into two separate parts, see Fig. 3c, and so is the exciton wave function of I^1 in aBPNR(5.3/4.6). For I^1 in aBPNR(3.7/0), there are two transitions (VBM-1@ $\Gamma \rightarrow$ CBM@ Γ and VBM@ $\Gamma \rightarrow$ CBM+1@ Γ) contributing 50% and 40% in probability, respectively. The exciton wave function of I^1 (Fig. 2d) thus reflects the two PCDs shown in Fig. 3b, which explains why the exciton is not quite as separated as that in Fig. 2e.

For aBPNR(6.8/6.8), an in-gap state moves down and becomes the lowest unoccupied state (Fig. 2a), which is in agreement with Refs. 49, 50. Due to this qualitative change of the bandstructure, the OP band gap is no longer a monotonic function of intensity of strain. In contrast with the lowest-energy excitons at Γ in the other nanoribbons, I^0 in aBPNR(6.8/6.8) is mainly composed of the transition from VBM@X' to the in-gap state at the X' point (CBM@X'). As expected, the PCD of CBM@X' (top panel in Fig. 3d) is similar to $|\psi(r_e; r_h)|^2$ of I^0 (top panel in Fig. 2f). On the other hand, the second lowest exciton I^1 in aBPNR(6.8/6.8) mainly consists of transitions to CBM+1@ Γ and CBM+2@ Γ . which is similar to the I^1 s in aBPNR(3.7/0) and aBPNR(5.3/4.6). As shown, these three excitons are associated with similarly separated PCDs. Moreover, this correspondence between excitonic distribution and PCD is also valid for I^2 , which is generated by the transition to the in-gap state around the Γ point (see PCDs in the Supplemental Material).

Although we did not plot $|\psi(r_e; r_h)|^2$ for the hole part (with fixed electron position), we have confirmed that the hole distribution can be deduced from the PCDs of corresponding valence bands (see Supplemental Material). For example, the PCD of VBM@ Γ is similarly split as the PCD of CBM+1@ Γ in aBPNR(5.3/4.6). This indicates that the whole exciton, i.e. electron-hole pair, locates around the edge regions of this bent aBPNR. For all other excitons discussed above, we find that the electron and the hole accumulate in the same region, except I^2 in aBPNR(6.8/6.8) (see the PCD of VBM-1@ Γ in the Supplemental Material). However, I^2 is not the lowest energy exciton, and contributes much less to the optical absorption around 1.7 eV. Therefore, we are not going to consider I^2 in the following.

3.1.2. Exciton formation and recombination: funnel effects

So far we have focused on the exciton energies and wave functions in bent nanoribbons. A discussion of excitonic funnel effects requires a spatially resolved picture of the formation and recombination of the excitons; this is achieved by introducing the concept of local VB and CB edges. In the Supplemental Material, we analyze the local band edges in different regions of aBPNR(5.3/4.6), by comparing the partial density of states (PDOS) projected onto P atoms at different positions. We find that the PDOS of P atoms near the edges of the ribbon, rather than P atoms in the middle, contribute the highest occupied states in the VB. This means that the local VB edge around the less strained region is higher than that around the more strained region, and vice versa for the local CB edge across the ribbon.

Figure 4 is a schematic illustration of excitonic funnels, based on the so defined local VB and CB edges and in-gap states in a generic bent BPNR. The "inverse funnel" and "ingap state funnel" are highlighted by the green dashed boxes on the left and right of the top panel, respectively. In the following, these pictures will be explained and discussed for different types of aBPNRs.

We first focus on the "inverse funnel" (left box of Fig.



Figure 4: Schematics of excitonic funnels in compressed aBP-NRs. In the upper panel, the CB and VB edges are represented by the black lines. The in-gap state is represented by the brown line. The blue arrows indicate the motion of the exciton due to carrier relaxation. In the bottom panel, the number of black dots represents the accumulation or dispersion of excitons. The schematic of funnel in an individual moderatecompressed aBPNR is shown in the left dashed-green box.

4) in aBPNR(5.3/4.6), an example for the moderately compressed case. As shown in Section 3.1.1, both the electron and hole of I^1 (VBM@ Γ and CBM+1@ Γ) are localized near the edge region of the ribbon. This means that the I^1 exciton will stay around the edge region until recombination. This simple process is represented by the pair of grey and white dots, associated with the arrows in the left-most part of the upper panel in Fig. 4. Note that the transition from VBM@ Γ to CBM@ Γ is dipole forbidden; this prohibits the electron of I^1 from transitioning to CBM@ Γ , even though this would be energetically favorable. Considering the small energy difference between CBM@ Γ and CBM+1@ Γ , we refer to CBM+1@ Γ as the CB edge (for excitons) of the bent ribbon in Fig. 4. Excitons with energies higher than I^1 , generated in regions of high ISF, will transition non-radiatively to I^1 , with their centers of mass moving from the central bent region to the edge region. This process is illustrated by the blue arrows in the left green box in Fig. 4.

Next, we discuss the less compressed aBPNRs with smaller curvatures than aBPNR(5.3/4.6), and thus with VB and CB edges in between those of aBPNR(0/0) and aBPNR(5.3/4.6). In Table 1, we listed the VBM and CBM levels of all the calculated aBPNRs, with respect to the vacuum level. The VBM and CBM of aBPNR(5.3/4.6) are 0.31 eV lower and 0.11 eV higher than the VBM and CBM in aBPNR(0/0), respectively. This indicates the VBM and CBM of a less compressed aBPNR are also lower and higher than those in aBPNR(0/0), respectively. Thus, the inverse funnel picture, although somewhat less pronounced, also applies to the less compressed aBPNRs.

The scenario may be different for the more strongly compressed aBPNRs with larger curvatures than aBPNRs(5.3/4.6). A key condition above is that the band structure of a less compressed aBPNR is similar to that of aBPNR(0/0) and aBPNR(5.3/4.6). Although an in-gap state exists in every bent aBPNR, it is only the lowest conduction band around the X point in aBPNR(3.7/0) and aBPNR(5.3/4.6). Thus the in-gap state hardly affects the behavior of low energy excitons. But this is no longer guaranteed under a strong ISF, since then the in-gap state becomes the global CBM in aBPNR(6.8/6.8). This causes the formation of the lowest energy exciton I^0 at X', giving rise to two funnels in aBPNR(6.8/6.8) as mentioned before.

The main features of the band structure (except the ingap state) in aBPNR(6.8/6.8) remain similar to those in the other three aBPNRs, which leads to the a similar inverse funnel scenario for I^1 type excitons as in aBPNR(5.3/4.6). As stated above, I^1 is here contributed by the VBM@ Γ , CBM+1@ Γ and CBM+2@ Γ . As shown in Fig. 3d, the PCDs of CBM+1@ Γ and CBM+2@ Γ (see also the VBM@ Γ plotted in the Supplemental Material) in aBPNR(6.8/6.8) are also separated, which causes the excited carriers to flow towards the edge region from the more compressed region. In addition, the PDOS analysis in the Supplemental Material shows that aBPNR(6.8/6.8) has similar local band edges as aBPNR(5.3/4.6), except the in-gap state. Therefore, the inverse funnel still applies in aBPNR(6.8/6.8), and accumulates the I^1 type excitons around the edge regions.

There is another type of exciton, I^0 , whose electrons are occupying the in-gap state, particularly around X'. Following the analysis above, we first investigate the PCDs of VBM@X' and CBM@X'. As shown in Fig. 3d, both PCDs are located around the most strongly bent region, which is further confirmed by the PDOS in the Supplemental Material. As a consequence, the excited carriers of I^0 type excitons can be pushed towards regions with strong ISF, and a "positive funnel" is formed in the strongly compressed aBP-NRs. This funnel mechanism is illustrated in the right green dashed-line box in Fig. 4. This makes it possible, in principle, to separate the two types of excitons. A potential application of such a dual funnel could be in the highly desirable intrinsic ultra-narrow linewidth excitonic photoluminescence [52] in near-infrared range.

We found the VBM and CBM at X' to be clearly lower than at Γ . There is thus a possibility for the holes around X' to move to Γ , which could lead to a competition between a charge-separation effect and the excitonic funnel effect. This competition will ultimately be decided by the strength of exciton binding energy [30]. Since the binding energies of lower-energy excitons in BPNRs are around 1 eV, which is larger than the energy differences (0.5 eV) between VBM@X' and VBM@ Γ (also CBM@X' and CBM@ Γ), it seems likely that the funnel effect will win.

3.2. Zigzag Nanoribbons

The electronic band structures (except the band gap) are not significantly changed in bent zBPNRs compared to the armchair NRs. The QP band gap energy of zBPNR (see Table 2) becomes smaller under a compressive strain, while it



Figure 5: (a) Exciton probability distributions $|\psi(r_e; r_h)|^2$ in real space as a function of electron position for the first excitonic states I^1 in zBPNR(0/0) and zBPNR(9.7/9.3), with holes fixed at the center. (b) Side views of partial charge densities for CBM@ Γ .

gets larger under a tensile strain. We note that this is different from aBPNRs, where both compressive and tensile strain make the gap larger. Similar to E_g , the E_I^1 becomes smaller or larger under a tensile or compressive strain, respectively (see Table 2). Our results are in agreement with experimental [36] and theoretical [37, 49] studies in the literature.

In contrast with aBPNRs, the ISF does not lead to a separated distribution of excited electrons $(|\psi(r_e; r_h)|^2)$ in bent zBPNRs. As an example, in Fig. 5a, we plot the electron probability distributions $|\psi(r_e; r_h)|^2$ in real space as a function of electron position for the first excitonic states I^1 of zBPNR(0/0) and zBPNR(9.7/9.3). It can be confirmed by the PCDs plotted in Fig. 5b. As listed in Table 2, the CBMs of zBPNR(4.7/0) and zBPNR(9.7/9.3) are even slightly lower than those in zBPNR(0/0). This helps the electron of I^1 to maintain the same distribution as in zBPNR(0/0).

By contrast, in zBPNR(4.7/0) and zBPNR(9.7/9.3) the VBMs are significantly changed compared to zBPNR(0/0). In fact, the PCDs of VBMs are quite similar to those of the CBMs shown in Fig. 5b. In addition, the projected density of states for P atoms at different positions are also similar to each other (see Figure 6 in Ref. 49). This means that there is hardly any energy difference between the arch and edge areas of the bent ribbon. Thus, there are neither different spatial distributions of the VBM nor strong exciton funnels in bent zBPNRs.

3.3. 2D BP nanosheets

Although we did not observe a clear funnel effect in zBP-NRs as a consequence of quantum confinement, excitonic funnels are reported to generally exist along different direcQuasiparticle (GW) band gaps E_g , VBM, CBM, E_I^1 , E_b^1 and E_I^2 in zBPNRs. All energies are in eV.

	E_{g}	VBM	СВМ	E_I^1	E_b^1	E_I^2
zBPNR(0/0)	2.35	-5.17	-2.82	1.41	0.94	1.46
zBPNR(4.7/0)	2.52	-5.40	-2.88	1.61	0.91	1.81
zBPNR(9.7/9.3)	2.11	-4.94	-2.83	1.24	0.87	1.43

tions in 2D BP nanosheets [36, 37]. In this section, based on the results obtained in nanoribbons, we discuss possible scenarios of the mechanism of excitonic funnels in 2D BP nanosheets.

A 2D nanosheet can be regarded as a nanoribbon in the limit of very large width. Alternatively, by joining large numbers of individual nanoribbons laterally one may also arrive at a 2D nanosheet. A wrinkled BP nanosheet can then be constructed by a suitable arrangement of flat and bent BPNRs. Consider, for example, the rippled BP monolayers that were experimentally studied by Qereda *et al.* [36]. As demonstrated in Fig. 6a, these can be simulated by alternating zBPNR(9.7/9.3) (up), zBPNR(0/0), zBPNR(9.7/9.3) (down), zBPNR(0/0), and so on. zBPNRs with different curvatures could be used as well.

In the next step, it is assumed that the VB and CB edges of the joined nanoribbons remain more or less unchanged; using the values listed in Table 2, this leads to a band alignment as shown in the upper panel of Fig. 6a. Thus, in the wrinkled monolayer BP nanosheet, the VBMs (CBMs) of the bending regions are higher (lower) than the corresponding VBMs (CBMs) in the flat areas. This immediately shows that excitons which are generated in the flat regions will move towards the bent regions (blue arrows in Fig. 6a), leading to excitonic funnels.

The above simple scenario can be generalized to fewlayer 2D BP, but will no longer apply in multiple layer 2D BP films, due to variations of the ISF. In monolayer BP, the upper sublayer of P atoms is subject to tensile stress, whereas the bottom sublayer is compressed [50]. As the number of BP layers increases, the sign of the strain field varies around different areas in the film, as illustrated in Fig. 6b. For a 10 nm thick BP film [36], the outermost few layers would need be simulated by an arrangement such as zBPNR(4.7/0)(up), zBPNR(0/0), zBPNR(9.7/9.3) (down), and so on. This leads to the schematic band alignment shown in the upper panel of Fig. 6b, where it is assumed that the excitonic effects occur in the top layers of the film. Thus, excitons which are generated in the green regions will move toward regions of higher strain, which are characterized by smaller gaps. This scenario is supported by the experimental observation that the absorption edge in wrinkled BP films is up to 0.7 eV smaller in the compressed regions [36].

The scenarios discussed here assume minimal changes of the band alignment when connecting different ribbons into a sheet. Another assumption is that the ISF causes similar changes of band structure BP nanosheets as in individ-



Figure 6: (a) Schematic illustrations of excitonic funnels in (a) monolayer wrinkled BP nanosheet (b) multi-layer wrinkled BP film. In the upper area of each picture, the blue arrows indicate the motion of optically excited carriers. In the bottom areas, the number of black dots represents the accumulation of excitons. Bent zBPNRs are linked up by flat zBPNRs, which are represented by dashed lines.

ual BPNRs. These two conditions are not satisfied in aBP-NRs. According to our calculations, the ISF causes larger band gaps for both tensile and compressed aBPNRs. This is contrary to the results that the tensile ISF makes the band gap smaller in 2D BP [49]. Thus, the tensile part of wrinkled 2D BP films cannot be simulated using tensile aBPNRs. To solve this problem, periodic rippled structures like those in Ref. 49 would need to be constructed. The necessary large-scale GW/BSE calculations are beyond the scope of this work. However, we can use results for rippled phosphorene to discuss the trends of aBPNRs with larger widths. The curvatures of the bent structures in Figs. 1f and 1h of Ref. 49 are similar to those of our aBPNR(0/0) and aBPNR(6.8/6.8). The band gap difference of the bent structures in Figs. 1f and 1h of Ref. 49 (0.37 eV) is only slightly larger than the band gap difference of our aBPNRs (0.2 eV). In addition, the band structures, in particular the featured in-gap states, are quite similar in 2D and aBPNRs. Therefore, we conclude that the funnel effects will be only weakly dependent on the width of the ribbon, but will be much more strongly influenced by the bending curvature (i.e., the intensity of the ISF).

Lastly, the exciton funnel effect is not the only effect to be induced by the ISF in low dimensional layered materials. At least two types of band alignment can be formed by the ISF [30]. Typically, the Type-I alignment leads to the funnel effect, which drives the electrons and holes towards the same direction. On the other hand, the Type-II alignment is found in other materials under ISF, which may make the charge separation easier [53, 54]. In particular, as the number of layers increases, the excitonic effects are weakened, i.e., the excitonic binding energies become smaller and the excited electrons and holes are more easily separated. In addition, the excited charges can be separated through interlayer transitions. This suggests that the funnel effects in multi-layer systems are not as strong as in the monolayer system. For an overall better understanding of all these effects, proper nonequilibrium dynamics simulations need to be developed and performed [55, 56], which is beyond the scope of this work.

Another interesting research direction would be the excitons in BP nanotubes (BPNTs). At present, BPNTs have only been theoretically studied [57, 58, 59]. The exciton binding in BPNTs is likely not very different from that in bent BPNRs with similar bending radius since the excitons are relatively strongly localized, similar to the more extensively studied boron nitride systems [60, 61]. To observe a funnel effect, one could look at bent nanotubes, whose structural properties have been well studied, see e.g. Ref. [62] for the case of carbon. One finds that nanotubes undergo buckling transitions which are accompanied by rather large strain fields, much larger than one could achieve in bent nanoribbons. Thus, one may speculate that buckled BPNTs exhibit quite significant exciton funnel effects.

4. Conclusions

In this paper, we theoretically investigated the electronic and excitonic properties of BPNRs under inhomogeneous strain, simulated by bending geometric models. In addition to tuning the band gap and optical absorption edge in BP-NRs, the ISF is responsible for creating excitonic funnels, which can not be achieved by homogeneous strain. It is possible to tune the funnels by both the intensity and sign (compressed or tensile) of the ISF. Our calculations also suggest highly anisotropic funnel effects in BPNRs in two aspects: first, the funnels in aBPNRs are more pronounced than those in zBPNRs; second, an additional funnel induced by the ingap state is present when the aBPNRs are strongly compressed. Furthermore, the discussion for the funnel effects in 2D BP nanosheet shows that the thickness of the layered material and quantum-size confinement effects are critical as well. This work offers a theoretical understanding for the unique excitonic funnel effect induced by the ISF, which is relevant for the development of future flexible optoelectronic devices.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this article.

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Supplemental Material Excitons in Bent Black Phosphorus Nanoribbons: Multiple Excitonic Funnels

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Figure S1 Side views of the PCDs of VBM-1@ Γ and CBM@ Γ corresponding to the exciton I^2 in aBPNR(6.8/6.8).



Figure S2 Side views of the PCDs of VBM@ Γ in (a) aBPNR(0/0), (b) aBPNR(3.7/0) and (c) aBPNR(5.3/4.6). (d) Side views of the PCDs of VBM@ Γ and VBM@X' in aBPNR(6.8/6.8).



Figure S3 Side views of the PCDs of (a) VBM@ Γ in zBPNR(0/0), (b) VBM@ Γ and CBM@ Γ in aBPNR(3.7/0) and (c) VBM@ Γ in zBPNR(9.7/9.3).

The local band edges in the compressed aBPNRs in Figure 4 in the main paper are analyzed via the partial density of states (PDOS) projected to *p*-orbitals of selected P atoms. Here we first discuss the local VB edges in both aBPNR(5.3/4.6) and aBPNR(6.8/6.8).



Figure S4 The PDOS, projected to *p*-orbitals of selected P atoms from different strained regions in (a) aBPNR(5.3/4.6) and (b) aBPNR(6.8/6.8), respectively. The Fermi levels are artificially adjusted to zero.

For aBPNR(5.3/4.6), we selected two P atoms, whose positions are shown in Figure S4a. The P1 atom is selected as the second nearest to the H atom, in order to cancel the influence from passivated atoms. The PDOS shows that the highest occupied *p*-orbital of the P1 atom is located clearly at a higher energy than that of the P2 atom in the middle of the nanoribbon. This means that the local VB edge around the less strained region is higher than that around the more strained region, which pushes the optically excited holes towards the edge regions.

For aBPNR(6.8/6.8), the highest occupied *p*-orbital of P3 atom is clearly lower than those of the P1 and P2 atoms (see Figure S4b). The density of states of the *p*-orbital of the P2 atom is smaller than that of P1 atom between -0.5 eV and the Fermi level, although the PDOS edges of P1 and P2 are quite similar. These result show that the local VB edge in aBPNR(6.8/6.8) is similar to that in aBPNR(5.3/4.6) as shown in Figure 4 in the main paper.

Let us now analyze the local CB edges via a comparison between the two nanoribbons. In aBPNR(5.3/4.6), the lowest unoccupied *p*-orbital of the P2 atom is closer to the Fermi level than that of the P1 atom. It can be seen that the PDOS peak of the P2 atom around 1 eV is much higher than that of the P1 atom. However, this peak is partially contributed by the in-gap state in aBPNR(5.3/4.6), though it is not the global lowest unoccupied state, as shown in Figure 2a in the main paper.

When the in-gap state is clearly separated from the main part of CB, in aBPNR(6.8/6.8), the structure of the PDOS of the main part of the CB can be better observed. The PDOS in Figure S4b above 1 eV shows that the edge of the main part of the CB hardly changes in P1, P2 and P3. Nevertheless, the electron of the lowest-energy exciton I^1 mostly hops to CMB+1@ Γ instead of CBM@ Γ , and the transition from VBM@ Γ to CBM@ Γ is dipole forbidden as stated in the main paper. Since the energy difference between these two states is smaller than 0.05 eV, we refer to CBM+1@ Γ as the CB edge (for excitons) of the bent ribbon. Therefore, the lowest local band edge

for excitons to transition to, $CBM+1@\Gamma$, is mostly distributed around the edge regions. In this sense, we plot the schematics of local CB edge as Figure 4 in the main paper for both ribbons.

Lastly, the in-gap state is found to be contributed by the *p*-orbital of the P3 atom, according to the PDOS between 0 and 1 eV in Figure S4b. This indicates that the in-gap state is mainly localized around the middle region of the nanoribbon, which is in agreement with the partial charge density distribution of CBM@X' given in the main paper.



Figure S5 Schematic of excitonic funnels in tensile aBPNRs. In the upper area, the normal CBs and VBs were represented by the black curves. The blue arrows indicate the drifts of carriers. In the bottom areas, the number of black dots represents the accumulation or dispersion of excitons.