Bandgap engineering in van der Waals heterostructures of blue phosphorene and MoS₂: A first principles calculation

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Abstract

Blue phosphorene (BP) was theoretically predicted to be thermally stable recently. Considering its similar in-layer hexagonal lattice to MoS₂, MoS₂ could be appropriate substrate to grow BP in experiments. In this work, the **van der Waals (vdW)** heterostructures are constructed by stacking BP on top of MoS₂. The thermal stability and electronic structures are evaluated based on first principles calculations with **vdW**-corrected exchange-correlation functional. The formation of the heterostructures is demonstrated to be exothermic and the most stable stacking configuration is confirmed. The heterostructures BP/MoS₂ preserve both the properties of BP and MoS₂ but exhibit relatively narrower bandgaps due to **the** interlayer coupling effect. The band structures can be further engineered by applying external electric fields. An indirect-direct bandgap transition in bilayer BP/MoS₂ is demonstrated controlled by the symmetry property of the built-in electric dipole fields.

Keywords: van der Waals (**vdW**) heterostructures; Blue phosphorene; MoS₂; Indirect-direct band gap transition; Built-in electric dipole field

PACS numbers:

1. INTRODUCTION

Since graphene was obtained as a transferable material in 2004 [1], there has been tremendous research interest in atomic two-dimensional (2D) materials for potential applications in next-generation electronic devices. Besides the intensely studied graphene, single- and few-layer hexagonal boron nitride (hBN) [2–4], molybdenum dichalcogenides such as MoS₂ and MoSe₂ [5–8], and recently exploited phosphorene [9–16] and arsenene [17–20] have been attracting intense attention. **Researches** on these 2D materials will undoubtedly continue to be one of the hottest topics for long time. Furthermore, as an emerging research area, to assemble the isolated atomic configurations layer by layer into various heterostructures in a precisely controlled sequence is an exciting research field [21]. It will provide a versatile platform for exploring new phenomena and designing novel nanoelectronic devices. In such heterostructures, strong covalent bonds assure in-plane stability, and meanwhile, the relatively weak van der Waals (vdW) interactions hold the stacking layers together and is expected to play as a degree of freedom to produce novel electronic properties. The stacked heterostructures are hence usually referred to as vdW heterostructures. In recent years, the feasibility to experimentally fabricate such vdW heterostructures has been demonstrated. Inspired by the report that graphene grown on hBN substrate showing a 10-fold increase in the electronic quality [2, 22], the heterostructure of graphene/hBN was developed [2, 22–25]. Along with this advance, combining graphene with other 2D materials, such as MoS₂ and WS₂ were conducted [26–29]. Furthermore, some other heterostructures such as MoS₂/WS₂ [30], MoS₂/MoSe₂ [31] and MoS₂/hBN [32] were also investigated.

Among the above mentioned 2D materials, single-layer MoS₂ possesses a direct bandgap of ~ 1.8 eV [33, 34], potentially to be applied in electronic devices. The Field effect transistor based on MoS₂ was fabricated [35]. In parallel with the research efforts on single-layer MoS₂, its vdW heterostructures with other atomic 2D materials, such as graphene [26–29], hBN [32] and other group-VI dichalcogenides [30, 31] have been constructed, demonstrating various electronic properties. In addition, blue phosphorene (BP) was recently theoretically predicted to be thermally stable by using *ab initio* method [14]. The bandgap of BP attains a large value of ~ 2 eV allowing the practical applications in optoelectronics devices [14, 15]. The bandgap can be further tuned in a large range through applying external electric fields [16]. Moreover, the in-layer hexagonal lattice of BP is close to that of MoS₂ and more

importantly, the lattice mismatch between them is reasonably low ($\sim 3\%$). So, MoS_2 could be an appropriate substrate to grow BP in experiments.

In this work, the vdW heterostructures of bilayer and multilayer BP/ MoS_2 are built by stacking BP on top of MoS_2 . First principles calculations with vdW-corrected exchange-correlation functional are devoted to evaluate the thermal stability and the electronic properties. Then, external electric fields are utilized to further tune the bandgap properties, which realize an indirect-direct bandgap transition in bilayer BP/ MoS_2 before the bandgap closes. The underlying mechanisms are discussed. The rest of this work is arranged as follows. In Sec. 2 we briefly describe the method used in this work. Results and discussion are presented in Sec. 3. Finally, we conclude our work in Sec. 4.

2. THEORETICAL APPROACH

Our calculations are conducted with VASP code based on the density functional theory (DFT) [37, 38]. The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) [39] is adopted to describe the exchange-correlation (XC) energy between electrons within the projector augmented wave (PAW) method [40]. The heterostructure c-11 is composed of monolayer MoS_2 with monolayer BP. Two starting stacking configurations, as indicated in Figs. 1a and 1d are considered and the most stable structure is confirmed. Then, c-12 is constructed with monolayer MoS_2 and bilayer BP, c-21 with bilayer MoS_2 and monolayer BP, and c-22 with bilayer MoS_2 and bilayer BP. The effect of vdW interaction is taken into account by using the empirical correction scheme proposed by Grimme [41]. The plane wave energy cutoff is set to 400 eV to ensure the convergence of total energy. Structural optimizations are applied by relaxing the positions of all the atoms until the convergence tolerance of force on each atom is less than 0.001 eV/Å. Periodic boundary condition is used to simulate the 2D infinite sheet. A vacuum space at least 10 Å is used to avoid the interaction between periodic images and simultaneously ensure the convergence of the total energy. The reciprocal space is sampled by a fine grid of Gamma-centered Monkhorst-Pack's mesh $24 \times 24 \times 1$ in the Brillouin zone. The tetrahedron method with Blöchl correction is used for the structural optimizations and density of states (DOS) calculations. Band structures are calculated employing the Gaussian smearing method along the high symmetric line of M-K- Γ -M. To further engineer the band structures of the heterostructures, external

electric fields are applied perpendicular to the stacking layers. In VASP, external electric field is applied to a system by introducing an electric dipole field.

3. RESULTS AND DISCUSSION

First, the lattice constants of monolayer BP and MoS₂ are optimized, which are obtained as 3.28 and 3.19 Å, respectively. These values are in line with that reported in previous studies [15, 33, 34, 36]. Accordingly, the lattice mismatch is evaluated to be about 3% between BP and MoS₂. Then, the heterostructures of bilayer BP/MoS₂ are constructed by stacking BP on top of MoS₂ **using the lattice of the former**. To obtain the equilibrium geometry, two starting configurations are considered, as indicated in Figs. 1a and 1d. We denote them as AB and AB' stacking, respectively. It is noticeable that a series other possible configurations can be obtained by translating the BP layer along the x and/or y directions with respect to the MoS₂ layer. To evaluate the thermal stability of the structures, we calculate the **average** binding energy **for a P atom** by using equation $E_b = (E_{\text{hetero}} - E_{\text{BP}} - E_{\text{MoS}_2})/N$, where E_{hetero} is the total energy of the heterostructures, E_{BP} and E_{MoS_2} are respectively the total energy of BP and monolayer MoS₂, and N is the total number of P atoms. The E_b is evaluated to be -438 and -429 meV for the AB and AB' stacking, respectively. Hence, the formation of **the heterostructures are exothermic from the thermodynamic point of view**. The lattice constants of the two heterostructures are optimized as ~ 3.24 Å. The interlayer distance (d_L) are estimated to be about 3.11 and 3.20 Å for the AB and AB' stacking, respectively.

Based on the AB-stacking c-11 structure as shown in Fig. 1a, further translating the BP layer relative to the MoS₂ layer along the $x(y)$ direction by a relative displacement $\delta_x(\delta_y)$ will result in an energy increase, as illustrated in Fig. 1b. The energy increase is mainly caused by the repulsion between the p_z orbitals of the S and P atoms. For instance, when $\delta_x(\delta_y) = \pm 50\%$ or $\delta_y = 33\%$, as shown in the insets of Fig. 1e, the P atom sits in an almost vertical position above the S atom, an obvious total energy increase is observed. The d_L is optimized to be ~ 3.11 Å for the c-11. Increasing or decreasing this value will make the total energy rise (Fig. 1c). When it comes to the AB' stacking (Fig. 1e), $\delta_y = -33\%$ corresponds to the most stable state. Oppositely, $\delta_y = 33\%$ leads to the highest total energy state. Similar to the case of the AB stacking, the phenomenon is dictated by the repulsion between the p_z orbitals of the S and P atoms. As can be found in the insets of Fig. 1e, when

$\delta_x(\delta_y) = \pm 50\%$ or $\delta_y = 33\%$, the P atom sits nearly vertically above the S atom raising largely the total energy. For the most stable AB' stacking structure, i.e. $\delta_y = -33\%$, the interlayer distance d_L is optimized to be around 3.14 Å, as illustrated in Fig. 1f. The E_b is estimated to be about -437 meV, which is slightly lower than that when $\delta_x(\delta_y) = 0$ (-429 meV) and almost the same as that of the AB stacking c-11 (-438 meV). In addition, our study finds that for both the AB and AB' stacking, a lower energy state usually exhibits a smaller d_L and the opposite is also true. For example, at $\delta_y = 33\%$ for both the AB and AB' stacking corresponding to the highest total energy, the d_L is optimized up to ~ 3.8 Å. In this case, the corresponding E_b is about -410 meV.

For both **the two types of the** bilayer BP/MoS₂ heterostructures discussed above, the band structures share similarity in profile except the bandgap energy (E_g) varies (~ 0.95 - 1.19 eV). As a representative, the band structure of the c-11 is presented in Fig. 2a. As can be found, the valence band maximum (VBM) locates at the Γ point while the conduction band minimum (CBM) appears at the the K point, claiming an indirect bandgap (~ 0.95 eV). **It is well known that the band gap based on the DFT is always underestimated due to the improper treatment of the Coulomb repulsion. In comparison, the HSE06 method [42] gives an enhanced band gap. In our case, the band gap value is enhanced to 1.39 eV by using the HSE06 method.** For the convenience of comparison, the band structures of BP and single-layer MoS₂ are calculated and shown in Figs. 2b and 2c, respectively. Our results agree well with the previous studies [15, 33, 34, 36]. The bandgap of BP is indirect with the E_g of ~ 1.92 eV. The VBM locates between the K and Γ points while the CBM appears between the Γ and M points. Single-layer MoS₂ exhibits a direct bandgap of ~ 1.73 eV with both the VBM and CBM located at the K point. It is clearly seen from Fig. 2 that the band structure of the c-11 preserve both the properties of BP and MoS₂. It is consistent with the DOS and partial DOS (PDOS) results, as displayed in Fig. 3. As can be seen, both the BP (p orbitals of P) and MoS₂ (p orbitals of S and d orbitals of Mo) contribute to the VBM. In contrast, the CBM comes mainly from the MoS₂ layer (p orbitals of S and d orbitals of Mo). On the other hand, it is found that the bandgap width of the heterostructure is relatively narrower than both of the constructing individuals of BP and MoS₂. The similar phenomenon has been observed in other heterostructures, such as MoS₂/WS₂ [30] and MoS₂/hBN [32]. It should be ascribed to the interlayer coupling effect [43]. Our finding is that a relatively larger interlayer separation usually corresponds to a

relatively wider bandgap. For instance, in the above discussed AB and AB' structures with $\delta_y = 33\%$ ($d_L = 3.8 \text{ \AA}$), the E_g claims a relative larger value of $\sim 1.19 \text{ eV}$.

Based on the above discussed AB stacking c-11, multilayer BP/MoS₂ heterostructures are constructed. We should note that the case is similar for the AB' stacking, which will not be elaborated here. As shown in Figs. 4a-4c, c-12 is comprised of monolayer MoS₂ with bilayer BP, c-21 of bilayer MoS₂ with **monolayer** BP, and c-22 of bilayer MoS₂ with bilayer BP. Wherein, for bilayer BP, we employ the **AB-stacking** configuration which is confirmed to be the most stable one in previous study [14] and in our calculation. The lattice constants of these multilayer structures are optimized to be $\sim 3.24\text{-}3.25 \text{ \AA}$. The interlayer separations exhibit a slight adjustment among the three structures, as indicated in Figs. 4a-4c. The calculated band structures are presented in Figs. 4d-4f. The bandgaps are all indirect in nature. The VBM is located at the Γ point. For the c-21 (Fig. 4e), the CBM appears at the K point, which is similar to that of the c-11 discussed in Fig. 2a. While for the c-12 (Fig. 4d) and c-22 (Fig. 4f), the CBM rises along the Γ -M line. This is because in the c-21, the CBM is comprised mainly of the MoS₂ layer. In comparison, in the c-12 and c-22, the CBM is composed not only of the MoS₂ layer, but also of the BP layer (the PDOS is not shown here). The E_g are determined to be 0.82, 0.77 and 0.72 eV for the c-12, c-21 and c-22, respectively. Generally, in layered materials, the bandgap width decreases with increasing the stacking layers until it finally converges. The similar rule should govern the BP/MoS₂ heterostructures. **In the present case, the band gap decreases to around 0.66 and 0.63 eV in c-15 (monolayer MoS₂ with five-layer BP) and c-24 (bilayer MoS₂ with four-layer BP), respectively.**

To further engineer the band structures of the heterostructures, external electric fields are applied perpendicular to the stacking layers. Four typical band structures of the c-11 at electric fields of 0, 0.3, 0.6 and 0.71 eV/ $\text{\AA}$ are presented in Figs. 5a-5d, respectively. Firstly, with external electric fields increasing, the bandgap width decreases until it finally closes due to the well known Stark effect [44, 45]. In addition, before the bandgap closes at $\sim 0.71 \text{ eV/\AA}$ (see Fig. 5d), two important transitions take place. First, the CBM moving from the K point at 0 eV/ $\text{\AA}$ (Fig. 5a) to that between the K and Γ points at around 0.3 eV/ $\text{\AA}$ (Fig. 5b). Then, when the electric field is further increased, the CBM shifts to the Γ point at around 0.6 eV/ $\text{\AA}$ (Fig. 5c), corresponding to an indirect-direct bandgap transition. **A study on the PDOS reveals that as the band gap turns to be direct until it closes, the CBM is**

contributed primarily from the BP (p orbitals of P) while the VBM comes mainly from the MoS₂. The typical PDOS is displayed in the right panel of Fig. 5c. It is in a sharp contrast to the case that without applying external electric field as discussed above in Fig. 3. It can be anticipated that when such materials are excited by light irradiation, electrons and holes will be localized within different layers and the electron-hole recombination possibility will be largely reduced. It would be a very interesting research topic in fields of such as solar cells and photo-catalysts.

To unveil the mechanism behind the changes in the band structures under electric fields, the differential charge density distributions under four typical electric fields with respect to zero field are given in Figs. 6a-6d. As shown in Fig. 6a, at a relatively lower electric field (0.1 eV/Å), there is a charge density redistribution extending spatially the p_z orbitals of the P and S atoms. With electric field intensifying (0.3 eV/Å, see Fig. 6b, built-in electric dipole fields are formed due to charge polarization. Such electric dipole fields occur in three forms: (1) between the adjacent S and P atoms in the interlayer region; (2) between the top P and bottom S atoms; (3) on the Mo atoms. Obviously, the former two predominate, and in addition, the p_z orbitals of the S and P atoms are mainly involved. As seen from Fig. 6b, the charge polarization is nearly balanced between the adjacent S and P atoms in the interlayer region. In others words, the positive charge density on the P is nearly as much as the negative charge density on the S. The case is similar between the top P and bottom S atoms and it is that negative charge density on the P and positive charge density on the S are nearly the same. On the other hand, as a result of charge density polarization, the P are relatively more negatively charged, which makes itself more pronounced in the electronic states near the bandgap. This is why the CBM shifts to that between the Γ and M points in Fig. 5b. Further increasing electric field up to around 0.6 eV/Å or larger results in a change in the symmetry of the polarized charge density distributions. As seen from Figs. 6c and 6d, there are more positive charge density on the interlayer P than the negative charge density on the interlayer S; oppositely, there are more negative charge density on the top P than the positive charge density on the bottom S. This effect is believed to be responsible for the observed indirect-direct bandgap transition exhibited in Figs. 5c and 5d. Similar phenomenon was clarified in our previous work [45]. It was demonstrated that the symmetry of the built-in electric dipole field controlled the indirect-direct bandgap transition in bilayer MoS₂ subjected to external electric fields. In several other bilayer BP/MoS₂ heterostructures

such as the AB stacking with $\delta_y = 30\%$ and the AB' stacking with $\delta_x(\delta_y) = 0$ and $\delta_y = -30\%$ subjected to external electric fields, the same results are obtained. In addition, in the multilayer structures c-12, c-21 and c-22, external fields of ~ 0.31 , ~ 0.24 and ~ 0.07 eV/Å close the bandgap, respectively. However, no indirect-direct bandgap transition is observed and the differential charge density distributions are featureless at different electric fields.

4. CONCLUSION

Stacking BP and MoS₂ into heterostructures of BP/MoS₂ are demonstrated to be exothermic, suggesting the possibility to grow BP using MoS₂ as the substrate. The heterostructures preserve **both the properties of** BP and MoS₂. Whereas, due to the interlayer coupling effect, the bandgaps of the heterostructures are narrower than both of the comprising components of BP and MoS₂. The band structures are further engineered by applying external electric fields. In bilayer BP/MoS₂, an indirect-direct transition is realized when the electric field is applied around 0.6 eV/Å. Our results demonstrate that the symmetry of the built-in electric dipole fields controls the indirect-direct bandgap transition. We believe these results will provide a solid foundation for future engineering the electronic properties of 2D van der Waals heterostructures.

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- [1] K.S. Novoselov, A.K.Geim, S.V.Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov, Science 306 (2004) 666-669.
 - [2] C.R. Dean, A.F. Young, I. Meric, C. Lee, L. Wang, S. Sorgenfrei, K. Watanabe, T. Taniguchi, P. Kim, K.L. Shepard, J. Hone, Nat. Nanotech. 5 (2010) 722-726.

- [3] G.H. Lee, Y.J. Yu, C. Lee, C. Dean, K.L. Shepard, P. Kim, J. Hone, Appl. Phys. Lett. 99 (2011) 243114.
- [4] L. Britnell, R.V. Gorbachev, R. Jalil, B.D. Belle, F. Schedin, M.I. Katsnelson, L. Eaves, S.V. Morozov, A.S. Mayorov, N.M. Peres, A.H. Neto, J. Leist, A.K. Geim, L.A. Ponomarenko, K.S. Novoselov, Nano Lett. 12 (2012) 1707-1710.
- [5] R.A. Gordon, D. Yang, E.D. Crozier, D.T. Jiang, R.F. Frindt, Phys. Rev. B 65 (2012) 125407.
- [6] H. Zeng, J. Dai, W. Yao, D. Xiao, X. Cui, Nat. Nanotech. 7 (2012) 490-493.
- [7] K.F. Mak, K. He, J. Shan, T.F. Heinz, Nat. Nanotech. 7 (2012) 494-498.
- [8] P. Tonndorf, R. Schmidt, P. Böttger, X. Zhang, J. Börner, A. Liebig, M. Albrecht, C. Kloc, O. Gordan, D.R.T. Zahn, S.M. Vasconcellos, R. Bratschitsch, Opt. Express 21 (2013) 4908-4916.
- [9] J. Qiao, X. Kong, Z.-X. Hu, F. Yang, W. Ji, Nat. Commun. 5 (2014) 4475.
- [10] H. Liu, A.T. Neal, Z. Zhu, Z. Luo, X. Xu, D. Tománek, P.D. Ye, ACS Nano 8 (2014) 4033-4041.
- [11] L. Li, Y. Yu, G.J. Ye, Q. Ge, X. Ou, H. Wu, D. Feng, X.H. Chen, Y. Zhang, Nat. Nanotech. 9 (2014) 372-377.
- [12] F. Xia, H. Wang, Y. Jia, Nat. Commun. 5 (2014) 4458.
- [13] A. Castellanos-Gomez, L. Vicarelli, E. Prada, J.O. Island, K.L. Narasimha-Acharya, D.J. Groenendijk, M. Buscema, G.A. Steele, J.V. Alvarez, H.W. Zandbergen, J.J. Palacios, H.S.J. Zant, 2D Mater. 1 (2014) 025001.
- [14] Z. Zhu, D. Tománek, Phys. Rev. Lett. 112 (2014) 176802.
- [15] J. Xie, M.S. Si, D.Z. Yang, Z.Y. Zhang, D.S. Xue, J. Appl. Phys. 116 (2014) 073704.
- [16] B. Ghosh, S. Nahas, S. Bhowmick, A. Agarwal, Phys. Rev. B 91 (2015) 115433.
- [17] Z. Zhu, J. Guan, D. Tománek, Phys. Rev. B 91 (2015) 161406(R).
- [18] Z.Y. Zhang, J. Xie, D.Z. Yang, Y.H. Wang, D.S. Xue, M.S. Si, Appl. Phys. Express 8 (2015) 055201.
- [19] J. Han, J. Xie, Z.Y. Zhang, D.Z. Yang, M.S. Si, D.S. Xue, Appl. Phys. Express 8 (2015) 041801.
- [20] C. Kamal, M. Ezawa, Phys. Rev. B 91 (2015) 085423.
- [21] A.K. Geim, I.V. Grigorieva, Nature 499 (2013) 419-425.
- [22] P.J. Zomer, S.P. Dash, N. Tombros, B.J. van Wees, Appl. Phys. Lett. 99 (2011) 232104.
- [23] R. Decker, Y. Wang, V.W. Brar, W. Regan, H.Z. Tsai, Q. Wu, W. Gannett, A. Zettl, M.F. Crommie, Nano Lett. 11 (2011) 2291-2295.

- [24] Z. Liu, L. Song, S. Zhao, J. Huang, L. Ma, J. Zhang, J. Lou, P. M. Ajayan, *Nano Lett.* 11 (2011) 2032-2037.
- [25] T. Tanaka, A. Ito, A. Tajiima, E. Rokuta, C. Oshima, *Surf. Rev. Lett.* 10 (2003) 721-726.
- [26] Y. Shi, W. Zhou, A.Y. Lu, W. Fang, Y.H. Lee, A.L. Hsu, S.M. Kim, K.K. Kim, H.Y. Yang, L.J. Li, J.C. Idrobo, J. Kong, *Nano Lett.* 12 (2012) 2784-2791.
- [27] S. Bertolazzi, D. Krasnozhan, A. Kis, *ACS Nano* 7 (2013) 3246-3252.
- [28] Y. Hu, X. Li, A. Lushington, M. Cai, D. Geng, M.N. Banis, R. Li, X. Sun, *ECS J. Solid State Sci. Tech.* 2 (2013) M3034-M3039.
- [29] W. Fu, F.H. Du, J. Su, X.H. Li, X. Wei, T.N. Ye, K.X. Wang, J.S. Chen, *Sci. Rep.* 4 (2014) 4673.
- [30] K. Kósmider, J. Fernández-Rossier, *Phys. Rev. B* 87 (2013) 075451.
- [31] J. Kang, J. Li, S.S. Li, J.B. Xia, L.W. Wang, *Nano Lett.* 13 (2013) 5485-5490.
- [32] Z. Huang, C. He, X. Qi, H. Yang, W. Liu, X. Wei, X. Peng, J. Zhong, *J. Phys. D: Appl. Phys.* 47 (2014) 075301.
- [33] K.F. Mak, C. Lee, J. Hone, J. Shan, T.F. Heinz, *Phys. Rev. Lett.* 101 (2010) 136805.
- [34] A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim, C.Y. Chim, G. Galli, F. Wang, *Nano Lett.* 10 (2010) 1271-1275.
- [35] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, A. Kis, *Nat. Nanotech.* 6 (2011) 147-150.
- [36] J. He, K. Hummer, C. Franchini, *Phys. Rev. B* 89 (2014) 075409.
- [37] G. Kresse, J. Furthmüller, *Comput. Mater. Sci.* 6 (1996) 15-50.
- [38] G. Kresse, J. Furthmüller, *Phys. Rev. B* 54 (1996) 11169.
- [39] J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 77 (1996) 3865.
- [40] P.E. Blöchl, *Phys. Rev. B* 50 (1994) 17953.
- [41] S. Grimme, *J. Comput. Chem.* 27 (2006) 1787-1799.
- [42] J. Heyd, G.E. Scuseria, M. Ernzerhof, *ibid. J. Chem. Phys.* 124 (2006) 219906.
- [43] T. Cheiwchanchamnangij, W.R.L. Lambrecht, *Phys. Rev. B* 85 (2012) 205302.
- [44] A. Ramasubramaniam, D. Naveh, E. Towe, *Phys. Rev. B* 84 (2011) 205325.
- [45] Z.Y. Zhang, M.S. Si, Y.H. Wang, X.P. Gao, D. Sung, S. Hong, J. He, *J. Chem. Phys.* 140 (2014) 174707.

FIG. 1: (Color online) Top and side views of bilayer BP/MoS₂ heterostructures with (a) AB and (d) AB' stacking. The blue, red and grey represent the P, Mo and S atoms, respectively. The evolution of the total energy with a function of $\delta_x(\delta_y)$ in (b) AB and (e) AB' stacking. $\delta_x(\delta_y)$ represents the transilation shift of the BP layer relative to the MoS₂ layer along the $x(y)$ direction. The insets (from left to right) in (b) and (e) indicate the structures corresponding to $\delta_x(\delta_y) = -50\%$, $\delta_y = -33\%$, $\delta_y = 33\%$, $\delta_x(\delta_y) = 50\%$, respectively. (c) Total energy as a function of the interlayer distance d_L in (c) AB and (f) AB' stacking.

FIG. 2: Calculated band structures of (a) bilayer BP/MoS₂ (c-11) with PBE functional (black line) and by using the HSE06 method (red line), (b) blue phosphorene (BP) and (c) monolayer MoS₂. The horizontal dotted lines represent the Fermi level energy (E_F).

FIG. 3: (Color online) The total density of states (DOS) and orbital-resolved partial DOS (PDOS) of c-11. The total DOS is mainly comprised of p orbitals of P and S and d orbitals of Mo. The p_x and p_z orbitals of P (S) are degenerate. The d_{xy} and $d_{x^2-y^2}$ (d_{xz} and d_{yz}) orbitals of Mo occupy the the same energy; the d_{z^2} orbitals locate close to the d_{xy} and $d_{x^2-y^2}$ orbitals energetically. The vertical dotted lines represent the Fermi level energy (E_F).

FIG. 4: (color online) Stacking structures of multilayer BP/MoS₂: (a) c-12 of monolayer MoS₂ with bilayer BP, (b) c-21 of bilayer MoS₂ with BP, and (c) c-22 of bilayer MoS₂ with bilayer BP. The interlayer separations are indicated correspondingly. The calculated band structures of (d) c-12, (e) c-21 and (f) c-22. The indirect bandgaps are indicated with tilted black arrows. The gap energy are 0.82, 0.77 and 0.72 eV, respectively. The horizontal dotted lines represent the Fermi level energy (E_F).

FIG. 5: Band structures of BP/MoS₂ under various external electric fields: (a) 0 eV/Å, (b) 0.3 eV/Å, (c) 0.6 eV/Å (left panel) and (d) 0.71 eV/Å. The tilted black arrows mark indirect bandgaps and the vertical black arrow indicates direct bandgap. The bandgap closes at 0.71 eV/Å in (d). The right panel in the (c) shows the corresponding PDOS at 0.6 eV/Å. The horizontal dotted lines represent the Fermi level energy (E_F).

FIG. 6: (color online) Differential charge density distributions of the c-11 under various external electric fields with respect to zero field: (a) $0.1 \text{ eV/\AA}$ with isovalue of $8 \times 10^{-2} \text{ e/\AA}^3$, (b) $0.3 \text{ eV/\AA}$ with isovalue of $1.2 \times 10^{-3} \text{ e/\AA}^3$, (c) $0.6 \text{ eV/\AA}$ with isovalue of $1.9 \times 10^{-3} \text{ e/\AA}^3$, and (d) $0.71 \text{ eV/\AA}$ with isovalue of $1.3 \times 10^{-3} \text{ e/\AA}^3$. The blue, red and grey represent the P, Mo and S atoms, respectively. The greenish yellow and the light blue represent positive and negative charge density, respectively.