Prediction of the trends on electronic and native defect properties in few-layer phosphorene

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Using hybrid density functional theory together with a semiempirical dispersion correction of Grimme’s DFT-D2 method, we systematically investigated the band structure and intrinsic conductivity in few-layer phosphorene. We found that the layer number plays important roles in determining the electronic and the native defect properties of phosphorene. More specifically, our results theoretically predict that the host band gap, and formation energies as well as transition energies of P vacancy and interstitial P defects decrease with increasing P layer number. The fact that the valence band maximum and conduction band minimum are shifted upward and downward respectively in reference to the vacuum level are primarily responsible for these observed trends. Consequently, both P vacancy and interstitial P defects become shallow acceptors and act as sources of the experimentally observed p-type conductivity in few-layer phosphorene. On the other hand, these native defects would behavior as electron compensating centers as they have low formation energies and are stable in the positively charged state in n-type doping phosphorene. We also showed that the substitutional and interstitial sites on the outermost layer are more energetically favorable than those sites in internal configurations for the incorporation of P vacancy and interstitial P defects.

I. INTRODUCTION

The discovery of two dimensional (2D) materials such as graphene and transition metal dichalcogenides (TMDCs) arouses a huge interest of researchers due to their attractive electronic, mechanical, optical, and thermal properties. However, as novel functional materials, they also have some deficiencies in future electronic industry. For example, the applications of graphene in electronic and photonics devices are limited by its gapless nature most of the TMDCs currently being studied, such as MoS$_2$, but its carrier mobility of around 200-500 cm$^2$/V-s restricts its wide applications in nanotransistors. Despite it shows rather high on-off current ratios, excellent current saturations and direct band gaps properties. Moreover, most pristine TMDCs show unintentionally n-type conductivities owing to the presence of donor-like S vacancies and the partial Fermi level pinning near the conduction band edge of these materials.

Very recently, a new 2D few-layer black phosphorus, namely, phosphorene, has been successfully fabricated. It was excitingly reported that the phosphorene-based field effect transistor (FET) exhibits a carrier mobility up to 1000 cm$^2$/V-s and an on/off ratio up to $10^4 \sim 10^5$. Similar to graphite, black phosphorus is also a layered material in which the interlayers are held together by weak van der Waals (vdW) interaction. Inside a layer, each phosphorus atom bonds with its three neighbors by sharing all three valence electrons to form a $sp^3$ hybridization in a puckered honeycomb structure. Black phosphorus has a direct band gap of 0.31$\sim$0.35 eV. A novel finding that the band gap of phosphorene is found to be layer-number dependent. Previous first-principles calculations have predicted that

the band gap values range from 2.0$\sim$1.5 eV for a mono-layer to $\sim$0.6 eV for a five-layer. In addition, theoretical studies have showed that few-layer phosphorene goes through a semiconductor-metal or direct-indirect band gap transition by applying strain. Most recently, Liu et al. experimentally constructed an inverter by using MoS$_2$ for the n-type transistor and phosphorene as a p-type transistor, both integrated on the same Si/SiO$_2$ substrate. They observed that typically few-layer phosphorene show unintentional p-type conductivity. In addition, a number of other experiments also achieve intrinsic p-type phosphorene. Then a question arises: What is the origin of the reported intrinsic p-type conductivity?

It is well known that native defects and impurities have important effects on the properties of semiconductors. Despite the fact that there are a large number of theoretical studies on the layer-dependent electronic structure of few-layer phosphorene, a full picture of detailed and systematic analysis of the layered effects on the native defect properties of few-layer phosphorene is still missing. In the present work, we investigated formation energies and transition levels of native defects, with aiming of gaining a deeper understanding of the possible source of the p-type conductivity in few-layer phosphorene based on the hybrid density functional theory coupling with a semiempirical vdW correction approach developed by Grimme and co-workers. The recent development of hybrid density functional theory can correct the band gap and provide more reliable description of transition levels and formation energies of defects in semiconductors. Our calculated results demonstrate that (i) the host band gap systematically reduces as the P layer number of phosphorene increases since the valence band maximum and conduction band minimum are
shifted upward and downward respectively in reference to the vacuum level; (ii) the calculated formation energies and acceptor transition levels of both P vacancy and interstitial P defects in monolayer are lower in energy than those in monolayer; (iii) both P vacancy and interstitial P are expected to be possible sources of the intrinsic p-type conductivity in few-layer phosphorene. (iv) these native defects have low enough formation energies to act as compensating centers in n-type phosphorene. The remainder of this paper is organized as follows. In Sec. II, the details of the methodology and computational details are described. Sec. III presents our calculated formation energies and transition energies of various defects in few-layer phosphorene. Finally, a short summary is given in Sec. IV.

II. METHODS

Our total energy and electronic structure calculations were carried out within a revised Heyd-Scuseria-Ernzerhof (HSE06) range-separated hybrid functional as implemented in the VASP code. In the HSE06 approach, the screening parameter was set to 0.2 Å⁻¹. The Hartree-Fock (HF) mixing parameter α (meaning α of HF exchange with 1-α of PBE exchange) were tuned to produce accurate band gap values for few-layers phosphorene systems. The core-valence interaction was described by the frozen-core projector augmented wave (PAW) method. The electronic wave functions were expanded in a plane-wave basis with a cutoff of 300 eV. Previous theoretical calculations have shown that the vdW interaction need to be accounted for properly describing the geometrical properties of black phosphorus. We incorporated the vdW interactions through employing a semiempirical correction scheme of Grimme’s DFT-D2 method, which has been proven to be successful in describing the geometries of various layered materials.

The initial structures of few-layer phosphorene were modeled from the bulk phase of black phosphorus. In the black phosphorus as presented in Fig. 1 the sp³ hybridization between one P atom with its three neighbors lead to the tripod-like local structure in the two sub-planes along z direction inside a layer. A vacuum distance of ≥ 40 Å along the vertical (z) direction to the phosphorene slab was applied to avoid interactions between neighboring images. We carefully checked the convergence of the calculated total energies of charged defects with respect to the vacuum thickness and a more detailed discussion is given in the next sections. A 8×6×1 k-mesh generated according to the Monkhorst-Pack scheme including Γ point was applied to the Brillouin-zone integrations in total-energy calculations. During the geometric optimization, lattice sizes, lattice shapes and internal structural parameters are fully relaxed until the residual force on atoms less than 0.01 eV/Å.

Since no experimental data available for the electronic properties of few-layer phosphorene. An accurate description of the band structures of phosphorene is prerequisite for obtaining reliable predictions regarding their defect properties, which is an ultimately key factor determining the electronic conductivities in phosphorene. Thus, we also employed more accurate quasiparticle GW0 approximation to estimate the band gaps of few-layer phosphorene. The GW0 approximation can provide more reliable descriptions on the electronic and dielectric properties in many semiconductors and insulators. In the GW0 calculations, the total band number is 80 times of the total number of involved atoms to achieve converged dielectric function. The converged HSE06 with 25% HF exact exchange eigenvalues and wavefunctions were chosen as the initial input for the GW0 calculations. It should be pointed that only the quasiparticle energies are recalculated in GW0 calculations; the wavefunctions are not updated and remain fixed at the HSE06-25% level. For visualization purposes, the GW0 calculated band structures were interpolated based on Wannier orbitals as implemented in the WANNIER90 code.

The defect systems were modeled by adding (removing) an P atom to (from) a 3×2 supercell of phosphorene. The native defects, i.e., P vacancy (V_P) and interstitial P (P_i) were considered in the present work. Similar to the cases of interstitial sites in hexagonal BN and graphene, there are three possible interstitial configurations in the monolayer. Additionally, in the few-layer phosphorene, both V_P and P_i defects reside either at the sites on the outermost layer or on the interlayer. We label as X^in and X^out (X=V_P and P_i) respectively. For example, six possible interstitial sites in bilayer are visualized in Fig. 2. We have previously pointed that the contribution of vdW interaction to the stability of adsorbate on graphene, even in the chemisorption case could not be ignored. It is therefore expect that the HSE06 plus DFT-D2 method would be give a better accurate
description on the local structures of interstitial defects in few-layer phosphorene. A Γ-centered 2×2×1 k-mesh was adopted in the spin-polarized defect calculations.

\[ \Delta E^f_{D}\left(\alpha, q\right) = E_{\text{tot}}\left(\alpha, q\right) - E_{\text{tot}}\left(\text{slab}, 0\right) - n_\alpha \mu_\alpha + q\left(\mu_e + \varepsilon_v\right) + E_{\text{corr}}\left[q\right], \]  

where \( E_{\text{tot}}\left(\alpha, q\right) \) and \( E_{\text{tot}}\left(\text{host, 0}\right) \) are the total energies of the supercells with and without defect \( \alpha \). \( n_\alpha \) is the number atoms of species \( \alpha \) added to \( (n_\alpha > 0) \) or and removed from \( (n_\alpha < 0) \) the perfect supercell to create defect \( \alpha \). \( \mu_\alpha \) is the atomic chemical potential equal to the total energy per atom in the corresponding phosphorene configuration. \( q \) is the charge state of defect and \( \mu_e \) is electron chemical potential in reference to the host valence band maximum (VBM). Therefore, \( \mu_e \) varies between zero and the band-gap \( (E_g) \) of few-layer phosphorene. The final term accounts for both the alignment of the electrostatic potential between the bulk and defective charged supercells, as well as the finite-size effects resulting from the long-range Coulomb interaction of charged defects in a homogeneous neutralizing background. It can be evaluated by using the Freysoldt correction scheme with an average static dielectric constant \( (\varepsilon_0) \). A double k-point meshes with a Gaussian smearing of 0.01 eV was employed in the calculations of static dielectric tensors, and the procedure we have detailed in a previous work. The defect thermodynamic transition (ionization) energy level \( \epsilon_\alpha(q/q') \) is defined as the Fermi-level \( (E_F) \) position for which the formation energies of these charge states are equal for the same defect, namely,

\[ \epsilon_\alpha(q/q') = \frac{\Delta E^f_{D}\left(\alpha, q\right) - \Delta E^f_{D}\left(\alpha, q'\right)}{(q' - q)}. \]  

More specifically, the defect is stable in the charge state \( q \) when the \( E_F \) is below \( \epsilon_\alpha(q/q') \), while the defect is stable in the charge state \( q' \) for the \( E_F \) positions above \( \epsilon_\alpha(q/q') \).

### III. RESULTS AND DISCUSSION

#### A. Fundamental properties of pristine few-layer phosphorene

We start our analysis by first checking the geometric and electronic properties of pristine few-layers phosphorene. For comparison purposes, the changes of geometric properties as a function of P layer number using PBE, PBE with vdW correction (PBE+vdW) and HSE06-25%+vdW approaches are listed in Table I. It is found that the lattice parameter \( b \) increases by 0.07–0.15 Å from bulk to monolayer depending on the selected approach. In contrast, the lattice parameter \( a \) shortens only within 0.01 Å and the interlayer distance between two adjacent P layers \( \Delta d \) is also insensitive to the number of layer. Similar trends were theoretically found in previous studies by Qiao et al. As for the bulk phosphorene, its experimental lattice parameters are \( a=3.31 \) Å, \( b=4.38 \) Å and \( \Delta d=5.24 \) Å. Note that the PBE approach without vdW correction overestimates around 3.6% for \( a \) and 5.5% for \( \Delta d \); while the calculated results using PBE+vdW and HSE06+vdW, especially the latter, are quite good agreement with the experimental values. However so far there are no experimental data available that could verify our predicted results for few-layer phosphorene systems. We believe that the reliability of PBE+vdW and HSE06+vdW results still hold true for the geometries of few-layer phosphorene. Hence, the following calculated results include vdW correction unless otherwise stated.

In general, the DFT calculations within PBE functional underestimate the band gaps of materials. The standard HSE03 method with 25% exact exchange well reproduces the band gaps of small- to medium-gap systems but still underestimates the gap values of large-gap systems. Recently, Fuchs et al. theoretically have shown that the mean absolute relative error (MARE) of G0W0 (GWO) approach upon the HSE03 eigenvalues and wave functions on the calculated band gaps of some representative traditional semiconductors is 6.8% (8.0%). We summarize the PBE, HSE06, G0W0 and GW0 calculated band gap values of few-layer phosphorene in Table II. We note that the G0W0 approach gives a calculated \( E_g \) of 0.58 eV for bulk phosphorus, overestimating the band gap by near 100% comparing with the experimental value of 0.31–0.35 eV. This surprising overestimation may be attributed to the magnitude of bulk gap value is rather small. As expected, the HSE06 calculated value
TABLE I. Lattice constants $a$, $b$ and interlayer distance between two adjacent P layers $\Delta d$ as a function of the number of layers in black phosphorus using PBE, PBE+vdW and HSE06-25%+vdW approaches respectively.

| Systems | PBE | PBE+vdW | HSE06-25%+vdW |
|---------|-----|---------|---------------|
|         | $a$ (Å) | $b$ (Å) | $\Delta d$ (Å) | $a$ (Å) | $b$ (Å) | $\Delta d$ (Å) | $a$ (Å) | $b$ (Å) | $\Delta d$ (Å) |
| monolayer | 3.30 | 4.61 | - | 3.32 | 4.56 | - | 3.30 | 4.50 | - |
| bilayer | 3.31 | 4.58 | 5.57 | 3.32 | 4.50 | 5.21 | 3.30 | 4.45 | 5.17 |
| trilayer | 3.31 | 4.58 | 5.58 | 3.32 | 4.47 | 5.22 | 3.30 | 4.44 | 5.18 |
| quadrilayer | 3.31 | 4.57 | 5.59 | 3.32 | 4.46 | 5.23 | 3.30 | 4.44 | 5.19 |
| bulk | 3.31 | 4.54 | 5.53 | 3.33 | 4.41 | 5.23 | 3.31 | 4.37 | 5.19 |

* Experimental lattice constants: $a=3.31$ Å, $b=4.38$ Å and $\Delta d=5.24$ Å in reference [58].

is quite good agreement with experiment. The G0W0 (HSE06-25%) approach predicts the band gap values of 2.37 (1.56) eV for monolayer, 1.66 (1.04) eV for bilayer, 1.18 (0.74) eV for trilayer and 1.04 (0.71) eV for quadrilayer. We therefore expect that the GW0 and HSE06-25% approaches would give a reasonable upper and lower bounds for the gap values of few-layer phosphorene respectively.

All approaches are observed to predict similar decrease trends of $E_g$ with increasing of layer number, which is mainly attribute to the energy level splitting induced by the interlayer interaction. More specifically, the more number of layer, the stronger the interlayer interaction; and thus the more significant the dispersion spectrum for band structure, giving rise to a smaller band gap. Considering the fact that no experimental data as a reference, the optimized Hartree-Fock mixed parameter $\alpha$=35% for monolayer, $\alpha$=30% for bilayer, and $\alpha$=25% for quadrilayer was set to more closely reflect the G0W0 calculated band gaps in the underlying HSE06 studies of defect properties.

Figure 3 displays the HSE06 and GW0 calculated band structure of phosphorene monolayer. Note that both VBM and conduction band minimum (CBM) are located at the $\Gamma$ point, leading to a direct band gap character. This is consistent with the findings in previous theoretical studies. The partial charge density analyses show that the VBM are derived from the bonding states between P atoms in two sublayer and the anti-boding states between P atoms in the same sublayer, supposing that we view along the direction perpendicular to the $z$ axis as shown in Fig. 3 (b). The opposite is true for the case of CBM. The band structure characteristics of bilayer are similar to that of monolayer, except for the former in which the interlayer vdW interaction results in the degenerate energy level splitting as observed in Fig. 4 (b). Overall, both HSE06 and GW0 yields similar band dispersion curves. The main difference is that the HSE06 calculated energy levels of the states lying 10 eV below VBM are pushed downward in energy relative to those obtained using GW0 approach.

The band alignments for few-layer phosphorene are shown in Fig. 5. One can note that all approaches produce similar trends: (i) As the P layer number increases, namely, from monolayer to quadrilayer, the VBM of few-layer phosphorene move upward, while the CBMs move downward. This can be understood in terms of a simple quantum confinement effect. (ii) Overall, the band offset of valence band is more significantly than that of conduction band. This suggests that the transition levels of acceptors are more sensitively dependent layer number than those of donors. The HSE06 calculated static dielectric tensors $\epsilon_0$ (including ionic contributions) of few-layer phosphorene parallel to $a$ ($\epsilon_{0x}^{ax}$), $b$ ($\epsilon_{0y}^{bx}$), and $c$ ($\epsilon_{0z}^{cz}$) axes are listed in Table I. The decrease trend in the band gap of few-layer phosphorene is primarily responsible for the upward trend of static dielectric tensors.

B. Properties of native defects in few-layer phosphorene

Considering that the electrostatic screening effect of vacuum slab perpendicular to the $z$ direction is small, we take phosphorene monolayer as an example to check...
TABLE II. The calculated band gap ($E_g$) as a function of the number of layers in phosphorene using PBE, HSE06 and GW0 methods respectively.

| Systems  | PBE   | HSE06-25% | HSE06-opt | G0W0  | GW0  | Previous work$^a$ | Exp. |
|----------|-------|-----------|-----------|-------|------|------------------|------|
| monolayer| 0.91  | 1.56      | 1.91$^c$  | 2.37  | 2.41 | 1.5-2.0          | -    |
| bilayer  | 0.45  | 1.04      | 1.23$^c$  | 1.66  | 1.66 | 1.0-1.3          | -    |
| trilayer | 0.20  | 0.74      | 0.98$^c$  | 1.18  | 1.20 | 0.7-1.1          | -    |
| quadrilayer | 0.08 | 0.71      | 0.71$^d$  | 1.04  | 1.08 | 0.5-0.7          | -    |
| bulk     | 0.10  | 0.28      | 0.28$^d$  | 0.58  | 0.65 | $\sim$0.3       | 0.31-0.35$^e$ |

$^a$ References [16, 21] and [22]
$^c$ HSE06-35% calculated value.
$^d$ HSE06-30% calculated value.
$^e$ HSE06-25% calculated value.
$^f$ References [17-20]

FIG. 4. (Color online) (a) HSE06 and GW0 calculated band structure; top and side views of wavefunction squared of (b) VBM and (c) CBM of phosphorene bilayer, respectively. The vacuum level is taken as zero energy reference. The charge density isosurfaces are shown at 40% of their maximum values.

FIG. 5. (Color online) Band alignments for few-layer phosphorene. The vacuum level is taken as zero energy reference.

The formation energies of charged defects with respect to the vacuum thickness. Test calculations show that a vacuum thickness of 12 Å can ensure the charge-neutral systems were well converged within 0.01 eV in total energies. Figure 6 (a) reveals that the numerical errors on the relative total energies of monolayer systems containing one singly negative charged V$^{\text{out}}_P$ or P$^{\text{out}}_i$ defect reach to 0.1 eV when a vacuum space of 40 Å was applied. However, one interesting observation is that that the total energies of supercells containing one singly positive charged defect with a 40 Å vacuum space differ by about 1.0 eV from those of ones with a 32 Å vacuum space. A better convergence within 0.1 eV can be reached until a 80 Å vacuum space was adopted in donor doping monolayer. This implies that the formation energies of positively and negatively charged native defects would be observably overestimated and underestimated in few-layer phosphorene respectively when a typical 12 Å vacuum space was adopted. In other words, this leads to shallower transition levels for acceptors and deeper transition levels for donors.

The formation energies of V$^{\text{out}}_P$ and P$^{\text{out}}_i$ in phosphorene monolayer as a function of electron chemical potential $\mu_e$ are plotted in Fig. 7 (a). For simple reasons of convenience, we label V$^{\text{out}}_P$ and P$^{\text{out}}_i$ as V$^P$ and P$^i$ herein. For a given value of $\mu_e$, only the energetically stable charge state (with the lowest formation energy) of a specified defect is presented. The changes of slope in the curves correspond to the transition between charge states and hence to thermodynamic transition levels. We
find that V$_P$ are stable in the charge state of 1- for all values of $E_F$ in the host band gap. Considering that the high formation of the negatively charged V$_P$ (around 2.6 eV) when the $E_F$ near the VBM, the V$_P$ might be not an efficient p-type defect due its low concentration as grown phosphorene monolayer under equilibrium growth conditions. It is found that the nearest P neighbor on the top sublayer relaxes toward V$_P$. Finally, this P atom is observed to bond with its four neighbors with two different bond lengths of 2.41 Å and 2.28 Å respectively when V$_P$ is in the 1- charge state, as shown in Fig. 7 (b). This P atom is more close to the P pair on the top sublayer. It should be pointed that the the donor ionization levels of V$_P$ or P$_i$ are unstable for all positions of $E_F$ in the band gaps of few-layer phosphorene, suggesting that both V$_P$ and P$_i$ are expected to be acceptor-like defects.

As for interstitial P, the configuration with P$_i$ serving as a bridge between two host P atoms is found to be the most energetically favorable structure as displayed in Fig. 2 (a). Note that P$_i$ is lower by $\sim$1.0 eV than V$_P$ when the $E_F$ is near the VBM, suggesting that P$_i$ is a dominant native defect under p-type conditions. The (-1/0) acceptor level of P$_i$ is predicted to be 0.88 eV above VBM, implying that P$_i$ is a deep acceptor. On the other hand, when the $E_F$ is close to CBM, both V$_P$ and P$_i$ have lower formation energies (less than 0.9 eV) and are energetically stable in the charge state of 1-, meaning that they can act as a compensating center in n-type doping monolayer. In the neutral charge state, P$_i$ is bonded to two host P atom with identical bond lengths of 2.14 Å. A small asymmetry was observed in these two bonds (2.06 Å versus 2.20 Å), accompanied by a distinct local lattice distortion around P$_{i}^{1-}$ defect.

In the phosphorene bilayer, both P$_{i}^{out}$ and V$_P^{out}$ are energetically more stable than the corresponding P$_{i}^{in}$ and V$_P^{in}$ as shown in Fig. 8 (a). This suggests that the outermost layer is energetically favored by $\sim$0.7 eV than the intermediate layer for the formation of native defects. From Fig. 9 (a), it is seen clearly that the relaxed local structure of V$_P^{out}$ is very similar to the case of monolayer. In contrast to V$_P^{out}$, the neighboring P atoms of the negatively charged V$_P^{out}$ undergoes no significant distortion from their ideal lattice positions as displayed in Fig. 9 (b). This in turn leads to week bond strength between the neighbors and V$_P^{out}$ due to the large distance between them ($\geq$ 3.1 Å). The equilibrium local structure of the negatively charged P$_i^{out}$ in the bilayer is also similar to that in the monolayer. As for P$_i^{in}$, the upper layer pushes the negatively charged P$_i^{in}$ to move downward, leading to two identical bond lengths between P$_i^{in}$ and its two neighbors (2.14 Å). Meanwhile, the nearest-neighbors on the upper layer relax symmetrically away from P$_i^{in}$, as illustrated Fig. 9 (d).

![FIG. 6. (Color online) Vacuum thickness dependent total energies of the systems consisting of one V$_P^{out}$ or P$_i^{out}$ defect in the charge states of (a) -1; (b) +1 in phosphorene monolayer. The total energies of the configurations with a vacuum thickness of 12 Å are taken as zero energy references.](image)

![FIG. 7. (Color online) (a) Formation energies of V$_P$ and P$_i$ as a function of electron chemical potential in monolayer. (b) Local structures of V$_P$ and P$_i$. The defect and its nearest-neighbors are marked in blue balls.](image)

![FIG. 8. (Color online) Formation energies of V$_P$ and P$_i$ in (a) bilayer and (b) quantrilayer as a function of electron chemical potential.](image)
The acceptor transition levels for $V_p^{\text{out}}$ and $P_i^{\text{out}}$ are -0.64 eV and 0.19 eV with respect to VBM in bilayer, implying all possible native defects can contribute to the $p$-type conductivity in bilayer. Finally, all native defects are stable in the charge state of 1- for any position of the $E_F$ in the band gap of quantilayer. We tentatively partly attribute this trend as the upward trend of band offset for VBM (see Fig. 9). In addition, one can note the calculated formation energies of all possible native defects systematically decrease with the increase of P layer number. This means that the $p$-type doping by native defects in multilayer phosphorene becomes more efficient. On the other hand, since the formation energies of these acceptor-type defects are low enough when $E_F$ is near CBM, indicating that self-compensation would have been unavoidable in $n$-type phosphorene. Thus, using nonequilibrium growth techniques to reduce the concentrations of native defects in $n$-type phosphorene are necessary.

![Fig. 9](image)

**FIG. 9.** (Color online) Local structures of the single negatively charged (a) $V_p^{\text{out}}$, (b) $V_p^{\text{in}}$, (c) $P_i^{\text{out}}$ and $P_i^{\text{in}}$ in bilayer. The defect and related nearest-neighbors are marked in blue balls.

To gain insight into the origin of the trends on the conductive characteristics, we display the transition levels of native defects with respect to the vacuum level in Fig. 10. One can note that the transition levels of $V_P$ and $P_i$, which are referenced to the vacuum level generally decrease with increasing P layer number. This means that the magnitudes of the formation energies for negatively charged defects decrease more quickly than those for the corresponding neutral ones when from monolayer to quantilayer, which results in the shift of the transition levels of $V_P$ and $P_i$ toward lower energies. Therefore this trend will certainly contribute to the observed shallower acceptor levels of $V_P$ and $P_i$ in quantilayer, besides the band offset effects for VBM and CBM. We should keep in mind that three different values of HF mixing parameter $\alpha$ (25%, 30% and 35%) were adopted for monolayer, bi-layer and quantilayer systems respectively. However, it is noteworthy that the formation energies of defects also depends on the choice of $\alpha$, which was already pointed out in our previous studies[61]

![Fig. 10](image)

**FIG. 10.** (Color online) Transition levels of $V_P$ and $P_i$ referenced to the vacuum level in few-layer phosphorene.

We take $V_P^{\text{out}}$ and $P_i^{\text{out}}$ as examples to investigate the roles of $\alpha$ in their stability and conductivity. From the results presented in Fig. 11 a slight deviation of around 0.4 eV is observed for the formation energy of $P_i^{\text{out}}$, while the calculated transition levels of $V_P^{\text{out}}$ and $P_i^{\text{out}}$ which are referred to the vacuum level differ less than 0.1 eV when reducing the value of $\alpha$ from 35% to 25%. This suggests that the $\alpha$ has little effects on the transition levels of $V_P^{\text{out}}$ and $P_i^{\text{out}}$ on an absolute energy scale. It might be expected to hold true for more layer phosphorene.

**IV. SUMMARY**

In summary, we have systematically investigated the trends of electronic and native defect properties in few-layer phosphorene using first-principles calculations based on hybrid density functional theory including vdW correction within the Grimme’s DFT-D2 scheme. Our calculations show that all possible native defects, i.e., P vacancy and interstitial P defects exhibit acceptor-like behavior and their formation energies and transition levels decrease with increasing P layer number. The same trend is also observed in the host band gap. The reason for these trends can be explained by the band offsets for few-layer phosphorene. Specifically, we found that the valence band maximum and conduction band minimum systematically shift upward and downward in reference to the vacuum level as the layer number of phosphorene increases due to the quantum confinement effect. Additionally, we demonstrated that both P vacancy and interstitial P defects can act as sources of $p$-type conductivities reported experimentally in few-layer phosphorene.
FIG. 11. (Color online) Formation energies of V$_P$ and P$_i$ as a function of electron chemical potential in monolayer phosphorene. (b) transition energy levels referenced to the vacuum level using HSE06-35% and HSE06-25% approaches respectively. The gray region represents the HSE06-25% calculated band gap. The solid and dashed lines represent the HSE06-35% and HSE06-25% methods calculated results.

On the other hand, these native acceptors would have non-negligible concentrations and thus act as a compensating centers in $n$-type phosphorene.

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