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Magneto-electronic perturbation effects on the electronic phase of phosphorene

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Abstract. In the present paper, we address the influence of dilute charged impurity, the perpendicular electric field, and the perpendicular magnetic field on the electronic density of states (DOS) of phosphorene. This is done with the help of the continuum model Hamiltonian and the Green's function approach. Also, the magneto-electron-impurity interaction effect is carried out within the full self-consistent Born approximation for the small density of impurities. We observe a semiconductor-to-semimetal phase transition in both armchair and zigzag directions when the system is unbiased and infected by impurity atoms at strong magnetic fields, whereas there is no phase transition in biased case. Moreover, both impurity concentration and impurity scattering potential parameters lead to the decrease of the band gap. Further, these parameters play different roles in the degeneration of the midgap states-induced of unbiased and biased phosphorene in the presence of a magnetic field. Our findings improve the ability of experimentalists in controlling electronic and optical properties of phosphorene.

Keywords: Phosphorene; Green's function; Electronic phase transition; Born approximation; Density of states

1. Introduction

In graphene, the nearly relativistic velocities of the electrons and the lack of the band gap are two frustrating factors in the real application of graphene in field effect transistors (FET) [1, 2]. Compared to the graphene, phosphorene is more applicable as a FET [3, 4]. Phosphorene has a direct band gap about 1.5 eV [5] and has attracted great attention both theoretically and experimentally [4, 6, 7, 8, 9, 10, 11, 12, 13, 14]. This semiconductor gives the industry a hope as a good candidate on-off device better than graphene. The large mobility of carriers with different masses in different directions is the main reason for special recent studies on phosphorene. On the other hand, it has been reported that the pristine phosphorene is a non-magnetic semiconductor with interesting transport and optical properties in the presence of perpendicular magnetic field [15, 16]. Different Landau splitting of the conduction and valence bands in different directions is one of the nice results of this material when the perpendicular magnetic field is applied. Also, the direction-dependent electronic phase transition in magnetic field-induced gated phosphorene is studied in Ref. [17], which reminds once more the inherent anisotropy property of phosphorene. Further, theoretically, the Landau levels and magneto-transport properties of phosphorene under a perpendicular magnetic field within the framework of the effective $\vec{k} \cdot \vec{p}$ Hamiltonian and tight-binding model has been investigated in Ref. [18].

In addition to the magnetic field aforementioned above, electronic perturbations also affect the electronic and optical properties of low-dimensional materials. One of the electronic perturbations is charged impurity, leading to perturbed electronic DOS around the Fermi energy. Recently, in Refs. [19, 20, 21, 22], tuning of the band gap of different shapes of doped phosphorene has been investigated. They found that depending on the doping concentration, one obtains different behaviors for the electronic phase of the system. On the other hand, the effect of the perpendicular electric field has been studied in Refs. [23, 24, 25, 26], which demonstrate different electro-optical properties due to the modulated band gaps. However, to the best of our knowledge, a few numbers of studies have focused on the *combined* effects of both electronic and magnetic perturbations on phosphorene to date.

Accordingly, we aimed at studying the electronic phase transition of phosphorene in the presence of combined effects of: (i) dilute charge impurity, (ii) Zeeman magnetic field, and (iii) the perpendicular electric field. In so doing, an analytical procedure based on the Born approximation has been performed to describe electronic phase transition using the tight-binding model Hamiltonian and the Green's function method. The remainder of this paper is organized as follows: Sec. 2 introduces the required theoretical frameworks. In Sec. 3, we show the numerical results, and finally, our main conclusions are concluded in Sec. 4.

Magneto-electronic perturbation effects on the electronic phase of phosphorene 3

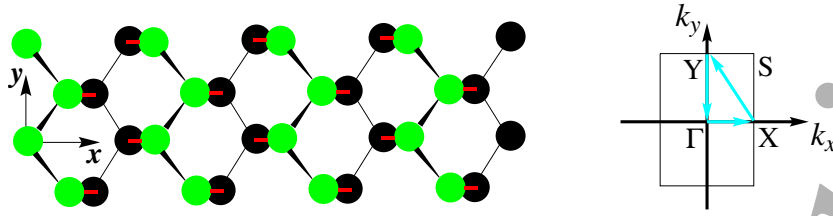


Figure 1. (Color online) Sketch of the top view of phosphorene including green and black circles in vertical heights. The buckling is shown by red bold lines. The primitive unit cell contains four atoms. The first Brillouin zone is also presented as a vertical rectangle in the right side with four high symmetry points Γ , X, S, and Y.

2. Theoretical framework

2.1. Non-interacting Green's function

Phosphorene has a puckered honeycomb atomic structure of phosphorus atoms with two sublayers, as shown in Fig. 1. The four phosphorus atoms are represented by green and black symbols at the bottom and top sublayer, respectively. In our calculations, the x - and y -axis correspond to the armchair (AC) and zigzag (ZZ) direction, respectively. Using the C_{2h} group invariance property and the Hamiltonian proposed in Refs. [10, 27], the continuum approximation of phosphorene around the Γ point (retaining the terms up to second-order in momentum) would be achieved as [28, 29, 30, 31, 32]

$$\mathcal{H}(\vec{k}) = \begin{array}{c} A \uparrow \\ B \uparrow \\ A \downarrow \\ B \downarrow \end{array} \left(\begin{array}{cccc} A \uparrow & B \uparrow & A \downarrow & B \downarrow \\ \epsilon_c + \eta_c k_x^2 + \nu_c k_y^2 & \gamma k_x + \alpha k_x^2 + \beta k_y^2 & g\mu_B \mathcal{B}/2 & 0 \\ \gamma k_x + \alpha k_x^2 + \beta k_y^2 & \epsilon_v - \eta_v k_x^2 - \nu_v k_y^2 & 0 & g\mu_B \mathcal{B}/2 \\ g\mu_B \mathcal{B}/2 & 0 & \epsilon_c + \eta_c k_x^2 + \nu_c k_y^2 & \gamma k_x + \alpha k_x^2 + \beta k_y^2 \\ 0 & g\mu_B \mathcal{B}/2 & \gamma k_x + \alpha k_x^2 + \beta k_y^2 & \epsilon_v - \eta_v k_x^2 - \nu_v k_y^2 \end{array} \right), \quad (1)$$

which means that we only consider the coupling between the magnetic field and spin of the same atoms in different sublayers, i.e. top and bottom sublayers. The corresponding Hamiltonian for this expression is given by $\hat{\mathcal{H}} = g\mu_B \mathcal{B}/2 \sum_i [\hat{a}_{1i,\uparrow}^\dagger \hat{a}_{2i,\downarrow} + \hat{b}_{1i,\uparrow}^\dagger \hat{b}_{2i,\downarrow} + \text{H.c.}]$. In the equation above, $\epsilon_c = -1.18$ ($\epsilon_v = 0.34$) eV are the energies from the bottom (top) of the conduction (valence) band at Γ point with a direct energy gap $\mathcal{E}_g = 1.52$ eV in quite agreement with Refs. [11, 13, 27]. We have used the knowledge of DFT results in order to get other coefficients [33]. Thus, we use $\eta_c = 0.008187$, $\eta_v = 0.038068$, $\nu_c = 0.030726$, $\nu_v = 0.004849$ in units of eVnm² and $\gamma = 0.48$ in units of eVnm. The momenta $\vec{k} = (k_x, k_y)$ belong to the first Brillouin zone (FBZ). As for the perpendicular magnetic field effect, the element $g\mu_B \mathcal{B}/2$ is introduced with g , μ_B , and \mathcal{B} corresponding to the degeneracy number (so-called the Lande g -factor), the Bohr magneton, and the Zeeman magnetic field strength, respectively. In Ref. [33], the value of coefficient α is

Magneto-electronic perturbation effects on the electronic phase of phosphorene 4

much less than coefficient γ . So, using the time-reversal invariant (TRI) feature and also $\alpha \ll \gamma$ in the system, the terms containing α and β can be removed. In our formulation, the perpendicular electric field is introduced using the applied bias voltage $V = eEd$ referring to the electric field E , the elementary charge e , and the sublayer separation d [22, 23, 28, 30, 31, 34, 35]. Accordingly, the new Hamiltonian has the following elements:

$$\mathcal{H}_{\text{eff}}(\vec{k}) = \begin{pmatrix} \epsilon_c + \eta_c k_x^2 + \nu_c k_y^2 + V/2 & \gamma k_x & g\mu_B \mathcal{B}/2 & 0 \\ \gamma k_x & \epsilon_v - \eta_v k_x^2 - \nu_v k_y^2 - V/2 & 0 & g\mu_B \mathcal{B}/2 \\ g\mu_B \mathcal{B}/2 & 0 & \epsilon_c + \eta_c k_x^2 + \nu_c k_y^2 + V/2 & \gamma k_x \\ 0 & g\mu_B \mathcal{B}/2 & \gamma k_x & \epsilon_v - \eta_v k_x^2 - \nu_v k_y^2 - V/2 \end{pmatrix}, \quad (2)$$

Thanks to the TRI and the non-interacting Green's function relation $G_0(\vec{k}, \mathcal{E}) = [\mathcal{E} + i\zeta - \mathcal{H}_{\text{eff}}(\vec{k})]^{-1}$ for $\zeta \simeq 5$ meV as the broadening factor, we deduce the following matrix in the momentum space in order to describe the correlations between carriers

$$G_0(\vec{k}, \mathcal{E}) = \begin{pmatrix} G_0^{11}(\vec{k}, \mathcal{E}) & G_0^{12}(\vec{k}, \mathcal{E}) & G_0^{13}(\vec{k}, \mathcal{E}) & G_0^{14}(\vec{k}, \mathcal{E}) \\ G_0^{21}(\vec{k}, \mathcal{E}) & G_0^{22}(\vec{k}, \mathcal{E}) & G_0^{23}(\vec{k}, \mathcal{E}) & G_0^{24}(\vec{k}, \mathcal{E}) \\ G_0^{31}(\vec{k}, \mathcal{E}) & G_0^{32}(\vec{k}, \mathcal{E}) & G_0^{33}(\vec{k}, \mathcal{E}) & G_0^{34}(\vec{k}, \mathcal{E}) \\ G_0^{41}(\vec{k}, \mathcal{E}) & G_0^{42}(\vec{k}, \mathcal{E}) & G_0^{43}(\vec{k}, \mathcal{E}) & G_0^{44}(\vec{k}, \mathcal{E}) \end{pmatrix}, \quad (3)$$

In the next section, we use this non-interacting Green's function matrix in order to treat the electronic phase transition by using the phase desegregation in the DOS at the Fermi energy, i.e. $\mathcal{E} = 0$ eV of the stable/optimized state of phosphorene. To this end, we have considered the absence and presence of perpendicular electric field, the impurity, and the perpendicular magnetic field. However, to consider the effect of electron-impurity interaction, we need a tool. The Born approximation is responsible for this in the present work.

2.2. Electron-impurity interaction and interacting Green's function

So far, the system was subjected to the Zeeman magnetic field and the electric field. In addition to these perturbations, now, we add dilute charged impurities characterized by impurity concentration n_i and scattering potential ν_i randomly to the system. The impurity concentration considered in the present work reaches up to 20%. In our theoretical model $n_i = x\%$ means that $x\%$ of the whole 1000×1000 unit cells are infected by impurities and for this huge unit cell, 20% is still dilute. The contact interaction between the electrons of phosphorene and external impurities within the tight-binding model is given by

$$\mathcal{H}_{\text{e-i}} = \sum_{\vec{q}} \nu_i c_{\vec{q}}^\dagger c_{\vec{q}} \quad , \quad c = \{\text{unit cell atoms}\} \quad (4)$$

where the induced momenta \vec{q} by impurities belong to the FBZ. Based on the Born approximation [22, 23, 28, 29, 30, 34, 36, 37, 38, 39, 40], the electronic self-energy

Magneto-electronic perturbation effects on the electronic phase of phosphorene 5

matrix elements of disordered phosphorene can be obtained as

$$\Sigma(\vec{q}, \mathcal{E}) = n_i \nu_i \left(1 - \frac{\nu_i}{N_a} \sum_{\vec{k} \in \text{FBZ}} G_0(\vec{k}, \mathcal{E}) \right)^{-1} \quad (5)$$

where N_a is the total number of atoms, which in our numerical calculations is 4000×4000 . Afterwards, to compute the interacting Green's function, we use the perturbed expansion for the Green's function of the disordered system via the Dyson equation [36]:

$$G(\vec{k}, \mathcal{E}) = G_0(\vec{k}, \mathcal{E}) + G(\vec{k}, \mathcal{E}) \Sigma(\vec{q}, \mathcal{E}) G_0(\vec{k}, \mathcal{E}). \quad (6)$$

Consequently, the electronic DOS can be calculated using the trace over the imaginary part of retarded Green's function [36, 37]

$$\mathcal{D}(\mathcal{E}) = -\frac{1}{\pi N_a} \sum_{\chi=1}^4 \sum_{\vec{k} \in \text{FBZ}} \text{Im} \left[G^{\chi\chi}(\vec{k}, \mathcal{E}) \right]. \quad (7)$$

In what follows, we intend to provide the main features of our results by the electronic DOS.

3. Results and discussions

In this section, we first write a general statement for the phase desegregation using the charge distributions in valence band maximum (VBM) and the conduction band minimum (CBM). Then we focus on the magneto-direction dependence of the electronic DOS of unbiased and biased phosphorene in the presence of impurity with $n_i = 8\%$ and $\nu_i = 0.4$ eV. Also, we analyze the effect of *the same* impurities by (i) changing the impurity concentration with a constant impurity scattering potential and (ii) varying the strength of the scattering potential as a factor for *different* impurity atoms with a constant impurity concentration on the electronic phase of the magnetic-field-induced phosphorene. It should be noted that throughout the paper the Fermi level is set to zero (the dashed magenta vertical lines in all figures).

The regulation for our key points refers to the behavior of DOS around the Fermi level. Since DOS becomes the zero and non-zero values for insulator/semiconductor and metal/semimetal materials, respectively, accordingly, we separate different phases using this point. In fact, the overlapped/unoverlapped states of the VBM and CBM determines the electronic phase of the system. Also, the degeneracy strength of the energy levels are given by the van Hove singularities. Furthermore, throughout the paper, we set the physical constants to unity for simplicity such as $k_B = g = \mu_B = e = m_e = 1$. It means that to have the main units of quantities, one needs to consider these values as 1 in their main units, e.g. $k_B = 1$ eV/K or $\mu_B = 1$ eV/T.

Magneto-electronic perturbation effects on the electronic phase of phosphorene 6

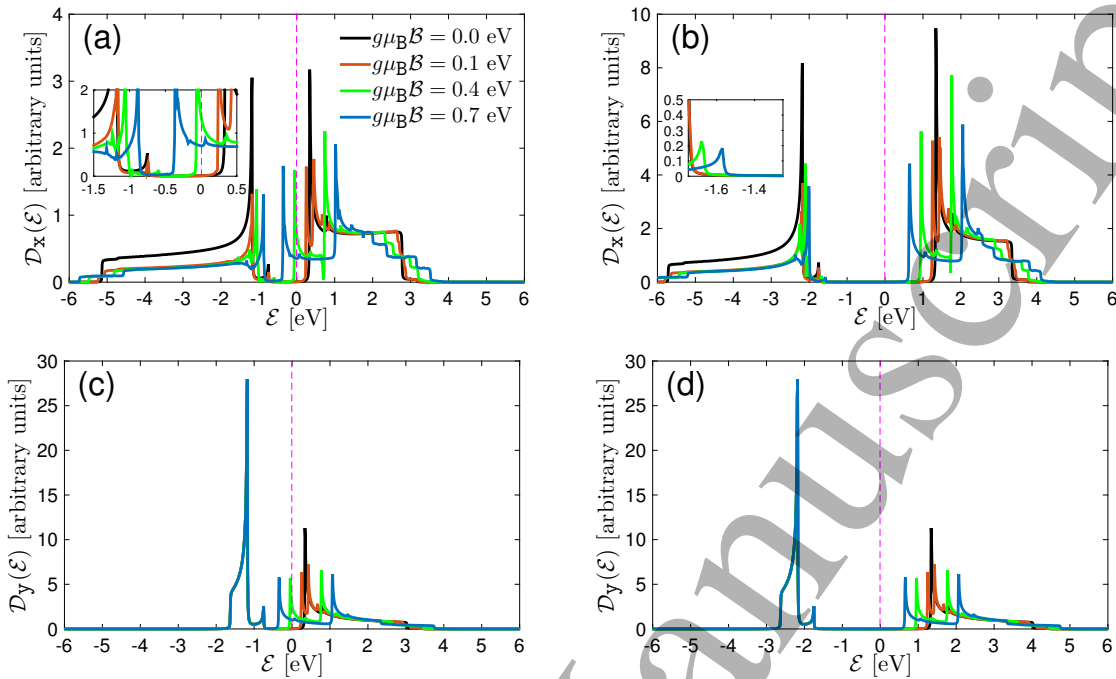


Figure 2. $D_x(\mathcal{E})$ in monolayer (a) unbiased and (b) biased [$V = 1.0$ eV] impurity-infected phosphorene for different Zeeman magnetic fields. The corresponding electronic DOS in the y -direction, i.e. $D_y(\mathcal{E})$ are plotted in panels (c) and (d). The impurity with $n_i = 8\%$ and $\nu_i = 0.4$ eV is fixed in these plots. The dashed magenta vertical line indicates the Fermi level.

Fig. 2(a) and (c) show the $\mathcal{D}(\mathcal{E})$ of unbiased phosphorene at various $g\mu_B\mathcal{B}$, namely 0, 0.1, 0.4 and 0.7 eV. At the first glance, one observes a midgap state for all panels inside the band gap in the presence of the impurity compared to the case of pristine phosphorene [11, 13, 27], which is an expectable result due to the added states from impurities to the unoccupied levels above (below) VBM (CBM). This result is in quite agreement with Ref. [41], too. It is bearing in mind that within the Born approximation, i.e. dealing with the finite but small density of impurities, peaks can show up in the DOS. Since they appear inside the band gap, the states associated with these peaks are called midgap states. These midgap states can be viewed as bound states attracted by the impurity potential. For many impurities with a small density, midgap states are related to the poles of self-energy function (T-matrix). On the other hand, we know from Eq. (7) that the DOS is related to poles of Green's function. Thus, midgap states stem from new poles associated with impurity. These midgap states, in turn, lead to the electronic phase transitions. Turning on the perpendicular magnetic field in the absence of electric field (bias voltage) splits the van Hove singularity around $\mathcal{E} \simeq 0.5$ eV in both directions into two singularities, confirming the Zeeman effect. The distance between these two singularities increases with magnetic field slightly. Also, the band gap decreases with the magnetic field and in the strong magnetic fields, interestingly, the system transits into the semimetallic phase provided by non-zero electronic DOS around $\mathcal{E} = 0$ eV in both directions. We continue our discussions by repeating the same calculation of the

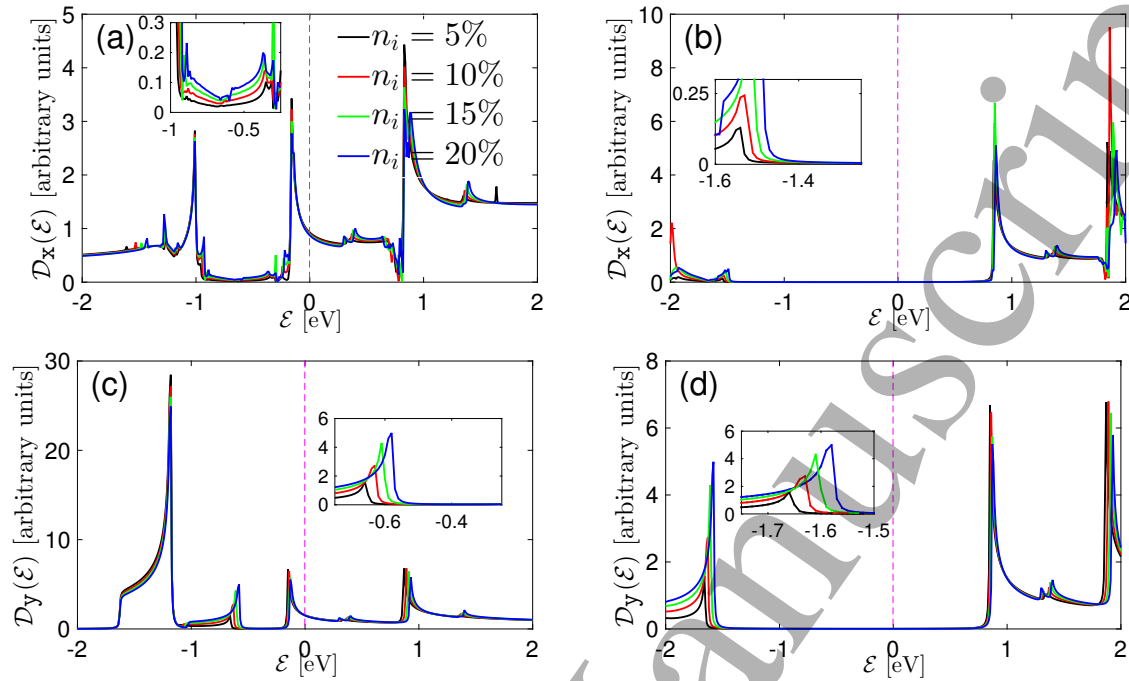
Magneto-electronic perturbation effects on the electronic phase of phosphorene 7

Figure 3. $D_x(\mathcal{E})$ in monolayer (a) unbiased and (b) biased [$V = 1.0$ eV] magnetic field-induced phosphorene for different impurity concentrations. The corresponding electronic DOS in the y -direction, i.e. $D_y(\mathcal{E})$ are plotted in panels (c) and (d). The impurity scattering potential $\nu_i = 0.5$ eV and the magnetic field $g\mu_B\mathcal{B} = 0.5$ eV are considered in these plots.

DOS of biased monolayer phosphorene in Fig. 2(b) and (d) in both directions. Since the electric field modulates the band gap [23], there is no phase transition when applying the electric field. Surprisingly, in panel (b), in contrast to the panel (a), we found that the midgap states disappear with the magnetic field in biased phosphorene in the x -direction, whereas there is no change in the y -direction. These different behaviors stem from the inherent anisotropy property of carriers in phosphorene. Similar to the x -direction, the band gap decreases with $g\mu_B\mathcal{B}$ in the y -direction, too. It is necessary to mention that the relation $D_y(\mathcal{E}) > D_x(\mathcal{E})$ is still valid here [11, 13, 27] when the system is subjected to the electric field or not.

Since the main features came up in the low-energy limits, we restrict ourselves to the low-energy limit in the following. Now, we investigate the magneto-DOS of phosphorene at $g\mu_B\mathcal{B} = 0.5$ eV for the case of different impurity concentrations with a constant impurity scattering potential $\nu_i = 0.5$ eV for both unbiased and biased phosphorene in Fig. 3. On the one hand, unlike the reported results in Refs. [22, 41], the impurity in the presence of Zeeman magnetic field does not affect the electronic phase of the system in the x -direction even at large concentrations [see panel (a)], whilst a phase transition from semiconductor to semimetal is observed in Refs. [22, 41] when there is no magnetic field. On the other hand, in the y -direction, one observes gradually increasing of the density of degenerate states around the Fermi level, as illustrated in inset panel of (c).

Magneto-electronic perturbation effects on the electronic phase of phosphorene 8

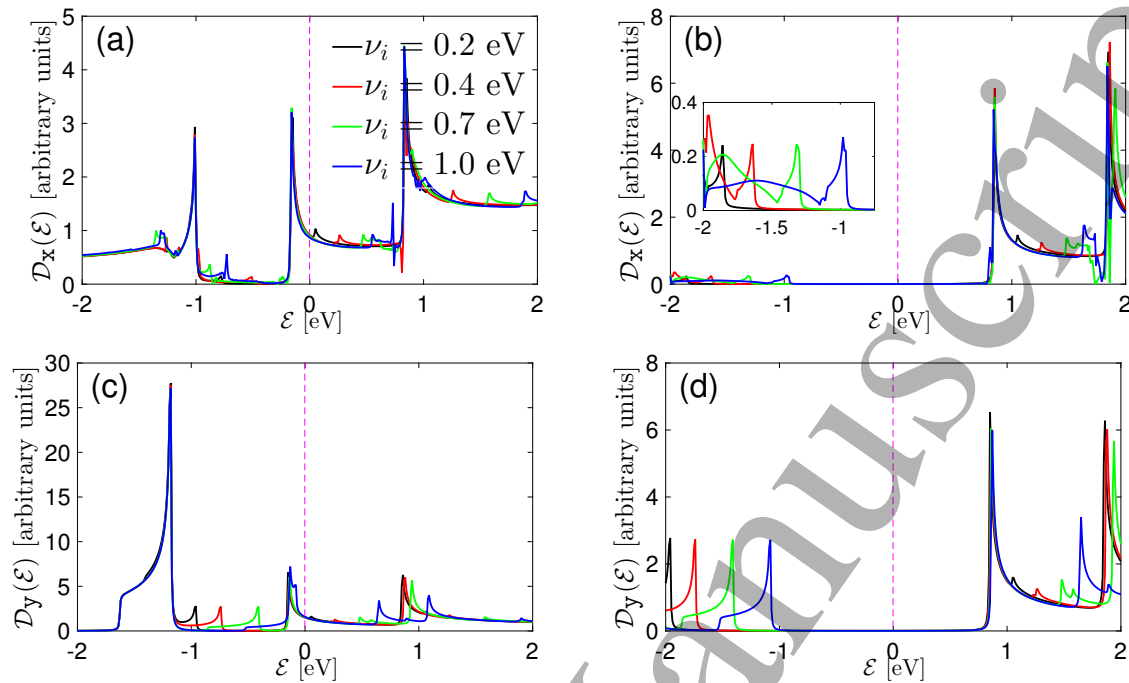


Figure 4. $\mathcal{D}_x(\mathcal{E})$ in monolayer (a) unbiased and (b) biased [$V = 1.0$ eV] magnetic field-induced phosphorene for different impurity scattering potentials. The corresponding electronic DOS in the y -direction, i.e. $\mathcal{D}_y(\mathcal{E})$ are plotted in panels (c) and (d). The impurity concentration $n_i = 10\%$ and the magnetic field $g\mu_B\mathcal{B} = 0.5$ eV are considered in these plots.

Also, we found that the band gap decreases slightly with n_i in biased phosphorene in both directions. Furthermore, the intensity of van Hove singularities increases with n_i in biased version [panels (b) and (d)].

Further, the calculations of the electronic DOS for different impurity scattering potentials are shown in Fig. 4. Like the previous case, there is a significant difference in the magneto-midgap states-induced in the unbiased and biased cases. We skip the analyse of the same results of panel (a) and, however, in contrast to the case of different n_i , the height of the midgap states of biased case in the x -direction [panel (b)] does not change with the impurity scattering potential ν_i and only the band gap decreases slightly. Panels (c) and (d) report a decreasing behavior for the band gap in the y -direction with ν_i .

4. Conclusions

To sum up, we have focused on the electronic phase of monolayer phosphorene in the presence of perpendicular electric field, charged impurity, and the Zeeman magnetic field. To this end, we have used the continuum Hamiltonian model, the Green's function technique, and the full self-consistent Born approximation in order to find the electronic correlation between the host and guest carriers. Our findings show that the impurity

Magneto-electronic perturbation effects on the electronic phase of phosphorene

induces midgap states. On the other hand, by increasing the magnetic field in both unbiased and biased impurity-infected phosphorene, the band gap decreases, leading to the semiconductor-to-semimetallic transition in unbiased phosphorene. Moreover, further considerations on the magnetic field-induced phosphorene showed that in both directions, the electronic states do not change significantly with impurity concentration and impurity scattering potential. However, in biased phosphorene, the band gap decreases slightly with (without) an increasing behavior of midgap states as a function of impurity concentration (scattering potential) in both directions.

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