Dirac fermions in blue-phosphorus

Yuanchang Li and Xiaobin Chen

1 National Center for Nanoscience and Technology, Beijing 100190, People’s Republic of China
2 Department of Physics and State Key Laboratory of Low-Dimensional Quantum Physics, Tsinghua University, Beijing 100084, People’s Republic of China
3 Collaborative Innovation Center of Quantum Matter, Tsinghua University, Beijing 100084, People’s Republic of China
E-mail: liyc@nanoctr.cn

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Abstract

We propose that Dirac cones can be engineered in phosphorene with fourfold-coordinated phosphorus atoms. The key is to separate the energy levels of the in-plane ($s$, $p_x$, and $p_y$) and out-of-plane ($p_z$) orbitals through the $sp^2$ configuration, yielding respective $\sigma$- and $\pi$-character Dirac cones, and then quench the latter. As a proof-of-principle study, we create $\sigma$-character Dirac cones in hydrogenated and fluorinated phosphorene with a honeycomb lattice. The obtained Dirac cones are at $K$-points, slightly anisotropic, with Fermi velocities of 0.91 and 1.23 times that of graphene along the $\Gamma K$ and $KM$ direction, and maintain good linearity up to $\sim$2 eV for holes. A substantive advantage of a $\sigma$-character Dirac cone is its convenience in tuning the Dirac gap via in-plane strain. Our findings pave the way for development of high-performance electronic devices based on Dirac materials.

Keywords: $\sigma$-character Dirac cone, phosphorene, four-fold coordinated, DFT

1. Introduction

Over the last decade, graphene has attracted tremendous attention and research interest owing to its possible applications in carbon-based nanoelectronics [1–3]. Graphene has the $\pi$-character Dirac cone: $\pi$ and $\pi^*$ bands, contributed by the carbon out-of-plane $p_z$ orbitals, intersect with each other at the $K$ and $K'$ points, respectively. The band structure is directly related to the honeycomb lattice symmetry of graphene, but unfortunately, the unique symmetry is usually disturbed or destroyed when graphene is coupled with the external world in device fabrication, e.g., bonding with the substrate [4]. At the same time, opening a tunable bandgap in graphene is
still a big challenge, but it is essential for controlling conductivity by electronic means in the semiconductor industry. Owing to the out-of-plane nature of graphene, the homogeneous strain behaves like the effective electronic scalar potential, and only a particularly designed strain distribution can gap the Dirac cone \[5–7\]. This raises an interesting question: whether there exists the $\sigma$-character Dirac cone spectrum, originating from the in-plane $p_x$ and $p_y$ orbitals. Such an in-plane characteristic will not only enrich Dirac physics in fundamental science but also may open up a new possibility for gap engineering in Dirac materials via in-plane strain for technological applications.

Phosphorene is another stable two-dimensional elemental matter besides graphene, but it has an inherent bandgap \[8–20\]. Recently monolayer phosphorene, which also possesses a hexagon skeleton like graphene, was exfoliated \[10\]. Phosphorus has several stable allotropes with different bandgaps, among which black phosphorus is the most stable. Unlike graphene, phosphorene exfoliated from black phosphorus exhibits a puckered non-planar structure, although it is composed of the basic hexagon, as shown in figure 1(a). Very recently blue phosphorus, a new member of the phosphorus family, was proposed as having stability equal to black phosphorus \[15\]; its phosphorene has a buckled honeycomb lattice, analogous to silicene \[21\] (see figure 1(b)). For clarity, we will use blue phosphorene as a prototype to illustrate our concept of engineering a Dirac cone spectrum in phosphorus, and we expect that the same concept also works in any other phosphorus allotrope that possesses an $sp^2$ configuration.

In this paper, we perform a theoretical study of a $\sigma$-character Dirac cone in one-atom-thick phosphorene. We show that the (quasi-)planar honeycomb lattice can separate the energy levels of the in-plane ($s$, $p_x$, and $p_y$) and out-of-plane ($p_z$) orbitals, resulting in the $\sigma$- and $\pi$-character Dirac cones, respectively. We then quench the $\pi$-character Dirac cone by out-of-plane saturation, leaving the $\sigma$-character Dirac cone behind. We take hydrogenated phosphorene as a model system to investigate the properties of the $\sigma$-character Dirac cone. Our obtained Dirac cones are at $K$-points, slightly anisotropic, with Fermi velocities of 0.91 and 1.23 times that of graphene along the $\Gamma K$ and $KM$ direction, and maintain good linearity up to $\sim 2$ eV for holes.
We demonstrate that a tunable bandgap can be engineered via in-plane strain apart from the breaking of AB sublattice symmetry. Finally, we discuss the possibility in incorporating the $\sigma$-character Dirac cone into the semiconductor industry through the fourfold-coordinated configuration, which also helps to overcome the instability of phosphorene when exposed to air.

2. Methods and model

The calculations were performed using density-functional theory (DFT) with the projector augmented wave [22] method and the Perdew–Burke–Ernzerhof [23] exchange and correlation potential, as implemented in the Vienna ab initio simulation package [24]. An energy cutoff of 400 eV was employed. A gamma-centered grid of $36 \times 36 \times 1$ was used to sample the Brillouin zone. The vacuum layer thickness was larger than 10 Å.

3. Results and discussion

Figure 2 plots the geometric and electronic structures of double-side hydrogenated monolayer blue phosphorene with different lattice parameters ($a_1 = a_2 = a$). Test calculations show that there is no net spin-polarization in the current cases. We begin with $a = 3.3 \text{ Å}$ due to the lattice parameter of 3.326 Å for monolayer blue phosphorene [15]. Substantially different from the $\sim 2 \text{ eV}$ bandgap of blue phosphorene, hydrogen-induced metallization is found, as reflected in

![Figure 2. Band structures of double-side hydrogenated monolayer blue phosphorene at the typical lattice parameters $a$. The two bands ultimately evolving into the Dirac cone are highlighted in orange with up-triangles and in violet with down-triangles as a guide to the eye. The Fermi level is set to zero. The insets are side views of the configurations. The large magenta and small green balls denote phosphorus and hydrogen atoms, respectively.](image-url)
figure 2(a). Structurally, phosphorene maintains a remarkably buckled hexagonal skeleton. Hydrogenation leads to phosphorus dimerization, and two kinds of P–P bond length appear, 2.20 and 2.59 Å. With increasing $a$, the system metallicity is gradually suppressed, whereas the P–P dimerization becomes stronger and stronger. Until $a = 3.6$ Å, the system shows a semimetal feature (see figure 2(b)).

When $a = 3.7$ Å, both the geometric and electronic structures change drastically, as shown in figure 2(c). At the same time, the hydrogenated phosphorene becomes nearly planar and dimerization is notably suppressed. In addition, interesting band crossing emerges at the $K$-point in sharp contrast with the original gapped behavior at all $k$ points. Further increasing $a$, the two highlighted bands continuously separate from the other bands and approach each other at the $K$-point, as illustrated in figures 2(d)–(f). In particular, when $a = 4.4$ Å, the system becomes a Dirac semimetal characterized by a $K$-point Dirac cone (note: the band crossing at the $\Gamma$ point is 0.09 eV above the Fermi level), and all P–P bond lengths become equivalent along with the disruption of the dimerization. Further increasing $a$, the $K$-point Dirac cone remains, whereas the crossing at the $\Gamma$ point shifts toward higher energy, e.g., it shifts to 0.56 eV when $a = 4.7$ Å. This trend holds until the hopping between near-neighboring phosphorus is sufficiently weak, and then a strong correlation effect dominates the properties. For example, the system with $a = 5.3$ Å does not have a Dirac cone anymore.

Apparently the lattice parameter increases as much as 33%, from $a = 3.3$ Å to $a = 4.4$ Å; however, the P–P bond length simply elongates from the 2.27 Å of pristine blue phosphorene to 2.54 Å in our hydrogenated phosphorene ($a = 4.4$ Å), corresponding to a stretch of 12%. This originates from the simultaneous release of out-of-plane buckling. As we show hereafter, the Dirac cone can be obtained even when the P–P bond is elongated only by 4.4%. Hence, it is not the strain but the structural phase transition from non-planar to planar that plays a key role in the presence of the exotic Dirac cone spectrum.

Following we take the $a = 4.4$ Å case as an example to discuss the properties of the Dirac cone. Figure 3(a) shows the three-dimensional band structure around the Dirac point. The same valley symmetry as in graphene is observed: two Dirac cones are located at the $K$ and $K'$ points. Thus, a series of interesting valley-related phenomena might occur in this system. Unlike in graphene, the energy spectrum is no longer electron-hole symmetric, and therefore neither the scattering mechanism nor the transport properties will be identical for the electron and hole doping situations. The linear dispersion holds up to $\sim 2$ eV for holes, whereas the massless electrons acquire mass rapidly away from the $K$-point. This implies that such a system is more promising for making unipolar ($p$-type) field effect devices than for making ambipolar ones with graphene. On the other hand, the linear dispersion region of electrons can be widened by increasing $a$, e.g., it reaches 0.5 eV when $a = 4.7$ Å, the same as in graphene [25]. Moreover, the Dirac cone is slightly anisotropic, with Fermi velocities of 0.91 and 1.23 times that of graphene along the $\Gamma K$ and $KM$ direction. It is worth emphasizing that the Fermi velocity depends weakly on $a$ provided the Dirac cone has formed.

A phosphorous atom has an intrinsically larger spin-orbit interaction than a carbon atom. This leads to many intriguing quantum phenomena in phosphorene, such as the quantum spin Hall effect [26], in addition to massless Dirac fermion as in graphene. As shown following, inversion symmetry is not necessary for the presence of Dirac cones anymore, and thus phosphorene is a natural candidate material for applications in valleytronics [27]; and, with the application of a perpendicular electric field, it exhibits the quantum valley Hall effect as well.
Moreover, phosphorus is necessarily fourfold-coordinated here, which provides us with new freedom for property modulation and device fabrication.

Next we turn to study the physical origin of the unique Dirac cone. Figure 3(b) shows the local density of states (LDOS) of hydrogenated phosphorene with \( a = 4.4 \, \text{Å} \), from which three hints are found. First, the Dirac cone dominantly arises from the phosphorus \( p_x, p_y, \) and \( s \) orbitals rather than from the \( p_z \) orbitals as in graphene, as is clearly reflected by the LDOS within 2 eV below the Fermi energy. Generally, \( p_x, p_y, \) and \( s \) orbitals form the in-plane \( \sigma \) bonds, indicating an in-plane characteristic of the Dirac cone. This in-plane characteristic is further confirmed by the decomposed charge density for the states within 1 eV below the Fermi energy, as shown in figure 3(c). Second, strong hybridization between P \( p_z \) and H states is observed in the energy region \( \leq -4 \, \text{eV} \), indicating the passivation of \( p_z \) states by H. Third, owing to the in-plane characteristic, the Dirac cone—not only the bandgap at the Dirac point but also the band shape—should be sensitive to in-plane strain.

We further calculate the electronic structure (see figure 3(d)) for the configuration as the inset of figure 2(e) but with H removed, in order to clarify the roles of the honeycomb lattice and hydrogenation. Two Dirac cones appear, both located at the \( K \)-point. The LDOS analysis

Figure 3. (a) Three-dimensional band structure around the Dirac point, (b) total and local density of states (LDOS), and (c) real-space charge distribution for the states in the energy range of \([-1, 0] \, \text{eV} \) (isosurface = 0.0024 e Å\(^{-3}\)) for double-side hydrogenated monolayer phosphorene with \( a = 4.4 \, \text{Å} \), corresponding to figure 2(e). In (b) the contributions from the phosphorus (P) \( p_z, p_x + p_y, \) and \( s \) orbitals and hydrogen (H) are shown. (d) Band structure and LDOS for the aforementioned system but with H removed. The red and green lines highlight the Dirac cones formed by the P \( p_z \) and \( s + p_x + p_y \) orbitals, respectively. The Fermi levels are at energy zero.

[28]. Moreover, phosphorus is necessarily fourfold-coordinated here, which provides us with new freedom for property modulation and device fabrication.
shows that the upper Dirac cone (green lines) originates from the $p_x$, $p_y$, and $s$ orbitals, whereas the lower one (red lines) originates from the $p_z$ orbitals. The upper Dirac cone is similar to those in figures 2(e) and (f), irrespective of the contributed orbitals or the band shape, whereas the lower Dirac cone is more similar to that in graphene [4]. This strongly implies that the planar honeycomb structure separates the in-plane ($p_x$, $p_y$, and $s$) and out-of-plane ($p_z$) orbitals, forming their own Dirac cones with $\sigma$ and $\pi$ characters. Hydrogenation with the delocalized $\pi$ orbitals quenches the $\pi$-character Dirac cone, leaving the $\sigma$ Dirac cone intact. As well, the two additional electrons contributed by H raise the Fermi energy to the Dirac point. In short, among the five valence electrons of phosphorus, three form the in-plane $\sigma$ bonds and the one from $p_z$ is localized by saturation, leaving the residual electron on the $\sigma^*$ levels and forming an in-plane-type Dirac cone. This is summarized in figure 4(a) as the energetic scheme of hydrogenated phosphorene.

The next question is, why and how does the $\sigma$-character Dirac cone form, and why does it from at the $K$-point? It is well known to us that the $\pi$-character Dirac cone originates from hopping between $p_z$ orbitals on a honeycomb lattice (see figure 4(b)), which can be obtained by directly solving a $2 \times 2$ spinless matrix; whereas the $\sigma$-character Dirac cone represents electron hopping among the three $\sigma^*$ bonds as illustrated in figure 4(a), and the effective Hamiltonian must be described by a $3 \times 3$ spinless matrix. If the P–P bond centers are viewed as lattice sites, it can be seen that a kagome lattice is formed as shown in figure 4(b). (The lattice sites are denoted by D, E, and F.) A $K$-point Dirac cone is then a natural consequence of the kagome lattice [29]. Note that such a kagome lattice is based on the assumption of the bond center as the lattice site, and hence it possesses a dynamic characteristic to some extent, which may be responsible for the anisotropy of the Dirac cone and the absence of a flat band. This is different from graphene or silicene, where the $\sigma^*$ bonds are fully unoccupied with no electron hopping; hence the absence of a $\sigma$-character Dirac cone.
In light of such a physics for the unique $\sigma$ Dirac cone, it should be very robust against saturated material species and site (double- or single-side), provided the injected electron eliminates the $\pi$ Dirac cone. To confirm this, we perform systematic calculations in double-side fluorinated, single-side hydrogenated, and single-side fluorinated monolayer blue phosphorene with different $a$. We find that the aforementioned Dirac physics remains valid in these systems. We show the results of double-side fluorinated ($a = 4.1 \text{ Å}$) and single-side hydrogenated ($a = 4.7 \text{ Å}$) cases in figures 5(a) and (b), respectively. We can see clearly the Dirac cone spectra resembling that in the double-side hydrogenated system. Notably, the P–P bond length in the $a = 4.1 \text{ Å}$ double-side fluorinated system is just 2.37 Å, corresponding to an elongation of 4.4% compared with that in pristine blue phosphorene.

Application of strain is usually employed to engineer the electronic properties of two-dimensional materials [5–7, 30–33]. Here, we indeed find the in-plane strain-induced gap of 0.35 (0.22) eV in single-side hydrogenated (fluorinated) phosphorene at $a = 4.4$ (4.7) Å. We must emphasize that the gap sizes are not optimized for $a$ and should set the lower bound in these systems. Even so, they are comparable to the maximum value of 0.25 eV in gate-controlled bilayer graphene [34]. So far as is known, it is still a big challenge to open a sizable bandgap in Dirac materials, both graphene [35] and topological insulators [36], for their incorporation into the existing semiconductor industry. In addition, we also investigate the system with one-side hydrogenation and other-side fluorination, whose band is shown in figure 5(c) ($a = 4.3 \text{ Å}$). Now an energy gap of 0.19 eV opens at the Dirac point (note: the gap is 0.12 eV when $a = 4.7 \text{ Å}$). It is worth emphasizing that at $a = 4.3 \text{ Å}$, the bandgaps are 0.03 and 0 eV, respectively, in double-side hydrogenated and fluorinated systems. Therefore, such a gap opening is related to the breaking of AB sublattice symmetry as in graphene. Both in-plane strain and symmetry breaking can yield a bandgap in our system, making manipulation more flexible.

Finally, let us discuss the experimental possibility. Since the discovery of graphene, tremendous efforts have been made to search for similar two-dimensional materials. Recently free-standing single-atom-thick iron membranes suspended in graphene pores were experimentally demonstrated with a square lattice at room temperature [37]. Silicene has also been
synthesized by depositing silicon on metal surfaces that do not interact strongly with the silicon atoms [21]. In fact, hydrogenation of phosphorene leads to an energy release of $\sim 3$ eV per H atom for systems with Dirac cones, nearly irrespective of $a$. The value is even a little larger than that for hydrogenated graphene [38], implying a good thermodynamic stability of the hydrogenated phosphorene. However, a Jahn–Teller-like structural distortion may be anticipated due to single electron occupation in three degenerate $\sigma^*$ orbitals. Our phonon dispersion calculations suggest that either double- or single-side hydrogenation or fluorination might not stabilize the (quasi-)planar honeycomb monolayer phosphorene due to the observation of imaginary frequency. Although the phonon calculations under such large strains are not as reliable as those under equilibrium conditions, it is quite possible that these systems may not exist individually at finite temperature, particularly as a freestanding form.

The fourfold-coordinated feature, i.e., necessary passivation out-of-plane, provides us with an alternative opportunity because the surface dangling bonds of the semiconducting materials can be used to anchor the P atoms and suppress the fluctuation. Three concerns should be considered about the material: (1) saturating the $p_z$ orbital of P, (2) enforcing the P atoms in the honeycomb arrangement, and (3) having an appropriate energy alignment to enable the Dirac cone residing in the gap of the host semiconductor. Given the existence of natural compounds between P and F as well as the huge bandgap ($>10$ eV), CaF$_2$ is taken as an example for illustration and the corresponding geometric and electronic structures are shown in figure 5(d). Note that the system can be obtained by replacing one layer of Ca atoms with P atoms. Obviously, the typical $\sigma$-character Dirac cone, as in hydrogenated or fluorinated phosphorene, remains unchanged, as highlighted by the thick green lines. The twofold degenerate bands (denoted by the red arrow) around the Fermi level arise from the imperfect saturation of F dangling bonds by H on the other side and thus do not reveal the intrinsic physics. In this way, phosphorene can be easily incorporated into the semiconductor industry, and importantly, such a sandwich structure also overcomes the fragility of phosphorene when exposed to air [12]. In any case, stabilizing the $sp^2$ configuration of phosphorus is undoubtedly important and deserves further investigation.

4. Conclusion

In conclusion, we show that Dirac cones can be engineered in phosphorene with fourfold-coordinated phosphorus atoms, potentially bringing about many intriguing phenomena related to Dirac fermions. Substantially different from the out-of-plane $\pi$-character in graphene, here the obtained Dirac cone exhibits the in-plane $\sigma$-character, with Fermi velocities of 0.91 and 1.23 times that of graphene along the $\Gamma K$ and $KM$ direction, which not only enriches the Dirac physics but also offers an excellent opportunity to tune the Dirac point gap via in-plane strain apart from the breaking of AB sublattice symmetry. The fourfold-coordinated feature provides us with a new and important freedom for modulating the properties and for incorporation into the existing semiconductor industry.

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