Theoretical studies of electronic transport in mono- and bi-layer phosphorene: A critical overview

Gautam Gaddemane,1 William G. Vandenberghe,1 Maarten L. Van de Put,1 Shanneng Chen,1 Sabyasachi Tiwari,1 Edward Chen,2 and Massimo V. Fischetti1
1Department of Materials Science and Engineering, The University of Texas at Dallas 800 W. Campbell Rd., Richardson, TX 75080, USA
2Corporate Research and Chief Technology Office, Taiwan Semiconductor Manufacturing Company Ltd. 168, Park Ave. II, Hsinchu Science Park, Hsinchu 300-75, Taiwan, R.O.C.
(Dated: January 29, 2018)

Recent ab initio theoretical calculations of the electrical performance of several two-dimensional materials predict a low-field carrier mobility that spans several orders of magnitude (from 26,000 to 35 cm² V⁻¹ s⁻¹, for example, for the hole mobility in monolayer phosphorene) depending on the physical approximations used. Given this state of uncertainty, we review critically the physical models employed, considering phosphorene, a group V material, as a specific example. We argue that the use of the most accurate models results in a calculated performance that is at the disappointing lower-end of the predicted range. We also employ first-principles methods to study high-field transport characteristics in mono- and bi-layer phosphorene. For thin multi-layer phosphorene we confirm the most disappointing results, with a strongly anisotropic carrier mobility that does not exceed ∼ 30 cm² V⁻¹ s⁻¹ at 300 K for electrons along the armchair direction.

I. INTRODUCTION

In the past couple of decades, the theoretical study of electronic transport in semiconductors has been affected by two new driving factors. First, the effort to scale transistors to the nanometer-size has stimulated interest in materials and devices that are quite different from the ‘conventional’ materials employed by the micro-electronics industry. References[1,3] constitute excellent recent overviews of the state of the art. Unlike silicon, germanium, or III-V compound semiconductors, for which decades of study have resulted in a reliable database of their electronic properties (e.g., band gap, effective mass, and carrier mobility), the atomic, electronic, and transport properties of many of these new materials are, at best, poorly known; at worst, even their existence and stability are known only from theoretical predictions. The infancy of the technology used to deal with these materials also casts doubts on the usefulness of experimental results, because of the large deviations from ideality that are expected from such an immature and fast-changing technology.

The second driving cause is the timely and welcome progress recently made in ab initio (or ‘first principles’) theoretical methods. Whereas in the past their predictions have been limited to small systems and had little or no connection to electronic transport, recent progress made in physical understanding, numerical algorithms, and computing hardware has broadened their range of applications, improved their accuracy, and extended their scope to electronic transport. Density functional theory (DFT) is now routinely used to predict the atomic and electronic structure of these new materials, thanks to the wide availability of computer packages, such as the Vienna Ab initio Software Package (VASP) or Quantum Espresso (QE). Even the strength of the electron-phonon interaction can now be calculated using DFT by using either finite ion displacement or Density function Perturbation Theory (DFPT)14,15, a remarkable evolution since the early ‘pioneering’ days in which the rigid-ion approximation and empirical pseudopotentials were painstakingly used to estimate deformation potentials in Si, intervalley deformation potentials in III-V compound semiconductors11,12, and used in Monte Carlo transport studies16,17. Even transport in open systems has been studied using DFT18, and such an ab initio formalism has also been used to study dissipative transport in the two-dimensional materials of current interest19.

Despite this remarkable progress, and limiting ourselves to the carrier mobility in covalent two-dimensional materials, theoretical predictions reported in the literature disagree wildly. Our purpose here to analyze critically the situation we face regarding phosphorene, taken as a striking example of this uncertainty and disagreement that is due to both physical and computational aspects, understand the underlying causes, learn from this how we should proceed, and consider in detail low-field and high-field electronic transport in phosphorene. Therefore, this paper is organized as follows: In Sec. II we discuss the state-of-the-art regarding the carrier mobility in phosphorene, presenting results obtained in a simplified but realistic model. In Sec. III we present a general theoretical framework to study low- and high-field electronic transport in 2D crystals using DFT. Finally, we present our results for mono- and bi-layer phosphorene in Sec. IV.
II. CARRIER MOBILITY IN PHOSPHORENE

Monolayer black phosphorus (bP), or phosphorene, is one of the many two-dimensional materials that have attracted enormous interest since the isolation of graphene.\(^{(20)}\) Considering only covalent crystals, notable examples that we shall mention or consider explicitly here include silicene\(^{(21-24)}\), germanene,\(^{(25,26)}\) phosphorene itself, of course,\(^{(27-35)}\) arsenene,\(^{(36,37)}\) antimonene,\(^{(38,39)}\) stanene\(^{(40,41)}\), and another large-band-gap two-dimensional topological insulator, bismuthene,\(^{(42,43)}\) which, known since the 1990s, has become the subject of recent renewed interest.\(^{(44,45)}\) Interest in phosphorene presumably originates from the very large carrier mobility measured in bulk black phosphorus.\(^{(39,46)}\) This interest has been reinforced by the good measured electrical properties of field-effect transistors (FETs) having many-layer phosphorene as channel material.\(^{(28,30)}\) Despite such wide interest, to our knowledge, the intrinsic charge-transport characteristics of monolayer phosphorene have not been widely studied experimentally, having been reported only in Ref.\(^{(31)}\) Moreover, theoretical predictions are in wild disagreement. We shall now review the experimental and theoretical information available at present, before discussing the causes of the theoretical confusion.

A. Available experimental and theoretical results

Given the large number of studies that have been published regarding the carrier mobility in phosphorene, it is convenient to summarize in Tables I and II the available experimental and theoretical results, before commenting on them. A necessary critical review will follow, as anticipated.

Experimental information. As we have mentioned above, interest in phosphorene has been stimulated by the relatively high room-temperature carrier mobility measured in black phosphorus: 300 to 1,100 \(\text{cm}^2\text{V}^{-1}\text{s}^{-1}\) for electrons and 150 to 1,300 \(\text{cm}^2\text{V}^{-1}\text{s}^{-1}\) for holes, depending on orientation.\(^{(39,47)}\) Information for multi-layers is limited to the hole mobility, since samples are almost invariably p-type. Only Cao et al.\(^{(48)}\) have observed ambipolar behavior in field-effect transistors with mono-, bi-, and tri-layer channels, finding an electron mobility much smaller than the hole mobility in all cases. They have also provided the only measurement for charge-transport properties of monolayers. In all cases, the hole mobility is strongly anisotropic and shows a strong dependence on the thickness of the film. Specifically, Cao et al.\(^{(48)}\) have measured a room-temperature hole mobility of 1, 80, and 1,200 \(\text{cm}^2\text{V}^{-1}\text{s}^{-1}\) in mono-, bi-, and tri-layers. Li et al.\(^{(49)}\) have also observed a thickness dependence, reporting a 300 K hole mobility of around several hundreds \(\text{cm}^2\text{V}^{-1}\text{s}^{-1}\) for thick layers, sharply decreasing in layers thinner than 10 nm, and reaching values as low as 1 to 10 \(\text{cm}^2\text{V}^{-1}\text{s}^{-1}\) for layers 2-3 nm-thin.\(^{(25,50)}\) A similar trend has been reported also by Liu et al.\(^{(48)}\), with a peak field-effect hole mobility of 286 \(\text{cm}^2\text{V}^{-1}\text{s}^{-1}\) in 5 nm-thick films. Xia et al.\(^{(49)}\) found a Hall mobility of about 600 \(\text{cm}^2\text{V}^{-1}\text{s}^{-1}\) in 15 nm-thick films and of about 400 \(\text{cm}^2\text{V}^{-1}\text{s}^{-1}\) in 8 nm-thick films. The general trend of an

---

### Table I. Experimentally measured hole mobility, \(\mu_h\), in phosphorene multilayers at 300 K.

| Reference       | \(\mu_h\) (\(\text{cm}^2\text{V}^{-1}\text{s}^{-1}\)) | Thickness |
|-----------------|---------------------------------|-----------|
| Akahama et al.\(^{(a)}\) | 150-1,300                       | bulk black phosphorus |
| Li et al.\(^{(b)}\)     | 300-1,000                       | > 10 nm    |
| Xia et al.\(^{(c)}\)   | 600                             | 15 nm      |
| Gillgren et al.\(^{(d)}\) | 400                           | ‘few layers’ |
| Doganov et al.\(^{(e)}\) | 189                           | 10 nm      |
| Xia et al.\(^{(f)}\)   | 400                             | 8 nm       |
| Liu et al.\(^{(g)}\)   | 286                             | 5 nm       |
| Xiang et al.\(^{(h)}\) | 214                             | 4.8 nm     |
| Cao et al.\(^{(i)}\)   | 1                               | monolayers |
| Cao et al.\(^{(j)}\)   | 80                              | bilayers   |
| Cao et al.\(^{(k)}\)   | 1,200                           | trilayers  |

(a) Ref.\(^{(49)}\)  (c) Ref.\(^{(51)}\)  (e) Ref.\(^{(32)}\)  (g) Ref.\(^{(33)}\)  (i) Ref.\(^{(34)}\)  (j) Ref.\(^{(34)}\)
(b) Ref.\(^{(35)}\)  (f) Ref.\(^{(35)}\)  (h) Ref.\(^{(33)}\)  (k) Ref.\(^{(33)}\)

### Table II. Theoretical calculations of the 300 K electron and hole mobility, \(\mu_e\) and \(\mu_h\), in monolayer and bilayer phosphorene.

| Reference       | \(\mu_e\) (\(\text{cm}^2\text{V}^{-1}\text{s}^{-1}\)) | \(\mu_h\) (\(\text{cm}^2\text{V}^{-1}\text{s}^{-1}\)) |
|-----------------|---------------------------------|---------------------------------|
| Qiao et al.\(^{(a)}\) | 1,100                          | 80                             |
| Jin et al.\(^{(b)}\) | 210                            | 40                             |
| Rudenko et al.\(^{(c)}\) | 738                           | 114                            |
| Rudenko et al.\(^{(d)}\) | ~700                          | ~250                           |
| Trushkov et al.\(^{(e)}\) | 625                           | 82                             |
| Liao et al.\(^{(f)}\) | 170                            | 50                             |
| This work\(^{(g)}\) | 20                             | 10                             |
| This work\(^{(h)}\) | 21                             | 10                             |
| This work\(^{(i)}\) | 25                             | 5                              |
| Qiao et al.\(^{(a)}\) | 600                            | 140-160                        |
| Jin et al.\(^{(b)}\) | 1,020                          | 360                            |
| This work\(^{(g)}\) | 14                             | 7                              |

(a) Ref.\(^{(51)}\)  (c) Ref.\(^{(53)}\)  (e) Ref.\(^{(54)}\)  (g) Ref.\(^{(55)}\)  (i) Ref.\(^{(56)}\)
(b) Ref.\(^{(52)}\)  (d) Ref.\(^{(54)}\)  (f) Ref.\(^{(55)}\)  (h) Ref.\(^{(55)}\)  (k) Ref.\(^{(56)}\)

---
increasing mobility in thicker films is also confirmed by the results of Xiang et al., who have measured a hole mobility of 214 cm$^2$V$^{-1}$s$^{-1}$ in 4.8 nm-thick films, compared to a Hall mobility of 400 cm$^2$V$^{-1}$s$^{-1}$ observed in ‘few-layers’ phosphorene by Gillgren et al. As a rare example of information on electron transport, Doganov and coworkers have reported an electron mobility of about 106 cm$^2$V$^{-1}$s$^{-1}$ in 10 nm-thick films. For holes, they have measured a value of 189 cm$^2$V$^{-1}$s$^{-1}$. Note that these are field-effect mobilities. Finally, a similar thickness dependence has been observed also at low temperatures by Tayari and coworkers, who have considered black-phosphorus films with thickness in the range of 6.1-to-47 nm and have measured a maximum mobility of about 600 (below 80 K) and 900 (300 mK) cm$^2$V$^{-1}$s$^{-1}$ in their thickest films. In most of these experiments, the highest field-effect hole mobility has been measured for channels presumably oriented along the armchair direction (‘presumably’ only, since this information is not always given).

**Theoretical results:** Restricting again our attention to room-temperature data, in monolayers a relatively large hole mobility of about 640-to-700 cm$^2$V$^{-1}$s$^{-1}$ has been calculated by Qiao and coworkers for transport along the armchair direction. Surprisingly, a huge hole mobility, 10,000-to-26,000 cm$^2$V$^{-1}$s$^{-1}$ has been predicted along the heavy-mass zigzag direction, a result allegedly due to an extremely small deformation potential. For electrons, Qiao et al. have calculated a mobility of 1,100 (armchair) and 80 (zigzag) cm$^2$V$^{-1}$s$^{-1}$. Monte Carlo simulations based on the DFT-calculated band structure and carrier-phonon scattering rates have been performed by Jin et al. They have obtained a hole mobility of 460 and 90 cm$^2$V$^{-1}$s$^{-1}$ for transport along the armchair and zigzag directions, respectively. For electrons, these values are, instead, 210 (armchair) and 40 (zigzag) cm$^2$V$^{-1}$s$^{-1}$. They have also predicted a higher mobility in bilayers: 1,020 cm$^2$V$^{-1}$s$^{-1}$ (armchair) and 360 cm$^2$V$^{-1}$s$^{-1}$ (zigzag) at 300 K for electrons, 1,610 cm$^2$V$^{-1}$s$^{-1}$ (armchair) and 760 cm$^2$V$^{-1}$s$^{-1}$ (zigzag) for holes. This enhanced mobility has been attributed to the smaller hole effective mass in bilayers, especially along the ‘flat’ Γ − Y (zigzag) direction, as indicated by Qiao et al.15. We shall later discuss (or, better, speculate about) possible causes for the observed thickness dependence of the hole mobility. More recently, Trushkov and Perebeinos have calculated the electron mobility as a function of carrier density and temperature, obtaining values of 625 cm$^2$V$^{-1}$s$^{-1}$ (armchair) and 82 cm$^2$V$^{-1}$s$^{-1}$ (zigzag) at 300 K and at an electron density of 10$^{13}$ cm$^{-2}$. Rudenko and coworkers have obtained similar values of 738 (armchair) and 114 (zigzag) cm$^2$V$^{-1}$s$^{-1}$ for electrons, of 292 (armchair) and 157 (zigzag) cm$^2$V$^{-1}$s$^{-1}$ for holes. At the lower range of predicted mobility, Liao et al. have also used DFT to calculate the band structure and carrier-phonon matrix elements, obtaining the values of 170 (armchair) and 50 (zigzag) cm$^2$V$^{-1}$s$^{-1}$ for electrons, of 170 (armchair) and 35 (zigzag) cm$^2$V$^{-1}$s$^{-1}$ for holes.

### B. Why such a disagreement?

It is probably premature to compare the experimental and theoretical results summarized in Tables II and III. Indeed, different experimental results may be due to expected deviations from ideality of the material, such as impurities and defects, resulting from an immature technology. Moreover, experimental data have been obtained in supported – and often gated – layers, whereas theoretical calculations have considered ideal free-standing films. A proper discussion of this issue would distract us from the main focus of this paper. Here we shall only remark that changes of the phonon spectra may be expected when moving from free-standing layers to supported and gated materials. This, obviously and in principle, may affect the carrier mobility. For van der Waals materials such as graphene, in-plane acoustic modes are left largely unaffected by interactions with a substrate, even when as strong as coupling with metals, whereas optical phonons are slightly softened by the dielectric screening of the metal. An excellent review of phonon dynamics in 2D materials also highlights the 2D nature of the layer(s) as the major effect that controls the vibrational frequency. Moreover, as we have already remarked, most calculations have been performed assuming intrinsic materials, whereas experiments usually deal with gated layers at a high carrier density. Given this ‘circumstantial’ evidence, and ignoring scattering with non-idealities of the substrate/gate (charges and defects), coupling with hybrid plasmon/substrate-optical modes, and considering that acoustic flexural modes – indeed affected by the substrate and the gate – do not play any role in phosphorene, we should not expect gross changes of the electronic-transport properties, at least in van der Waals materials. However, as discussed below, phosphorene is not a pure ‘van der Waals’ material. Therefore, it may couple rather strongly with a substrate or gate insulator. Depending on the vibrational stiffness (e.g., SiO$_2$) or softness (e.g., HfO$_2$) of this layer, the spectrum of the acoustic and especially of the optical modes of phosphorene will be affected accordingly. Nevertheless, here we wish to focus on the wide variations of the theoretical predictions for free-standing layers listed in Table III.

Indeed, besides an obvious thickness and orientation dependence, we have already observed that the wide variations of the experimental data shown in Table II may be explained by deviations from ideality of the material. No such plausible explanation can easily be found to make sense of the surprisingly wide range of theoretically predicted values shown in Table III. This is a disconcerting observation, since most of the theoretical results have been obtained by using ‘first principles’ calculations (DFT), often from the same software packages.

Obviously, *even ab initio* DFT calculations, despite their elegance and predictive power, exhibit some limitations. For example, the behavior of the electronic dispersion near the top of the valence band in mono and multi-layer phosphorene is very flat. The details of this...
dispersion (that is, effective mass and velocity) depend strongly on the exact details of the calculation\textsuperscript{59,60}, so much so that a hole effective mass along the zigzag direction cannot be defined. Such details may matter only marginally when considering the overall band structure, but the equilibrium transport properties are strongly affected by such tiny differences, being extremely sensitive to variations of the order of the thermal energy. These variations affect the carrier velocity and the density of states that, in turn, affects the scattering rates. Moreover, the carrier-phonon matrix elements obtained from DFT calculations may suffer from errors and uncertainties related not only to the choice of pseudopotentials and exchange-correlation functionals, but also to the subtle issue of dielectric screening. This has been observed to be the case for graphene\textsuperscript{61–63}, resulting in underestimated deformation potentials\textsuperscript{64}, as discussed in Ref. \textsuperscript{65}. Therefore, different choices of pseudopotentials or exchange-correlation functionals (local density approximation – LDA, generalized gradient approximation – GGA, or hybrid exchange-correlation functionals), or the use of GW corrections, will result in different bandstructures and values of the total-energy, and so in different phonon spectra and electron-phonon matrix elements.

However, it is difficult to see how such uncertainties, as large as they might be, may result in almost 4 orders of magnitude variations seen in Table\textsuperscript{11} for the hole mobility along the zigzag directions, from 10,000-26,000 cm\(^2\)V\(^{-1}\)s\(^{-1}\) (Ref. \textsuperscript{51}) to the small values of the order unity that we shall present below.

In our opinion, opinion that is also shared by Nakamura and coworkers\textsuperscript{66}, a first major source of errors is the use of the so-called Takagi formula\textsuperscript{67} to calculate the carrier mobility for a two-dimensional electron gas (2DEG):

\[
\mu = \frac{e\hbar^3 C_{2D}}{k_B T m^* m_d E_1^2}.
\]  

In this expression, \(m^*\) and \(m_d\) are the conductivity and density-of-states effective masses, respectively, \(C_{2D}\) is the longitudinal or transverse elastic constant of the 2D materials, and \(E_1\) is the so-called ‘deformation potential’. In this context, this last all-important quantity is defined as the energy-shift, \(\Delta E_{c,v}\), of the relevant band-edge (conduction for electron transport, valence for holes), under a relative change, \(\Delta a/a_0\), of the lattice constant \(a_0\),

\[
E_1 = a_0 \frac{\Delta E_{c,v}}{\Delta a}.
\]

Equations equivalent to those implied by Eq. \textsuperscript{11} have also been used to calculate extremely high values for the carrier mobility in silicene (\(\approx 2 \times 10^5\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) for both electrons and holes\textsuperscript{68} and germanene (\(\approx 6 \times 10^5\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) for both electrons and holes\textsuperscript{69}), ignoring coupling to flexural acoustic modes\textsuperscript{70}. Equation \textsuperscript{11} must be used with extreme care. It was originally derived by Takagi \textit{et al}\textsuperscript{67} in the context of electron transport in Si inversion layers. It was intended to be used to calculate the mobility limited by scattering with acoustic phonons, only one of the many scattering processes that affect electron transport in those systems, such as intersubband/intervalley process, scattering with optical phonons, with ionized impurities, and with surface roughness. Even when taken in this originally limited context, Eq. \textsuperscript{11} is of a semi-empirical nature, since longitudinal and transverse acoustic phonons are lumped into one single ‘effective’ mode, with an isotropic deformation potential \(E_1\), which for Si is typically in the range of 9-14 eV, fitted to reliably known experimental data. Indeed, within the framework of the deformation potential theorem\textsuperscript{71}, the electron/acoustic-phonon matrix elements in Si are known to be anisotropic,\textsuperscript{72} a property that plays a crucial role in explaining the electron mobility in strained Si (Ref. \textsuperscript{73}) and Si inversion layers\textsuperscript{58}. Arbitrarily extending Eq. \textsuperscript{11} to the more general context of 2D crystals presents severe problems: Scattering with optical modes and intervalley processes, when present, are neglected by Eq. \textsuperscript{11}. Moreover, as we have emphasized, only one phonon mode is considered, LA or TA, depending on the choice of \(E_1\) and \(C_{2D}\); also neglected is the anisotropy of the deformation potential, an effect that, as we have already noted, is extremely important in Si (Refs. \textsuperscript{72–75} and that has also been shown to be equally important in phosphorene\textsuperscript{55}. Finally, the symmetry of the initial and final wavefunctions affects the magnitude and angular dependence of the carrier-phonon matrix elements, and these ‘wavefunction-overlap effects’ are also ignored altogether. Therefore, the results of Qiao \textit{et al}\textsuperscript{51} should be regarded as no more than extremely optimistic upper bounds.

A second likely source of errors is the use of the ‘band deformation potential’, Eq. \textsuperscript{2}, to approximate the electron-phonon matrix elements. Even when moving beyond Eq. \textsuperscript{11} by using, for example, the Kubo-Greenwood expression to calculate the carrier mobility, the shifts of the band-edges under various strain conditions give only a qualitative approximation for the scattering matrix elements, since the effects mentioned above – mainly, wavefunction-overlap and angular dependence – are still neglected. Such models have been employed by Trushkov and Perebeinos\textsuperscript{52} and by Rudenko and coworkers\textsuperscript{53}. With a proper choice of elastic constants, the latter authors have accounted for both LA and TA phonons and for two-phonon processes between electrons and flexural modes. Yet, even in this case, their results, while not quite so impressive, are still quite large.

The fact that such models employing isotropic deformation potentials result in an optimistic overestimation of the mobility has been shown by the work performed by the late professor Dresselhaus’ group\textsuperscript{55}. Accounting for all modes, for the anisotropy of the matrix elements – due mainly to wavefunction-overlap effects – and accounting also for a non-parabolic band structure, they have predicted much smaller values. The results that we report here, listed in Table\textsuperscript{11} are even smaller. We shall speculate below on possible causes for such a disappointing
disagreement.

In order to illustrate the importance of the anisotropy of the carrier-phonon matrix elements, we now present calculations of the electron mobility in monolayer phosphorene in the simple case of scattering with acoustic modes only, parabolic bands, linear phonon dispersion, elastic, and equipartition approximation. The results are sufficiently accurate to emphasize the importance of the effects ignored by Eqns. (1) and (2). We shall later present in Sec. IVV calculations based on numerically calculated electronic and vibrational spectra. While more accurate, they are also less transparent.

C. Electron mobility: A Kubo-Greenwood calculation

Considering only scattering with acoustic phonons in the elastic, equipartition approximation, the electron mobility, \( \mu_\theta \), along a crystallographic direction at an angle \( \theta \) with respect to the armchair \( \Gamma - X \) direction, is given by the usual Kubo-Greenwood expression:

\[
\mu_\theta = \frac{2e}{nk_B T} \int \frac{dk}{(2\pi)^2} v_\theta(k) \tau_{p,\theta}(k) \frac{\partial f(k)}{\partial k_x}
\]

\[
= \frac{e}{nk_B T} \int \frac{dk}{(2\pi)^2} v_\theta(k)^2 \tau_{p,\theta}(k) f(k)[1 - f(k)]
\]

\[
= \frac{2e}{nk_B T} \int_0^\infty \frac{dk}{2\pi} \int_0^{2\pi} \frac{d\phi}{2\pi} v_\theta(k,\phi)^2 \tau_{p,\theta}(k,\phi) \times f[E(k,\phi)][1 - f[E(k,\phi)]] ,
\]

where \( e \) is the elementary charge, \( T \) is the temperature, \( k_B \) is the Boltzmann’s constant, \( n \) is the carrier density, \( E(k,\phi) \) and \( v_\theta(k,\phi) \) are the energy and group velocity along the direction \( \theta \) of an electron with wave vector of magnitude \( k \) along a direction at an angle \( \phi \) with respect to the armchair direction. Finally, \( f(E) \) is the Fermi-Dirac distribution function.

The momentum relaxation rate, \( 1/\tau_{p,\theta}(k) \), along the crystallographic direction \( \theta \) results from collisions with longitudinal (LA) and transverse (TA) acoustic phonons, \( 1/\tau_{p,\theta}(k) = 1/\tau_{p,\theta}^{(LA)}(k) + 1/\tau_{p,\theta}^{(TA)}(k) \). Using Fermi’s golden rule, each rate \( 1/\tau_{p,\theta}^{(\eta)}(k) \), with \( \eta = \text{LA or TA} \), can be expressed as follows:

\[
\frac{1}{\tau_{p,\theta}^{(\eta)}(k)} = \frac{2\pi}{\hbar} \int \frac{dk'}{(2\pi)^2} \frac{\hbar^2 DK_\eta^2(k,k')}{2\rho\omega_\eta^{(q)}} \frac{k_B T}{\hbar\omega_\eta^{(n)}} \times \left[ 1 - \frac{v_\theta(k')}{v_\theta(k)} \tau_{p,\theta}(k') \right] \delta[E(k) - E(k')] .
\]

Here \( DK_\eta(k,k') \) is the deformation potential (implicitly defined by Eq. (9) below) for initial and final electron wave vectors \( k \) and \( k' \) and \( \omega_\eta^{(q)} \) is the frequency of a phonon of branch \( \eta \) and wave vector \( q \). The phonon-branch index \( \eta \) takes the value LA or TA. Note that the term \( 2(k_B T/\hbar\omega_\eta^{(n)}) \) represents the equilibrium occupation number for \( \hbar\omega_\eta^{(n)} << k_B T \), the additional factor of 2 accounting for emission and absorption processes.

For simplicity, we approximate the low-energy range of the phosphorene band structure, calculated as we shall discuss in Sec. III IIA below, with an elliptical parabolic dispersion with a light ‘armchair’ mass, \( m_x = 0.14 m_0 \) (where \( m_0 \) is the free electron mass) and a heavy ‘zigzag’ mass, \( m_y = 1.2 m_0 \). These values have been obtained from the DFT calculations discussed in Sec. IV below.

The ‘deformation potential’ \( DK_\eta(k,k') \), has also been calculated from DFT, following Ref. 10 as discussed in Sec. III B below. The deformation potential exhibits the typical behavior of the electron/acoustic-phonon matrix elements, vanishing at long wavelength (that is, at small \( q = |k - k'| \)). We find it convenient to calculate \( DK_\eta(k,k') \) on the energy-conserving shell at an arbitrary (small) electron kinetic energy, \( E_0 \), and express its complicated but extremely important angular dependence as:

\[
DK_\eta(k,k') = (DK)_0,\eta \left( \frac{E}{E_0} \right)^{1/2} g_\eta(\phi,\phi') ,
\]

Tabulating the functions \( g_{LA}(\phi,\phi') \) and \( g_{TA}(\phi,\phi') \) obtained numerically. Figure (I) shows the quantities \( \Delta_{LA}(\phi') \) and \( \Delta_{TA}(\phi') \), defined as \( \Delta_{\eta}(\phi') = DK_{\eta}(k,k')/q \), where \( \phi' \) is the angle between the armchair direction and the direction of the final state \( k' \) for the particular case of an initial state, \( k \), along the armchair direction (\( \phi = 0 \)).

We also use the DFT results shown in Fig. (9) to approximate the frequency of the acoustic phonons in the neighborhood of the \( \Gamma \) point with linear dispersions via a longitudinal and a transverse sound velocity, \( c_{\eta}(\alpha) \), that depends on the angle \( \alpha \) between the \( \Gamma - X \) symmetry line

\[\text{Figure 1. Acoustic deformation potentials, } \Delta_{LA} \text{ and } \Delta_{TA}, \text{ as of the final scattering angle } \phi' \text{ (with respect to the armchair direction) for an initial angle } \phi = 0, \text{ that is, for an initial } k \text{ state along the armchair direction.}\]
below. Yet, our results are significantly different from those reported in Refs. 52 and 55. In Ref. 55 the local density approximation (LDA) was used for the exchange correlation functional, as opposed to the Perdew-Burke-Enzerhof generalized-gradient approximation (GGA-PBE) we have used. This likely yields a difference in both electronic and phononic structure, which may at least in part, account for the observed difference. We preferred PBE over LDA since it is known to yield a better approximation for the exchange-correlation functional than LDA. This observation, coupled to possible and likely different phonon polarization vectors, may be the cause of the much larger deformation potential we have obtained for the electron/TA-phonon interaction in

\[
\mu_\rho = \frac{e}{\pi m_\rho} \int_0^{2\pi} d\phi \left( \frac{\cos \phi \cos \theta/m_x + \sin \phi \sin \theta/m_y}{\cos^2 \phi/m_x + \sin^2 \phi/m_y} \right)^2 \tau_{p,\phi}(\phi). \tag{7}
\]

The electron mobility obtained from Eq. (7) is shown in Fig. 1. Despite the relatively simple models we have used so far, the results are in excellent qualitative agreement, and even reasonable quantitative agreement, with our more accurate full-band Monte Carlo results presented in Sec. IV A below. Yet, our results are significantly different from those reported in Refs. 52 and 55.

Such a disagreement is not too surprising when considering the hole mobility: The ‘flatness’ of the dispersion of the highest-energy valence band along the zigzag direction seems to depend very strongly on the computational method used, as already pointed out by Lew Van Yoon and coworkers. This uncertainty affects the velocity and density of states of thermal holes, so that, sadly, results vastly different should not come as a surprise.

More disconcerting is the situation regarding the electron mobility. We can only speculate on possible physical and numerical causes of the difference between our results and those reported in Refs. 52 and 55. In Ref. 55 the parabolic-band and elastic-equipartition approximations, the momentum relaxation rate does not depend on the electron kinetic energy.

and the phonon wave vector \( \mathbf{q} \), that is, \( \omega_\mathbf{q}^{(n)} \approx c_\mathbf{q}(\alpha)q \). Figure 2 shows the angular dependence of the sound velocity along the longitudinal (armchair) and transverse (zigzag) directions, whereas in Fig. 3 we show the angular dependence of the momentum relaxation rate.

With these approximations, the momentum relaxation rate \( 1/\tau_{p,\phi}^{(n)}(k, \phi) \) becomes independent of the magnitude of the wave vector (that is, of energy):

\[
\frac{1}{\tau_{p,\phi}^{(n)}(k, \phi)} = \frac{(DK)^2_{0,\phi}k_B T}{\hbar^3 \rho} \frac{E(k, \phi)}{E_0} \int_0^{2\pi} d\phi' \frac{2\pi}{2\pi} \nonumber
\]

\[
\times \frac{g_{\mathbf{q}}^{(\phi, \phi')}(\mathbf{q})}{c_\mathbf{q}(\alpha)q^2(\cos^2 \phi/m_x + \sin^2 \phi/m_y)} \left[ 1 - \frac{\mathbf{v}(k') \cdot \mathbf{v}(k)}{\mathbf{v}(k') \mathbf{v}(k)} \right]. \tag{6}
\]

Note that in this equation we have approximated the ‘velocity-loss’ factor (given by the last factor in square brackets inside the integrand in Eq. (4)) with the expression suggested in Refs. 19 and 55, an expression that depends only on the angle between the initial and final group velocities, \( \mathbf{v}(k) \) and \( \mathbf{v}(k') \), not on their magnitude, thanks to the elastic approximation. Therefore, in Eq. (3) the integration over \( k \) simplifies and the electron mobility can be simplified to the following expression that does not depend on the carrier density \( n \) (or Fermi energy):
particular. Indeed, as we shall emphasize below, great care must be taken, by using large supercells for the phonon calculations, to avoid ‘imaginary’ frequencies for the low-energy vibrational modes and, even when obtaining a ‘correct’ vibrational spectrum, the resulting eigenvectors are only known with relatively small accuracy. Moreover, the calculation of the mobility requires numerical integrations over the Brillouin zone and we have found that the results require a fine discretization to perform such integrations. Specifically, as we shall see below, we have used a very fine mesh around the Γ symmetry point, equivalent to $145 \times 205$ $k$-points in the first quadrant. On the contrary, a much coarser mesh, presumably $12 \times 12$ points in the entire BZ, has been employed in Ref. 52. Despite the quantitative disagreement with the $ab\ initio$ results presented in Refs. 52 and 53, we confirm their main conclusion: Besides the obviously strong anisotropy of the mobility, due mainly to the anisotropy of the conduction bands, these results show how important the matrix-element anisotropy really is, an effect that explains the large values calculated by Qiao et al.21 and also those reported in Refs. 53 and 54.

### III. FIRST-PRINCIPLES PHYSICAL MODELS AND NUMERICAL METHODS

Having used a simplified model to draw some early conclusions, we now consider more accurate but less transparent $ab\ initio$ methods.

A. Band structure and phonon spectrum

For the calculation of the band structure of the systems considered here, we have primarily used the Vienna $Ab\ initio$ Simulation Package (VASP)52,53 with the Perdew-Burke-Enzerhof generalized-gradient approximation (GGA-PBE) for the exchange-correlation functional54 and a projector augmented wave (PAW)55 pseudopotential. A vacuum ‘padding’ of 20 Å was used in constructing the unit-cell to obtain free-standing layers and avoid interaction with periodic images. Initially, we have always performed structural optimization by minimizing the total energy in order to determine the lattice constants and ionic positions. VASP also handles van der Waals (vdW) interactions, important in multilayer systems, with Grimme’s model56. We have chosen the ‘optPBE’ functionals57 among the various other vdW-corrected functionals58,59 for the bilayers. We shall further discuss this issue below. The phonon spectra have been obtained using the PHONOPY computer program60 which calculates the force constants using small-displacement method, using an interface to VASP to obtain the atomic forces. In our calculations, we have found that a supercell of size of at least $8 \times 8 \times 1$ unit-cells is required to avoid unphysical imaginary frequencies for low-energy acoustic phonons, especially for the flexural out-of-plane (ZA) modes.

In light of the large discrepancies seen in literature when using different methods, we have decided to verify the results obtained from VASP using a different implementation of DFT, the Quantum Espresso (QE)61 DFT package, so that we can independently calculate the atomic configuration and electronic structure for monolayer phosphorene using ultrasoft pseudopotentials, and the PBE-GGA exchange-correlation approximation. The phonon spectra have been obtained by using QE, which yields the dynamical matrix using Density Functional Perturbation Theory (DFPT)62, as opposed to the small-displacements method of PHONOPY. The phonon spectra obtained from QE are calculated on a coarse $q$-points grid and interpolation to a fine grid, as required for the proper estimation of the scattering rates, is performed with minimal loss of accuracy by using maximally localized Wannier functions as implemented in the EPW63,64 package. In QE, the $k$-point grid used in the self-consistent calculation of the electronic structure must be a multiple of the $q$-point grid to obtain an accurate phonon dispersion.

For both the VASP and QE methods, the self-consistent calculations should be performed using a large cutoff energy to avoid negative frequencies, especially for the ZA-phonons. Distinguishing among longitudinal and transverse, and between acoustic and optical modes, has proven difficult or impossible (and even unphysical), especially for the many optical phonons in bilayers. The computational parameters we used are shown in Table III. It was observed that, even though the methods differ significantly in their approach, both VASP...
Table III. Computational parameters for DFT calculations.

| Parameters | VASP | QE |
|------------|------|----|
| $E_k$ cutoff | 500 eV | 50 Ry |
| Ionic minimization threshold | $10^{-6}$ eV | $10^{-6}$ Ry |
| SCF threshold | $10^{-8}$ eV | $10^{-10}$ Ry |
| $k$ points mesh | $11 \times 11 \times 1$ | $12 \times 12 \times 1$ |
| EPW meshes | coarse | fine |
| $k$ points mesh | $12 \times 12 \times 1$ | $50 \times 50 \times 1$ |
| $q$ points mesh | $6 \times 6 \times 1$ | $50 \times 50 \times 1$ |

$E_k$: Kinetic Energy  
SCF: Self consistent field

and Quantum Espresso yield matching crystal structure, band structure, and phonon dispersion for monolayer phosphorene.

B. Carrier-phonon interaction

We have treated the electron-phonon interaction following the general theory developed in Refs. 10–12 and 64. The matrix elements for the electron-phonon interaction can be expressed as:

$$
\langle k'n' | V_q^{(\eta)} | k\eta \rangle = \left\{ \frac{n_q^{\eta}(1/2)}{(1 + n_q^{\eta}(1/2))} \right\} \sum_{\gamma,l} \frac{1}{2N_c M_{\gamma} \omega_q^{(\eta)}} \frac{\hbar}{2N_c M_{\gamma} \omega_q^{(\eta)}} \right)^{1/2} \\
\times \hat{e}_{q\gamma} R_{l\gamma}^\star \hat{e}_{q\gamma} \right| \int_{\Omega} dr \psi_{k'n'}(r)^\star \frac{\partial U(r)}{\partial R_{l\gamma}} \psi_{k\eta}(r),
$$

where $N_c$ is the number of cells, $M_\gamma$ the mass of ion $\gamma$ in each cell, $\Omega$ is the volume of the crystal, the index $l$ labels the cells, $R_{l\gamma}$ the equilibrium position of ion $\gamma$ in cell $l$, $k$, $k'$ and $n,n'$ are the wave vectors and band indices of the initial and final electronic states, respectively, $\psi_{k\eta}(r)$ are the associated Bloch wavefunctions, $\omega_q^{(\eta)}$ the phonon frequency and $\hat{e}_{q\gamma}$ the unit displacement vector of ion $\gamma$ for a phonon of branch $\eta$ and wave vector $q = k' - k$. Here, $r$, $\hat{e}_{q\gamma}$ and $R_{l\gamma}$ are 3D-vectors while $k$, $k'$ and $q$ are 2D-vectors. The quantity $n_q^{\eta}$ is the Bose-Einstein phonon occupation number (obtained after having implicitly traced-out the phonon modes, assumed to be at equilibrium) for phonons of branch $\eta$ and wave vector $q$.

The upper (lower) term within the curly brackets applies to phonon absorption (emission) processes, finally, the term $\partial U(r)/\partial R_{l\gamma}$ represents the change of total energy of the lattice under a shift $\delta R_{l\gamma}$ of the position of ion $\gamma$ in cell $l$. Following from the two methods used in the evaluation of the electron and, in particular, the phonon spectra, we have evaluated (Eq. (8)) using two distinct methods.

In our primary method, based on the VASP and PHONOPY packages, the term is approximated by identifying $U(r)$ with the Hartree component of the Kohn-Sham Hamiltonian, $U_H(r)$, and is evaluated using finite differences. Of course, the periodicity of the lattice implies that this quantity does not depend on the cell-index $l$. We have numerically evaluated this term following Ref. 10 using VASP. In our second method, the term is evaluated entirely within the DFPT formalism using the Quantum Espresso and EPW packages, where $U(r)$ now accounts for both the Hartree and the exchange/correlation components of the potential. Once again, we have used both methods for monolayer phosphorene to verify our results, and we have found that the obtained results are in excellent agreement. Perhaps surprisingly, we must therefore conclude that our results are not very sensitive to the actual method used, provided that sufficient care is taken to use very low tolerances and fine grids in order to capture all the relevant physics.

We shall also make frequent reference to the ‘deformation potential’, $DK_{\eta}(k\eta,k'n')$, a quantity defined implicitly by:

$$
\langle k'n'| V_q^{(\eta)} | k\eta \rangle = \left\{ \frac{n_q^{\eta}(1/2)}{(1 + n_q^{\eta}(1/2))} \right\} \sum_{\gamma,l} \frac{1}{2N_c M_{\gamma} \omega_q^{(\eta)}} \frac{\hbar}{2N_c M_{\gamma} \omega_q^{(\eta)}} \right)^{1/2} \\
\times DK_{\eta}(k\eta,k'n') \left( \frac{\hbar}{2M_{\text{cell}} \omega_{k-k'}} \right)^{1/2},
$$

having gone to infinite-area normalization, where $M_{\text{cell}}$ is the total mass of the supercell. The scattering rate of an electron in band (or subband) $n$ and in-plane wave vector $k$ due to a perturbation potential $V_q^{(\eta)}$ can now be expressed as an integral only over 2D states as follows:

$$
\frac{1}{\tau^{(\eta)}(k,n)} = 2\pi \frac{\hbar}{\omega_{k-k'}} \sum_{\gamma'j} \int d\textbf{k}' \left| \langle k'n'| V_q^{(\eta)} | k\eta \rangle \right|^2 \\
\times \delta[\varepsilon_n(k) - \varepsilon_{n'}(k')] \pm \hbar \omega_{k-k'},
$$

where $\varepsilon_n(k)$ is the energy of an electron or hole with wave vector $k$ in band $n$.

C. Monte Carlo simulations

In order to calculate electronic transport properties employing the first-principles information we have discussed, we have followed the well-known ‘full-band Monte Carlo’ method to solve numerically the Boltzmann’s transport equation for a two-dimensional electron gas. Such a method, described, for example, in Refs. 52, 64 or 65 requires the discretization of the BZ into elements centered at points $k_l$. The energy $E_{jn} = E_n(k_l)$ and gradients $\nabla E_{jn} = \nabla k E_n(k_l)$ for each band $n$ are computed, stored in tables, and used to interpolate the carrier energy and group velocity. Using the Gilat-Raubenheimer algorithm in two-dimensions, the same discretization in reciprocal space is used to evaluate numerically the carrier-phonon scattering rates, Eq. (10), as a sum over
energy-conserving mesh elements in the BZ:

\[
\frac{1}{\tau(n)(k,n)} \approx \frac{2\pi}{\hbar} \sum_{j,n'} \Omega_{xy} \left| (\mathbf{k}_j n') \left| \psi_{jk}^{(n)} \right| \mathbf{k}_n \right|^2 \times \frac{1}{(2\pi)^2} \frac{L(w_{jn'})}{|\nabla E_{jn'}|}.
\]

(11)

where \( \Omega_{xy} \) is the area in the \((x,y)\) plane. In the notation of Eqns. (7) and (8) of Ref. 52, here \([1/(2\pi)^2] \frac{L(w_{jn})}{|\nabla E_{jn}|}\) is the density of states on band \(n\) in the \(j\)th element with energy \(E_{jn'} = E_n(k) \pm \hbar \omega_{k-\mathbf{k}}^{(n)}\) and gradient \(|\nabla E_{jn'}|\) at the center of the element, \(\mathbf{k}_j\). Details about the discretization depend on the particular crystal structure considered and will be given below. In all cases, energy conservation is numerically maintained within a root-mean-square error of less than 1 meV.

We have employed a synchronous ensemble Monte Carlo method, in light of its possible extension to the study of transients and inhomogeneous cases, although such an extension is not required here. The ensemble typically consists of 500-to-1,000 ‘particles’, with a time step of 0.2 fs, and followed until steady-state is reached in the uniform electric field we consider. Usually steady-state is only reached after several hundreds of ps at high fields, or even ns at low fields. We have also assumed a non-degenerate situation in order to avoid complications originating from Pauli’s exclusion principle. Therefore, our study is constrained to the low-density limit. Moreover, we have obtained the low-field carrier mobility using Einstein relation by calculating the diffusion constant \(D_\theta\) along the direction \(\theta\), a calculation that is less affected by stochastic noise when the drift velocity is much smaller than the thermal velocity.\(^{58}\) The diffusion constant is evaluated from the Monte Carlo estimator:

\[
D_\theta = \frac{1}{2} \frac{d}{dt} \left( \langle x_\theta \rangle - \langle x_\theta \rangle_0 \right)^2,
\]

(12)

where \(\langle x_\theta \rangle_0\) is the time-dependent ensemble-average position along the direction \(\theta\) of electrons initially at the origin, \(r = 0\), diffusing in the absence of an electric field.

IV. ELECTRONIC TRANSPORT

The lattice constants obtained from the structure-relaxation procedure described above are 4.62 Å and 3.30 Å for monolayer and 4.51 Å and 3.30 Å for bilayer phosphorene, both for the VASP and QE methods, and in agreement with the trend reported in Ref. 51. For the bilayer, we obtain a van der Waals gap of 3.20 Å, a value that is in excellent agreement with the value calculated by Qiao et al.\(^{52}\). For the tabulation and interpolation of the band structure and phonon spectra obtained using VASP and required by the Monte Carlo simulations, the band structure has been tabulated over two nested meshes in the first quadrant of the \(\pi/a \times \pi/b\) Brillouin zone: A ‘coarse’ mesh consisting of 49×68 elements of size \(\Delta k_x \approx \Delta k_y \approx 1.38 \times 10^8/m,\) and a ‘fine’ mesh – of 44×205 elements, of size \(\Delta k_x \approx \Delta k_y \approx 4.63 \times 10^7/m\) – in a rectangle with sides of length \(0.3\pi/a\) and \(\pi/b\) with the ‘lower left corner’ at the \(\Gamma\) point. We found empirically that the use of such a very fine mesh is necessary to account correctly for the anisotropy and strong non-parabolicity of the electronic dispersion around the center of the BZ and in proximity of the local energy minimum along the symmetry line \(Q\). The phonon spectra and carrier-phonon matrix elements have also been calculated and tabulated over the same meshes. However, when using the small displacement, finite differences method, \(DK_\theta(k,n,k'n')\) has been stored for \(k'\)-points on nested meshes with elements of the same size, but covering the entire BZ, whereas symmetry permits the tabulation for \(k\)-points on the irreducible wedge (i.e., the first quadrant of the BZ).

The size of the tabulated data and the computation time required to calculate them has been optimized by considering only ‘energy conserving’ matrix elements; that is: the deformation potential \(DK_\theta(k,n,k'n')\) has been calculated and stored only when \(|E_n(k) - E_{n'}(k')| \leq \hbar \omega_{k-\mathbf{k}}^{(n)}\). We should stress that initial attempts to calculate the deformation potentials over a coarser mesh have resulted in an inaccurate treatment of the scattering-angle dependence of the deformation potentials and in an overestimation of the carrier mobility. For the DFPT method, using the QE and EPW packages, we have calculated the carrier-phonon matrix elements using a coarse \(q\) and \(k\) mesh and interpolated them to a fine \(q\) and \(k\) mesh using maximally localized Wannier functions. The coarse and fine mesh sizes used are shown in Table 1. During the Monte Carlo simulation, the carrier-phonon matrix element is further interpolated on our band structure meshes using bi-linear interpolation.

Given the high computational cost of calculating the deformation potentials, we have tabulated them only for the first bands (highest-energy valence band and lowest-energy conduction band) for monolayer phosphorene, since the next lowest-energy bands are separated by more than 0.7 eV from the band edges. Therefore, the higher-energy bands we have ignored are not expected to play any role in the limited set of cases we have considered and may be ignored. On the other hand, for bilayers, we had to account for the next lowest-energy conduction band, since the first and second conduction bands are degenerate at the local minimum along the point \(Q\), so that the second band is expected to be populated by electrons at the highest fields we have considered.

The electronic band structure and phonon dispersion plotted along the symmetry points for mono- and bi-layer phosphorene from VASP and QE are shown in Fig. 5. DFT calculations are known to underestimate the band gap. Indeed, the values we obtain for monolayer and bilayer phosphorene are 0.90 eV and 0.41 eV, lower than experimental values\(^{51,59,90}\) and also smaller than the results obtained from GW calculations for mono-layers, \(\approx 2.0\) eV (Ref. 51). However, besides the obvious and unavoidable impact on the effective mass (usually slightly underesti-
Figure 5. The calculated band structure (left frames, (a) and (c)) and phonon dispersion (right frames, (b) and (d)), for monolayer phosphorene in (a) and (b), for bilayer phosphorene in (c) and (d).

mated when the band gap is also underestimated), the underestimated band gaps are not expected to significantly affect the transport properties of interest, since interband transitions between the valence and conduction band are not included in our calculations.

The contour plot of the first conduction band is shown in Fig. 6 only for monolayers (bilayers look qualitatively very similar). It indicates the presence of two satellite valleys, one with a minimum at the symmetry point $Q$, and a second valley, called the $Y$-valley minimum here, with its minimum in proximity to a point close to the $Y - S$ symmetry line. For monolayers, the energy separation between the $\Gamma$ and the $Q$-valley minima, $\Delta E_{\Gamma Q}$ is about 0.21 eV, whereas the energy separation between the $\Gamma$ and the $Y$-valley minima $\Delta E_{\Gamma Y}$ is about 0.27 eV. The electron effective masses in the nearly-isotropic $Q$-valley are 0.25 and 0.30 $m_0$ along the armchair and zigzag directions, respectively, as obtained from the band structure shown in Fig. 5a. For bilayers, Fig. 5c, we find similar values, both for the valley energies, $\Delta E_{\Gamma Q} = 0.14$ eV and $\Delta E_{Y} = 0.29$ eV, and for the electron effective masses in the $Q$-valley, 0.25 and 0.32 $m_0$ along the armchair and zigzag directions, respectively.

Comparing the phonon spectra for monolayers, shown in Fig. 5b, to those calculated for bilayers, shown in Fig. 5d, we note the presence of low-energy optical modes for bilayers. The existence of such low-frequency soft modes is related to the weakness of the inter-layer coupling (discussed more at length in Sec. IV C below) and also because of the heavy mass of entire unit cells in different layers oscillating out-of-phase in either the in-plane (LO, TO) or out-of-plane (ZO) direction. The presence of low-energy optical modes in bilayer phosphorene was also recently discussed by Xin-Hu et al.\textsuperscript{92} and has been already discussed in other multilayer systems, such as bilayer graphene.\textsuperscript{93,94} Moreover, coupling of these modes with electrons was also shown to be strong.\textsuperscript{94} We shall discuss below how these modes do indeed affect electronic transport in bilayer phosphorene.

A. Phosphorene monolayers

In Figs. 7 and 8 we show the angle-averaged scattering rates as a function of carrier kinetic energy obtained from VASP and Quantum Espresso, both for electron-phonon and hole-phonon processes. Since phosphorene is a $\sigma_h$-symmetric crystal, the ZA phonons con-
Figure 6. Contour plot in the irreducible wedge of the Brillouin zone of the energy of the first conduction band in monolayer phosphorene.

Figure 7. Electron-phonon (left) and hole-phonon (right) scattering rates in monolayer phosphorene at 300 K where, the matrix element is obtained from VASP.

Figure 8. Electron-phonon (left) and hole-phonon (right) scattering rates in monolayer phosphorene at 300 K. The matrix elements have been calculated using QE.

distribution is negligible to at first order in the electron-phonon interaction\textsuperscript{50}. Therefore electron/ZA-phonon and hole/ZA-phonon scattering has been ignored in our transport studies. Figure 9 shows the electron-phonon and hole-phonon matrix element, as in Eq. (9), calculated for an initial kinetic energy of $\approx 40$ meV, as a function of the final scattering angle $\phi'$ (with respect to the armchair $\Gamma - X$ direction) for an initial wave vector $k$ along the armchair direction. The highly anisotropic nature of the electron/acoustic-phonon matrix elements indicates the importance of using angular dependent deformation potentials, as already observed in Ref. 53. For electrons, intravalley scattering is dominated by in-plane acoustic phonons with strong backward scattering (Figs. 9a and 9b). Intervallelley scattering is controlled mainly by an optical phonon ($\approx 32$ meV) with an intervalley deformation potential of about $1.7 \times 10^6$ eV/cm. For holes, when calculated from VASP, scattering is dominated by the intravalley ZO mode with an energy of about 43 meV and a high deformation potential of $1.7 \times 10^6$ eV/cm (Fig. 9c). However, when calculated from Quantum Espresso, we notice that the in-plane acoustic modes dominate the scattering for holes (Fig. 9d). Comparing these results to reports in literature using similar physical models, we note that Jin et al.\textsuperscript{52}, using Quantum Espresso, have concluded that acoustic phonons are the limiting factor in the hole transport, which is consistent with our Quantum Espresso results. Note that this difference between VASP and QE does not translate to large differences in transport characteristics at room temperature since the 43 meV ZO mode has a low thermal population.

In Table II, we list the values for the electron and hole mobility we have obtained from the diffusion constant, both in the armchair and the zigzag directions. We obtained very similar mobilities for electrons and holes from both VASP and Quantum Espresso. We have already observed that our results are significantly different from those presented in Refs. 52 and 55 and we have speculated about possible causes for this difference. The velocity-field and energy-field characteristics for electron and hole transport are shown in Fig. 10 for a uniform electric field applied along the armchair and zigzag directions. For transport along the armchair direction, the low-field mobility obtained for electrons from the velocity-field characteristics (Fig. 10a) is in agreement with both the Kubo-Greenwood results presented above as well as with the value obtained from the diffusion constant. In contrast, for electron transport along the zigzag direction, the Monte Carlo simulations predict a low-field mobility a factor of $\approx 2$ higher than the analytic Kubo-Greenwood estimate.

We note a rather disappointing saturated velocity of $5 \times 10^6$ cm/s for electrons, especially for a field along the zigzag direction. Interestingly, Fig. 11 shows the occurrence of significant intervalley transfer to the $Q$ valley and even to the $Y$ valley. However, this does not translate
Figure 9. (a) Acoustic (left) and optical (right) electron/hole-phonon matrix element for electrons obtained from VASP, (b) for holes obtained from VASP, (c) for electrons obtained from QE and (d) for holes obtained from QE, in monolayer phosphorene. The quantities plotted here have been calculated following Eq. (9) for an initial and final electron kinetic energies ($\approx 40$ meV) as functions of the angle $\phi'$ of the final wave vector $k'$ with respect to the armchair direction. The initial electron wave vector $k$ is taken to be along the armchair direction.

into any negative differential mobility, since the effective masses in these satellite valleys are similar to those in the $\Gamma$ valley. The hole mobility obtained from the velocity-field characteristics (Fig. 10c) and diffusion constant in the armchair direction is about the same as for electrons. However, the hole mobility is significantly lower along the zigzag direction due to ‘flatness’ of the valence band along the zigzag direction. The velocity tends to deviate from linearity for electrons at very high fields. However, we do not observe any saturation even at high fields of $10^5$ V/cm. At low fields, the velocities for both electrons and holes in the zigzag direction are lower than the thermal velocity, making it difficult to extract the mobility from the velocity-field characteristics numerically. Up to a field of 100 kV/cm, the average carrier energy for electrons remains at the thermal energy ($\approx 25$ meV) and the electrons are in the ohmic regime (Fig. 10b). For holes, the ohmic regime extends to even higher fields, especially in the zigzag direction (Fig. 10d).

B. Phosphorene bilayers

For bilayers, the angle-averaged scattering rates as a function of carrier kinetic energy are shown in Fig. 12. Similar to monolayers, scattering with ZA phonons is ignored. Fig. 13 shows the electron/hole-phonon matrix element, Eq. (9), at a small electron kinetic energy, plot-
Figure 10. (a) Drift-velocity vs. field (left) and (b) average-energy vs. field (right) characteristics at 300 K for electrons, and (c) and (d) for holes, in monolayer phosphorene calculated using full-band Monte Carlo simulations. The dashed lines in the velocity plots show the Ohmic behavior based on the mobility determined from the zero-field diffusion constant calculations. The electric field is assumed to be along the armchair or zigzag direction, as indicated. In the armchair direction, the electron-phonon matrix elements required for transport, are obtained using both VASP AND QE. The shaded region in the high field regime indicates the approximate onset of scattering to higher bands, which was excluded from our model, results in this region only show a qualitative trend.

Scattering matrices are presented as a function of final scattering angle $\phi'$ for an initial wave vector $k$ along the armchair direction. Similar to our findings for electrons in monolayers, intravalley scattering is controlled to a large extent by in-plane acoustic phonons but with a stronger backward scattering. However, the many optical phonons seen in Fig. 13a (right frame) all contribute significantly to intravalley processes. For intervalley scattering, similar to monolayer, the optical mode with an energy of 32 meV exhibits the largest deformation potential, $\approx 1.7 \times 10^9$ eV/cm. However, among the optical modes, because of their low energies, scattering is dominated by a low-energy inter-layer optical mode ($\approx 1.5$ meV), despite its low deformation potential (ranging from $5.4 \times 10^3$ to $2 \times 10^8$ eV/cm). This is due to the large phonon population and the large amplitude of the squared matrix element that is inversely proportional to the phonon energy. For holes, as seen in Fig. 13b (left frame), intravalley scattering is dominated by strong backward scattering due to acoustic modes and low-energy inter-layer optical modes with an energy of about 1.5 meV and 7 meV. The associated deformation potentials reach maximum values of about $2.2 \times 10^8$ eV/cm and $6.2 \times 10^8$ eV/cm, respectively.

In Fig. 13, we show that the acoustic modes have mul-
Figure 11. Distribution in reciprocal space for electrons in monolayer phosphorene for a field of $3 \times 10^3$ (left), $3 \times 10^4$ (center), and $3 \times 10^5$ V/cm (right), along the armchair direction. Note the $\Gamma - Q$ intervalley transfer at center, the $\Gamma - Y$, and $Q - Y$ intervalley transfer at the highest field.

Figure 12. Electron-phonon (left) and hole-phonon (right) scattering rates (VASP) in bilayer phosphorene at 300 K.

tiple branch crossings with the low-energy optical modes, making it difficult or impossible to distinguish between acoustic and optical modes. Therefore, we believe that the contribution by low-energy optical modes might be much higher than what we observe in Fig. 11. Note that our conclusion that low-energy inter-layer optical modes play such a dominant role in bilayers is not consistent with the results presented by Jin et al. Their results show that acoustic phonons dominate the scattering for both electrons and holes and that total scattering rates are much lower than what we obtained, leading to higher mobility for bilayer phosphorene. However, as we have mentioned above, a strong coupling between electron and inter-layer optical phonons has been previously shown in the case of graphene bilayers.\cite{94}

Finally, the velocity-field and energy-field characteristics for electron and hole transport in bilayers are shown in Fig. 14. The carrier mobilities for electrons and holes obtained from velocity-field characteristics (Fig. 14) and Fig. 14 along the armchair and zigzag directions are in agreement with the values obtained from the diffusion constants (Table III). As seen in monolayers, the saturated velocity for electrons in bilayers is relatively low as well, which can be attributed to intervalley transfer to $Q$ and $Y$ valleys (Fig. 15). The hole mobility in the armchair direction is about the same as for electrons, whereas in the zigzag direction, the mobility is significantly lower due to ‘flatness’ of the valence band along the zigzag direction. The results we have obtained show that the carrier mobility decreases slightly when moving from monolayers to bilayers. This can be attributed to scattering by low energy inter-layer optical modes. We believe that in the presence of a substrate and/or a gate dielectric, the mobility in bilayers should increase, especially for holes, thanks to the damping – or even suppression – of scattering with low-energy inter-layer optical modes. Similar to monolayers, the ohmic regime, extends up to a field of 100 kV/cm for electrons (Fig. 14) and it extends to higher fields for holes (Fig. 14).

We should note again that our results are in disagreement with those reported by Jin et al., despite the similarity of the methods and assumptions made. This is the case for both monolayers and bilayers. We only note that we have observed a notable dependence of the computed mobility on the discretization employed, as mentioned previously, mandating a very fine mesh in reciprocal space. A different band structure, resulting from different ‘flavors’ of the DFT numerical method used, may also be a plausible cause for this difference that, ultimately, we cannot explain.

C. Thickness dependence of transport properties

In light of the observation we have made in the previous section regarding the low-field carrier mobility in mono- and bi-layers, it is interesting to discuss more generally the dependence of the carrier mobility on the thickness of phosphorene multi-layers and bulk black phosphorus (bP).

As we have mentioned in Sec. 1A experiments show a hole mobility that is strongly dependent on thickness, with values hovering around several hundreds cm$^2$V$^{-1}$s$^{-1}$ in thick layers, sharply decreasing in layers thinner than 10 nm, being as low as 1-10 cm$^2$V$^{-1}$s$^{-1}$ in layers 2-3 nm-thin.\cite{28,30} Such a behavior can be understood as the result of several effects: An increasing effective mass, a stronger carrier confinement, a larger deformation potential, and softening of the inter-layer optical phonons as we move from bP to monolayers. We discuss each of these effects in turn.

1. Thickness dependence of the carrier effective mass.

We have calibrated the local empirical pseudopotentials for P given in Ref. 95 to reproduce the band structure of
monolayer phosphorene

\[ V_P(q) = \sum_{j=1}^{4} a_j e^{-b_j(q-c_j)^2} \left[ 1 - d_j e^{-f_j q^2} \right], \quad (13) \]

with parameters \(a_j, b_j, c_j, d_j,\) and \(f_j\) given in Ref. 59 except for \(b_1 = 0.834517\) and \(a_4 = 0.085232\) (in atomic and Rydberg units). The calibration has been performed using an energy cutoff of 5 Ry. The modifications of \(b_1\) and \(a_4\) have been made to obtain the desired band gap for monolayer phosphorene (\(\approx 1.5\) eV from Refs. 51, 89, and 90). The electron and hole effective masses we have obtained for bulk black phosphorus and of 1-, 2-, and 3-layer phosphorene are shown in Tables IV and V respectively. We have already observed that obtaining a meaningful effective mass for holes along the zigzag direction is not possible, since the dispersion of the valence band along this direction (\(\Gamma - Y\) in few-layer phosphorene, \(Z - A\) in bulk \(bP\)) is very flat and extremely sensitive on the way the calculations are performed, as also remarked in Ref. 59. Indeed, in some cases, the valence-band (VB) maximum is found slightly away from the \(\Gamma\) point \(59,97,99\), thus rendering the band gap of the material slightly indirect. Therefore, extracting a ‘curvature’ effective mass is impossible. In order to bypass this problem, we have calculated a conductivity mass \((i.e.,\) the slope of the dispersion) along that direction over an energy window of \(k_BT \approx 25\) meV as \(m_n = \hbar k_BT/\sqrt{30}\) meV where \(E(k_BT) = 25\) meV. The thus obtained conductivity mass will give an idea about the group velocity that enters the Kubo-Greenwood formula for the mobility. (Obviously, the high density-of-states associated with the flat dispersion still strongly depresses the mobility via the large momentum-relaxation rates).

The results are listed in Table IV and Table V also list the values of the effective masses we have obtained using DFT (VASP) calculations. These values are affected by a larger discretization error and are expected to be somewhat smaller compared to experimental results because of the smaller band gap predicted by DFT calculations. We see that the effective mass decreases with increasing thickness for both electrons and holes. This leads us to expect an increasing mobility when moving from monolayers to bulk black phosphorus. However, the masses decrease by an amount that is too small to explain the difference between bilayer and monolayer mobility behavior seen in Table II.

2. Quantum confinement effects. Intrinsically 2D materials have, among their many remarkable properties, two major advantages for the purpose of electronic devices when compared to thin ‘3D materials’. In thin 3D materials, quantum confinement is the result of conduction-band discontinuities with insulators (as for thin Si films confined by SiO\(_2\) or other oxides) whereas in 2D materials, electrons are naturally confined in two
Figure 14. (a) Drift-velocity vs. field (left) and (b) average-energy vs. field (right) characteristics at 300 K for electrons and, (c) and (d) for holes, in bilayer phosphorene (VASP) calculated using full-band Monte Carlo simulations.

Table V. Hole effective mass (in units of the free electron mass) in phosphorene layers and bulk black phosphorus calculated using empirical pseudopotentials and DFT (in parentheses).

|              | $\Gamma - X$ | $\Gamma - Y^{(a)}$ | $\Gamma - S$ | DoS |
|--------------|--------------|--------------------|--------------|-----|
| monolayer    | 0.20 (0.14)  | 1.7                | 0.59         | 0.59|
| bilayer      | 0.19 (0.09)  | 1.2 (3.08)         | 0.56         | 0.51|
| trilayer     | 0.21         | 0.91               | 0.62         | 0.49|
|              | $Z - Q$      | $Z - A$            | $Z - \Gamma$ | DoS |
| bulk         | 0.09         | 0.51               | 0.37         | 0.26|
| bulk (exp)$^{(b)}$ | 0.076      | 0.648              | 0.280        |     |

(a) Optical (slope) mass at 25 meV. The curvature mass along the $\Gamma - Y$ direction cannot be defined at $\Gamma$ due to the ‘flatness’ of the dispersion.
(b) Experimental data from Ref. 50

dimensions by ionic potentials (as for graphene). Bulk 3D material mobilities range from respectable to excellent, but in thin films the carrier mobility is severely depressed by ‘wavefunction-overlap’ effects. On the other hand, 2D materials have the potential of exhibiting excellent mobilities even in the limit of atomic thickness. Moreover, confinement by insulators leads to a problematic energetic up-shift of the ground-state subbands in semiconductor ultra-thin films or nanowires based on 3D materials$^{100}$, causing a potentially unacceptably high gate-current leakage. Again, the naturally ionic confinement in 2D materials will save them from such an unacceptable high gate leakage current.

Two-dimensional $sp^2$ (or $sp^2/sp^3$) group-IV materials and transition-metal dichalcogenides (TMDs) are typical examples of materials that exhibit these desired prop-
erties. In these materials, the presence of a lone electron (such as the electron occupying the $p_z$ orbital in $sp^2$ group-IV materials) or the absence of unpaired electrons (such as in TMDs, with the 2-4 $p$ electrons from the transition metal and the 6 hybrid-$sp$ electrons from the two chalcogens) results in either a $\pi$-band strongly localized in the out-of-plane direction (out of the “lone” $p_z$ electron in the $sp^2$ group-IV 2D crystals), or in out-of-plane-localized states inside the 2D crystal (TMDs).

In a multi-layer van der Waals heterostructure, ‘vertical’ band-discontinuities at the top and bottom surfaces or interfaces, do not significantly affect the band structure. Indeed, the van der Waals coupling between adjacent layers is too small (of the order of a few tens of meV per atom both in graphene\cite{101} and TMDs\cite{102}) to alter the bonding properties and, most important, the out-of-plane localization of the wavefunctions. These materials are indeed easily exfoliated and are relatively chemically stable – a result of the out-of-plane localization of the valence-band states. Moreover, they show a very low out-of-plane conductivity – a result of the out-of-plane localization of the conduction-band states. However, the in-plane mobility remains high, even in monolayers. Indeed, graphene exhibits an extremely high mobility, $\approx 10^5$ cm$^2$V$^{-1}$s$^{-1}$. Such a high mobility, even for carriers confined over a thickness of the order of 0.1 nm, is the result not only of pseudospin-conservation and reduced back-scattering, but also of the fact that the scattering form-factor of the wavefunctions does not depend on the confinement along the out-of-plane direction.

The recent studies by Qiao \textit{et al.}\cite{51} and by Xin-Hu and co-workers\cite{92} have shown that phosphorene (and, we speculate, other group-V materials, such as also arsenene and antimonene) is remarkably different: In multilayers, the lone $p$-orbital pairs hybridize into bonding and antibonding orbitals, weakly localized or even delocalized along the out-of-plane direction, with wavefunctions that spread across the interlayer gap. The interlayer coupling energy is now much larger: A value of 0.46 eV has been used for the interlayer coupling energy in calibrated tight-binding calculations of phosphorene\cite{60}, rendering this a ‘quasi-covalent’ bonding. This should be compared to the pure van der Waals interaction energy, of the order of a tens of meV/atom, as mentioned above. Such an effect, recently discussed at length by Xin-Hu \textit{et al.}\cite{92}, has been shown to be responsible for the poorly-understood behavior of phonon frequencies in few-layer phosphorene. These considerations imply that now the hybridized valence- and conduction-band wavefunctions can spread significantly across the interlayer. An additional strong hint that phosphorene multilayers are quite different from pure van der Waals materials is provided.
Figure 17. As in Fig. 16 but for a phosphorene trilayer. A vacuum of 3.1 nm was used in the construction of the supercell. Note how the valence-band wavefunction resembles a cosine-like standing wave, with a maximum in the central region, whereas the conduction-band wavefunctions show two broad peaks, as for the first excited state of a particle in a box. Therefore, the envelopes of these wavefunctions appear to be set more by the top and bottom trilayer surfaces than by the ionic potentials in each layer.

by the fact that that in bulk bP, the electron mobility along the z-axis (perpendicular to the plane of the layers) is about the same as along the zigzag direction: 400 cm$^2$V$^{-1}$s$^{-1}$ (out-of-plane) vs. 460 cm$^2$V$^{-1}$s$^{-1}$ (zigzag) at 200 K, compared to 2,300 cm$^2$V$^{-1}$s$^{-1}$ along the armchair direction. The situation is similar for holes, their mobility being 540 cm$^2$V$^{-1}$s$^{-1}$ along the out-of-plane direction, 1,300 cm$^2$V$^{-1}$s$^{-1}$ along the zigzag direction, and 3,300 cm$^2$V$^{-1}$s$^{-1}$ along the armchair direction, also at 200 K (Ref. [49]. This means that carriers move from one layer to the next with relative ease. On the contrary, for graphite, the measured in-plane electron mobility is quite high, about 13,000 cm$^2$V$^{-1}$s$^{-1}$ at 300 K, but the material behaves essentially as an insulator along the out-of-plane direction, with a conductivity (mobility) about 3,000 times lower. This means that carriers are not transferred between layers, instead being localized within each layer.

To illustrate the non-van der Waals nature of phosphorene, in Figs. 16 and 17 we show the squared amplitude of the wavefunctions corresponding to the highest-energy valence-band state and lowest-energy conduction-band state in bilayer and trilayer phosphorene. (The van der Waals gap of 3.20 Å reported in Ref. [51] has been assumed in these empirical-pseudopotential calculations.) The wavefunction can be seen to ‘spill’ into the interlayer region, especially for the conduction-band in bilayers (Fig. 16 (b) and (c)). Note also in Fig. 17 how the valence-band wavefunction reaches a maximum am-
amplitude in the central layer, as for the ground-state of a particle-in-a-box textbook problem. The next excited state, the wavefunction of the conduction band, exhibits instead two ‘bumps’, once more reminding us of the first excited state of confined bulk-like system compared to a 2D van der Waals material. As just mentioned, this indicates that the electronic states are more sensitive to the boundary conditions at the surfaces of the top and bottom layers than to the ionic potentials in each layer. To contrast how wavefunctions manifest themselves in a van der Waals material, we show the valence- and conduction-band wavefunctions in bilayer graphene (obtained using the empirical pseudopotentials given in Ref. 65 with a van der Waals gap of 3.35 Å) in Fig. 12. In this case the wavefunctions vanish in the inter-layer region, showing that in these material systems the wavefunctions strongly confine the 2DEG within each layer.

This discussion suggests that multi-layer phosphorene behaves more like a bulk covalent material than a van der Waals material, as already argued by Qiao et al. and Xin-Hu and co-workers. The ‘vertical’ confinement of the 2DEG appears to be mainly controlled by the ionic potentials but by the conduction/valence-band discontinuities at top/bottom interfaces. This situation is similar to the case of semiconductor thin films or quantum wells. In such cases, carrier-phonon scattering is mainly controlled by the well-known scattering form factor (a functional of the ‘envelope’ wavefunction along the out-of-plane direction z, ζn(z), for carriers in band n, averaged over an in-plane unit cell),

\[ I_{nm} = \int dz \ |ζ_n(z)|^2 \ |ζ_m(z)|^2, \]

originally derived by Price. This form factor increases as \(1/W^2\) as the well-width \(W\) (or multilayer thickness, in our case) decreases, resulting in a carrier mobility that vanishes as \(W^2\) for small \(W\). In a way, we are subjected to the same problems that govern Si thin film mobility: As the thickness decreases, the mobility is depressed because of this undesired ‘form-factor’ effect. In phosphorene, this may not be an effect as strong in the case of fully delocalized states, as for Si or Ge thin bodies, but it is also far removed from the more ideal cases of graphene, other group-IV monolayers, or TMDs.

Calculated form-factors for the wavefunctions in 1-, 2-, 3-layer phosphorene for valence band maximum (VBM) and conduction band minimum (CBM) are shown in Table VI. As expected, the form-factor decreases with increasing in thickness, however, they decrease by not more than a factor of 2. Therefore, going from mono- to bilayer phosphorene, we expect the mobility to increase by not more than a factor of 4 (the areal mass density in bilayers is twice that of monolayers). On the contrary, Cao et al. observed an increase in mobility by a factor of 80 moving from 1- to 2-layer phosphorene.

### 3. Deformation potentials

A survey of the literature shows that the band structure changes with strain in a way that depends on the thickness of the system. In monolayers, a 4-6% biaxial strain can have the huge effect of reversing the anisotropy, whereas in bulk bP strain seems to have a weaker effect. This seems to suggest that the deformation potentials decrease with increasing thickness, an effect that may contribute to boosting the carrier mobility in thicker films. We have confirmed this by using the empirical pseudopotential given by Eq. (10) to calculate the change of the band gap, \(E_G\), under hydrostatic stress, \(\nu_0 dE_G/d\nu\) (where \(\nu_0\) and \(V\) are the volume of the relaxed and hydrostatically strained crystal, respectively) for monolayer phosphorene and bP. This quantity yields the sum of the conduction-band, \(d_c\), and the valence-band, \(d_v\), dilatation deformation potentials. For bP, using the elastic constants measured in Ref. 107 and discussed in Ref. 108, we have obtained \(d_c + d_v\) ≈ 4.3 eV. This is about a half the value calculated in Ref. 109 and the values of 8.19-to-9.89 eV for \(d_c + d_v\) reported in Ref. 107. Such a discrepancy could be due to intrinsic limitations of the empirical pseudopotentials we have employed, to uncertainties in the values of the elastic constants, and to additional ‘internal’ atomic displacements that occur under strain. On the contrary, for monolayer phosphorene, we have obtained larger dilatation deformation potentials, \(d_c + d_v\) ≈ 6.6 eV. Of course, we cannot estimate separately the contribution of the conduction band and of the valence band (given as a 33%-66% split in Ref. 110). However, despite their uncertainty, these results constitute a highly suggestive argument to explain the larger carrier mobility in thicker films. From Figs. 9 and 13 we observe that the effective deformation potential (Eq. (9)) for the acoustic modes increases going from mono- to bi-layer. However, as mentioned earlier, in the case of bilayers, the low-energy optical modes have multiple branch crossings with the acoustic modes at small \(q\)-vectors, making it difficult or impossible to separate the contribution of the acoustic modes. We may argue that the effective deformation potential in acoustic modes might be much lower than what we see in Fig. 13 and low-energy optical modes might have a higher contribution to the scattering rates.

### 4. Stiffening of the inter-layer optical modes

Whereas when moving from monolayers to bilayers the carrier mobility is kept low by the presence of low-energy inter-layer optical modes, when moving to thicker multi-layer systems this effect is expected to be less significant and even show a qualitatively opposite behavior. Indeed, the amplitude of these optical modes decreases as their energy increases. This is the result of their increased stiffness
due to the coupling with various layers, as the energy of the lowest-frequency interlayer mode grows from ≈ 1.5 meV in bilayers to about 25 meV for TO phonons in bulk black phosphorus\(^5\). The situation is complicated by the splitting of several modes into ‘inner’ and ‘surface’ modes\(^9\) in layered structures, but this trend constitutes another possible cause for a mobility increasing in thicker films.

It would be extremely interesting to study in detail the thickness dependence of all of these effects. Unfortunately, it is impossible to treat correctly the 2D-to-3D transition – and so, also the Z-to-Γ direct-band-gap transition and the mobility change – when calculating the band structure and the vibrational properties of many-layer systems. Indeed, this would require accounting for inelastic, phase-breaking phonon scattering within a DFT (or even GW) framework, a task obviously still elusive. Yet, the results discussed here give a qualitative idea of why the carrier mobility decreases so sharply when moving from bulk black phosphorus to monolayer phosphorene. In particular, the observation that phosphorene behaves more like a conventional semiconductor than a van der Waals material – as discussed in item 2 above – seems to explain the strong thickness dependence of the carrier mobility shown in Fig. 4(c) of Ref.\(^{24}\) and suggested by Table 1.

V. CONCLUSIONS

The widely scattered theoretical predictions about the carrier mobility in 2D crystals that have been reported in the literature have prompted us to analyze critically the reasons for this confusion. Taking monolayer and bilayer phosphorene as examples of widely studied materials, we have identified the assumed simplifying isotropy of the electron-phonon matrix elements, the use of the ‘band’ deformation potential instead of the proper carrier-phonon matrix elements, and the associated neglect of the wavefunction-overlap effects as the main sources of this confusion. Using a simple – but, hopefully, not oversimplified – model, we have shown that, unfortunately, the most accurate models predict the less exciting values for the carrier mobility. These do not exceed ≈ 25 cm\(^2\) V\(^{-1}\) s\(^{-1}\) at 300 K for both electrons and holes. We have also employed Monte Carlo simulations – based on a band structure and carrier-phonon scattering rates calculated using two separate \textit{ab initio} DFT – methods to obtain both better estimates of the low-field mobility in phosphorene monolayers and bilayers, and information about high-field transport properties. We found that calculating the carrier-phonon interaction using small displacements and DFPT yield similar results. Our study further predicts a decrease in mobility moving from mono- to bi-layers. Most important, we have argued (unfortunately only at a qualitative level) that phosphorene, because of its lone-pair of ‘out-of-plane’ \(p\)-electrons, behaves more like a ‘conventional’ semiconductor than a van der Waals material, an observation that may explain the thickness dependence of the carrier mobility reported in the literature.

ACKNOWLEDGMENTS

This work has been supported by Taiwan Semiconductor Manufacturing Company, Ltd.. Edward Chen acknowledges Jack Sun for management support.

1 W. Zhang, Z. Huang, W. Zhang, and Y. Li, Nano Res. 7, 1731 (2014).
2 M. Houssa, A. Dimoulas, and A. Molle eds. (CRC Press -TaylorFrancis, Boca Raton, Florida, 2016), 2D Materials for Nanoelectronics.
3 A. Molle, J. Goldberger, M. Houssa, Y. Xu, S.-C. Zhang, and D. Akinwande, Nature Mat. 16, 163 (2017).
4 See for example the recent reviews of the history and state of the art of density functional theory by R. O. Jones, Rev. Mod. Phys. 87, 897 (2015) or by P. J. Hasnip, K. Refson, M. I. J. Probert, J. R. Yates, S. J. Clark, and C. J. Pickard, Phil. Trans. A: Math. Phys. Eng. Sci. 372, 20130270 (2014).
5 G. Kresse and J. Hafner, Phys. Rev. B 47, RC558 (1993).
6 G. Kresse, Ph. D. thesis, Technische Universität Wien (1993).
7 G. Kresse and J. Furthmüller, Comput. Mat. Sci. 6, 15 (1996).
8 G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).
9 P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, et al., J. Phys.: Condens. Matter 21, 395502 (2009).
10 W. G. Vandenbergh and M. V. Fischetti, Appl. Phys. Lett. 106, 013505 (2015).
11 S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, Rev. Mod. Phys. 73, 515 (2001).
12 F. Giustino, Rev. Mod. Phys. 89, 015003 (2017).
13 J. M. Ziman, Electrons and Phonons (Oxford University Press, Oxford, UK, 1958).
14 S. Zollner, S. Gopalan, and M. Cardona, Phys. Rev. B 44, 13446 (1991).
15 S. Zollner, S. Gopalan, and M. Cardona, Semicond. Sci. Technol. 7, B137 (1992).
16 M. V. Fischetti and J. Higman, in Monte Carlo Device Simulation: Full Band and Beyond, K. Hess ed., Kluwer Academic (Norwell, MA, 1991), pp. 123-160.
17 P. D. Yoder, V. D. Natoli and R. M. Martin, J. Appl. Phys. 73, 4378 (1993).
18 H. J. Choi and J. Ihm, Phys. Rev. B 59, 2267 (1999).
The fact that this expression does not depend on the density or Fermi energy is the result of the constant density of states in two dimensions for a parabolic dispersion. This implies an energy independent relaxation time. In turn, the energy integral appearing in Eq. (3), that depends on carrier density (or Fermi energy) via the Fermi-Dirac function \( f(x) = (1 + \exp(x - x_F))^{-1} \) (where \( x \) and \( x_F \) are the kinetic energy and Fermi energy in thermal units), becomes proportional to the carrier density \( n \) itself, so that 
\[
\int_0^\infty dx \, \frac{dF}{F} \left[ \int_0^\infty dx \, f(x) \right]^{-1} = 1 \text{ becomes independent of the Fermi energy.}
\]

J. P. Perdew and Y. Wang, Phys. Rev. B 45, 13244 (1992).

J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1997); Erratum Phys. Rev. Lett. 78, 1396 (1997).

P. E. Blochl, Phys. Rev. 50, 17953 (1994).

S. Grimme, J. Comp. Chem. 25, 46 (2004).

J. Klimsić, D. R. Bowler, and A. Michaelides, J. Phys. Condens. Matter 22, 022201 (2010).

A. D. Becke, Phys. Rev. A 88, 3098 (1988).

M. Dion, H. Rydberg, E. Schröder, D. C. Langreth, and B. I. Lundqvist, Phys. Rev. Lett. 92, 244601 (2004).

A. Togo and I. Tanaka, Scr. Mater. 108, 1 (2015).

J. Noffsinger, F. Giustino, B. D. Malone, C. H. Park, S. G. Louie and M. L. Cohen, Comput. Phys. Commun. 181, 2140 (2010).

F. Giustino, M. L. Cohen, and S. G. Louie, Phys. Rev. B 76, 165108 (2007).

G. Gilat and L. J. Raubenheimer, Phys. Rev. 144, 390 (1966); Erratum Phys. Rev. 147, 670 (1966).

M. V. Fischetti, B. Fu, S. Narayanan, and J. Kim, in Nano-Electronics Devices: Semiclassical and Quantum Transport Modeling, D. Vasilisaka and S. M. Goodnick Eds. (Springer, New York, 2011), pp. 183-247.

C. Jacoboni and L. Reggiani, Rev. Mod. Phys. 55, 645 (1983).

V. Tran, R. Soklaski, Y. Liang, and L. Yang, Phys. Rev. B 89, 235319 (2014).

S. Zhang, J. Yang, R. Xu, F. Wang, W. Li, M. Ghufran, Y. W. Zhang, Z. Yu, G. Zhang, Q. Qin, and Y. Lu, ACS Nano 8, 9590 (2014).

R. Fei, A. Faghaninia, R. Soklaski, J.-A. Yan, C. Lo, and L. Yang, Nano Lett. 14, 6393 (2014).

Z.-X. Hu, X. Kong, J. Qiao, B. Normanda, and W. Ji, Nanoscale 8, 2740 (2016).

J.-A. Yan, W. Y. Ruan, and M. Y. Chou, Phys. Rev. B 77, 125401 (2008).