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Quasiparticle band structure and tight-binding model for single- and bilayer black phosphorus

A. N. Rudenko$^1$ and M. I. Katsnelson$^1$

$^1$Institute for Molecules and Materials, Radboud University Nijmegen, Heijendaalseweg 135, 6525 AJ Nijmegen, The Netherlands

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By performing ab initio calculations for one- to four-layer black phosphorus within the GW approximation, we obtain a significant difference in the band gap ($\sim1.5$ eV), which is in line with recent experimental data. The results are analyzed in terms of the constructed four-band tight-binding model, which gives accurate descriptions of the mono- and bilayer band structure near the band gap, and reveal an important role of the interlayer hoppings, which are largely responsible for the obtained gap difference.

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Introduction. Black phosphorus (BP) is a layered material consisting of puckered atomic layers of elemental phosphorus coupled together by weak van der Waals forces [1]. BP is attracting attention because of the prediction of phosphorus nanotubes [2, 3] and especially in view of recent success in obtaining a few-layer BP, broadening the range of two-dimensional (2D) materials [4–8]. Preliminary investigations indicate a strong contrast in the electronic properties of bulk and few-layer BP, giving rise to the possibility of novel practical applications [4–8].

Since high-quality BP crystal became available [7], the electronic properties of BP have been extensively studied experimentally. In particular, bulk BP has been shown to be a semiconductor with a moderate band gap of 0.31–0.35 eV [10–12], whereas liquid He temperatures along pressure give rise to superconductivity [13]. Despite containing only one $p$ element, a theoretical description of BP turns out to be very challenging. Earlier attempts could not provide a reliable description of the band structure due to shortcomings of the computational methods [14–17]. Although the employment of more accurate nonempirical approaches reported in recent studies yields more consistent results [18–21], their performance is strongly dependent on the quality of the exchange-correlation approximation.

In contrast to semiconducting bulk BP, monolayer BP is predicted to be an insulator with a considerably larger band gap, strongly depending on the number of layers [5–7, 14, 16, 18, 20, 21], which is also supported by experimental observations [5–8]. However, the origin of a considerable band gap broadening in going from bulk to monolayer remains unclear.

In this Rapid Communication, we analyze in detail the electronic properties of monolayer, multilayer ($n=2–4$), and bulk BP within the quasiparticle GW approximation. Particularly, we address the problem of the variation of their electronic properties. To this end, we construct a tight-binding model, which sheds light on the mechanism of the band gap formation in BP and further can be used in large-scale calculations of transport and optical properties.

Structure and chemical bonding. A single layer of BP consists of a corrugated arrangement of P atoms and has a thickness of $\sim5$ Å [Fig. 1(a)] [22, 23]. Alternate stacking of the layers along the [001] direction gives rise to the structure of bulk BP, which is stabilized by weak dispersive interactions. The intralayer bonding in BP results from the $sp^3$ hybridization of P atoms, giving rise to three bonding orbitals per two atoms [Fig. 1(b)] augmented by lone pairs associated with each atom [Fig. 1(c)]. The latter plays a particular role in the pressure-induced transformations of BP, as well as accounts for a variety of structural modifications of solid P [24].

Electronic structure and a band gap in bulk BP. We first calculate the band structure of bulk BP along the high-symmetry lines of the Brillouin zone (BZ) by using two different theoretical approaches. The first method is the standard generalized-gradient approximation (GGA) [27], that is routinely used in density functional theory (DFT) calculations, while the second one corresponds to an explicit calculation of the self-energy (\(\Sigma = iGW\)) within the \(G_0W_0\) procedure [28, 29], where both the Green’s function \(G_0\) and screened exchange \(W_0\) are evaluated using DFT-GGA wave functions.

The calculations presented in this work were carried out by using the Vienna ab initio simulation package (VASP) [30, 31]. An energy cutoff of 280 eV for the plane-wave basis and the convergence threshold of \(10^{-8}\) eV were employed to obtain the DFT wave functions. The number of unoccupied bands in GW calculations was set to 90 per atom and 70 grid points were used for integration along the frequency axis. To sample the Brillouin zone, \(k\)-point meshes of \((10\times12\times4)\) and \((10\times12\times1)\) were used for bulk and multilayer calculations, respectively. An experimental lattice structure was adopted in all cases [22, 23]. For slab (multilayer) calculations, a vacuum layer of $\sim20$ Å was used. The chosen set of parameters ensures that the one-particle energies are accurate to within a few tens of meV.
In Fig. 2 we show the band structure of bulk BP calculated by using the two different methods. One can see that both GGA and GW band structures exhibit similar features with the exception of the relative position of the valence (VB) and conduction (CB) bands, which results in different band gaps \((E_g)\). In particular, the GGA approach leads to an overlap between the VB and CB in the vicinity of the \(\Gamma\) point (zero band gap), whereas the GW method gives rise to a band gap of \(~0.1\) eV. Although both approaches do not reproduce the experimental band gap of \(0.31–0.35\) eV, the GW method yields a qualitatively correct trend toward the band gap opening, which is expected to be improved by a self-consistent treatment of \(G\) and \(W\). Being in principle possible, such a treatment is highly demanding computationally and not considered within the present work. A qualitative difference between the results of the DFT-GGA and GW methods indicates an important role of electron correlations in BP, which requires a careful theoretical treatment.

To analyze the orbital composition of the bands close to the gap, we project the quasiparticle states onto the canonical \(s\) and \(p_i\) \((i = x, y, z)\) orbitals, which allows us to decompose the VB and CB into different orbital contributions. The decomposition at the \(\Gamma\) point yields \(\psi^{VB}(\Gamma) = 0.17 |s⟩ + 0.40 |p_x⟩ + 0.90 |p_z⟩\) and \(\psi^{CB}(\Gamma) = 0.57 |s⟩ + 0.44 |p_x⟩ + 0.69 |p_z⟩\), respectively, for VB and CB. One can see that the relevant bands represent a mixture of all the orbitals, with the exception of \(p_y\) having zero contribution at \(\Gamma\). Although the \(p_z\) orbital has the largest contribution in both cases, the role of the other orbitals \((s\) and \(p_x\)) in the formation of VB and CB cannot be considered as negligible. Therefore, we emphasize that in contrast to graphite (graphene), whose relevant bands are determined exclusively by the \(p_z\) states, the band structure of BP is considerably less trivial due to the mixture of states of different symmetry.

**Band structures of monolayer and a few-layer BP.** As a next step, we apply the GW approximation to the calculation of the band structure of monolayer and a few-layer BP. In Fig. 3 we show the corresponding spectra for a monolayer and a few-layer BP. The band gap decreases monotonically with the number of layers, reaching the value of \(0.46\) eV in the four-layer case. The observed trend is in line with previous DFT investigations \[5, 18, 21\], although the GW approach results in an appreciably larger band gap. It should be noted that although recent hybrid-functional DFT calculations within the HSE06 scheme \[32\] report a similar band gap for the monolayer BP \((1.51\) eV \[21\]), the application of the same approach to bulk BP leads to a substantial overestimation of its band gap \((0.82\) eV \[3\]), whereas the adjustment of the functional to give a better description for bulk BP conversely reduces the monolayer values \(~1.16\) eV).

Existing experiments on the photoresponse of BP-based field-effect transistors provide an estimation of the cutoff wavelength for the excitation of the carriers of a few-layer BP, which amounts to \(1.24\) eV \[6\]. Similarly, photoluminescence measurements provide indications of an even larger optical gap of \(1.6\) eV \[7\]. We note that a direct comparison between theory and experiment is not possible since the number of layers in the experimental samples is not clearly determined, while the GW approach does not capture excitonic effects, which are necessary for a correct description of the optical spectra. Nevertheless, the experimentally reported values...
FIG. 3. (Color online) Band structures for $n$-layer BP calculated within the GW approach for $n=1–4$. Zero energy corresponds to the center of the band gap. Blue circles show the band splitting near the gap.

can be considered as a lower limit for the band gap in monolayer BP, which indeed indicates that the gap in BP is strongly dependent on the number of layers. In comparison with previous DFT studies, the GW results presented above are appreciably closer to experimental observations. Moreover, taking into account some underestimation of the GW band gap in bulk BP, the same trend is expected for monolayer and multilayer BP, which suggest that the actual monolayer band gap is larger than the obtained value of 1.60 eV.

**Tight-binding parametrization.** We now turn to the tight-binding (TB) analysis of the band structure. Previously, a two-band model has been proposed within the $k\cdot p$ approximation for monolayer BP [20], which yields a reasonable description of the DFT bands near the $\Gamma$ point. However, the effective Hamiltonian proposed in Ref. 20 is determined in reciprocal space and does not involve any real-space interaction parameters, which is necessary to have an insight into the origin of the gap and its evolution with the number of layers.

Here, we further analyze the electronic structure of monolayer BP by performing TB parametrization of the GW Hamiltonian by using the following four-band model,

$$H = \sum_i \varepsilon_i n_i + \sum_{i \neq j} t_{ij}^{||} c_i^\dagger c_j,$$

where the summation runs over the lattice sites of single-layer BP (four sites per unit cell), $\varepsilon_i$ is the energy of the electron at site $i$, $t_{ij}^{||}$ is the hopping parameter between the $i$th and $j$th sites, and $c_i^\dagger (c_j)$ is the creation (annihilation) operator of electrons at site $i (j)$. To obtain an effective Hamiltonian in the form of Eq. (1), we first construct a set of four maximally localized Wannier functions $|w_i(r)\rangle$ [25, 26] by freezing the states in the region of 0.3 eV above and below the band gap. We then obtain the matrix elements of the original GW Hamiltonian in the Wannier function basis $\langle w_i | H | w_j \rangle$, which can be directly associated with the $\varepsilon_i$ and $t_{ij}^{||}$ parameters appearing in Eq. (1). Finally, we cut less significant parameters by employing the criteria $|t_{ij}^{||}| < 0.1$ eV, and reoptimize the remaining parameters in order to obtain a better band description within the relevant energy region.

In Table I, we list the obtained TB parameters for monolayer BP, which is described by five in-layer hoppings up to a distance of 4.23 Å [see Fig. 4(c)]. We note that due to symmetry, the electron energies ($\varepsilon_i$) appearing in Eq. (1) are equivalent for all lattice sites. The corresponding model band structure is shown in Fig. 4(a) in comparison with the original GW bands. One can see that both electron and hole states are accurately reproduced within the region of $\sim 0.3$ eV each. Beyond that region, the four-band model does not give a reliable description due to the presence of additional bands of different symmetry. As can be seen from Table I, the band structure of monolayer BP is determined predominantly by the first two parameters, which describe the nearest-
TABLE I. Inlayer (t||) and interlayer (t⊥) hopping parameters obtained in terms of the TB Hamiltonian [Eqs. (1)] for monolayer and bilayer BP. d and N denote the distances between the corresponding interacting lattice sites and the coordination number at the given distance, respectively. The hoppings are schematically shown in Fig. 4(c).

| No. | t||, eV | d||, Å | N|| | t⊥, eV | d⊥, Å | N⊥ |
|-----|--------|-------|------|--------|-------|------|
| 1   | −1.22  | 2.72  | 2    | 0.295  | 3.60  | 2    |
| 2   | 3.665  | 2.24  | 1    | 0.273  | 3.81  | 2    |
| 3   | −0.205 | 3.34  | 2    | −0.151 | 5.05  | 4    |
| 4   | −0.105 | 3.47  | 4    | −0.091 | 5.08  | 2    |
| 5   | −0.055 | 4.23  | 1    | 0.000  | 5.44  | 1    |

neighbor in-plane (t||) and nearest-neighbor out-of-plane (t⊥) hopping parameters obtained in terms of the TB Hamiltonian [Eqs. (1)] for monolayer and bilayer BP. d and N denote the distances between the corresponding interacting lattice sites and the coordination number at the given distance, respectively. The hoppings are schematically shown in Fig. 4(c).
FIG. 4. (Color online) Band structures calculated by using the tight-binding parametrization (see text for details) in comparison with the original GW bands for (a) monolayer and (b) bilayer BP. Hopping parameters of the TB model are sketched in (c). (d) and (e) show the dependence of the monolayer TB model on the inlayer ($t^{\parallel}_2$) and nearest-neighbor interlayer ($t_{NN}^\perp$) hopping parameters.

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