



Tight binding parametrization of few-layer black phosphorus from first-principles calculations

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ABSTRACT

We employ a tight-binding parametrization based on the Slater Koster model in order to fit the band structures of single-layer, bilayer and bulk black phosphorus obtained from first-principles calculations. We find that our model, which includes 9 or 17 parameters depending on whether overlap is included or not, reproduces quite well the *ab initio* band structures over a wide energy range, especially the occupied bands. We also find that the inclusion of overlap parameters improves the quality of the fit for the conduction bands. On the other hand, hopping and on-site energies are consistent throughout the different systems, which is an indication that our model is suitable for calculations on multilayer black phosphorus and more complex situations in which first-principles calculations become prohibitive, such as disordered systems and heterostructures with a large lattice mismatch. We also discuss the limitations of the model and how the fit procedure can be improved for a more accurate description of bands in the vicinity of the Fermi energy.

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1. Introduction

Since the experimental discovery of graphene in 2004, a strong scientific effort has been employed in the study of this material. Many interesting structural and electronic properties were uncovered, with potential applications in the near future [1,2]. Despite its large carrier mobility in comparison with current silicon based devices, graphene is a zero-gap semiconductor, which undermines its application in electronic devices such as field effect transistors, which require a band gap. As such, a lot of research has been done in finding ways to open a band gap in graphene. One of the most promising routes so far is the application of external electric fields or doping in multilayer systems [3–6].

The success of graphene research and the search for a band gap also led to the study of other materials that share some structural similarities to graphene, the so-called 2D materials. These materials form a single layer of thickness of one up to a few atoms, and can be metallic, semiconducting or insulating, thus being suitable for many different applications [7,8]. Moreover, the weak van der Waals interactions between such layers allows the possibility of stacking them in many different ways in order to target specific electronic and optical properties, resulting in a set of materials now known as van der Waals heterostructures [9,10]. Among such

materials, few-layer black phosphorus (BP) is a promising candidate for future applications. Like graphite, it is a natural layered material that can be exfoliated down to a single layer, which is known as phosphorene in analogy to graphene [11,12]. Fig. 1 shows the crystal structure of bulk and single layer BP. We can see that each layer is composed of puckered zigzag chains of P atoms, a structure that leads to highly anisotropic transport and optical properties [13–16]. Moreover, theoretical predictions and experimental observations have confirmed that few-layer BP is a semiconductor with a band gap that can be tuned by the number of stacked layers, ranging from 1.73 eV for single-layer down to 0.35 eV in the bulk, which is a very desirable property for applications in optoelectronic devices [14,17,18].

From a theoretical point of view, the electronic and structural properties of few-layer BP can be accurately determined by first principles calculations, such as those based on Density Functional Theory (DFT) and the GW approximation for quasiparticle corrections [13,18–21]. However, such methods quickly become prohibitive with an increasing number of atoms in the unit cell, as is the case in calculations for transport properties in disordered systems and heterostructures with a large lattice mismatch. In such situations, semi empirical tight-binding (TB) calculations are often preferred, but they require an adequate parametrization, which may be obtained from theoretical calculations such as DFT and GW, or experimental data. There are a few available parametrizations so far, with different degrees of success in describing the

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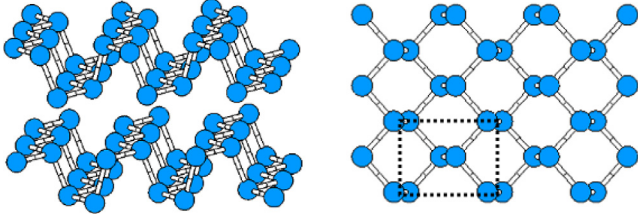


Fig. 1. Left: Crystal structure of black phosphorus, showing the puckered zigzag chains in each layer. Right: Top view of a single layer, also known as phosphorene. The dashed rectangle indicates an unit cell of the layer.

electronic properties of this material. In one class of parametrizations, based on projection techniques using Wannier functions and GW calculations, the proposed models include a single p_z -like orbital per atom [22,23]. Therefore, they do not fully capture the physics of sp^3 bonding in this system, due to the staggered nature of each layer. Such models include up to 15 parameters and are successful in describing the low energy properties of few-layer BP, specially near the Γ point of the Brillouin Zone, where the bands are mostly of p_z character. However, they do not fully describe these bands away from the Γ point, since they also contain contributions from s , p_x and p_y orbitals. Moreover, they describe only a limited number of bands, not taking into account most of the higher energy states. In a second class of parametrizations, based on atomic orbitals, the proposed models include all s and p orbitals, but employ a large number of parameters and can become very complex [24]. The reason for that is that the hopping between a pair of sites is parametrized individually (considering the symmetries of the structure), so they do not obey an analytical functional form with distance. Therefore, the number of parameters increases with the number of neighboring interactions considered, reaching up to 58 parameters for 8th neighbors. Such models can describe the valence and conduction bands of few-layer BP with a greater overall accuracy than the previous class of models, but they also fail to fully describe the higher energy bands, since the parameters are tailored to fit the low-energy states.

In this work, we provide a simple, yet reliable, tight-binding parametrization based on the Slater-Koster model for the electronic structure of few-layer BP, obtained from first-principles calculations. Our model includes s and p orbitals for each site and an exponential decay behavior for the hopping and overlap integrals, resulting in a number of parameters that range from 9 up to 17, depending on whether overlap parameters are included or not. The number of neighboring interactions can be controlled by a cut-off radius, whose value is chosen after convergence tests. The main advantages of this model, besides its simplicity, are that the associated TB parameters have a clear physical interpretation in terms of chemical bonding and that we can fit a larger number of bands in a wide energy range, as we describe below. Our paper is organized as follows: in the next section we present our methodology, including the first-principles calculations used to obtain the band structures, our tight-binding model used to fit them and the fitting procedure. In Section 3, we present our results by discussing calculations with and without overlap integrals, different energy ranges and how the resulting TB parameters compare with previous parametrizations. We also discuss the role of the basis choice in the first-principles calculations and the consistency of our results for single-layer, bilayer and bulk BP. Finally, in Section 4 we present our conclusions and discuss the suitability of our model for multilayer systems and more complex situations. We also discuss how the present model can be improved in order to reach a better fit quality.

2. Methodology

2.1. First-principles calculations

In the first step of our calculations, we perform first-principles calculations for single-layer, bilayer and bulk BP based on Density Functional Theory (DFT), as implemented on the SIESTA code [25–27]. We employ a double-zeta-polarized (DZP) pseudoatomic orbital basis to expand the wavefunctions. We have also performed calculations with a simpler single-zeta basis (SZ), which bears a closer correspondence to the sp^3 TB model used for the fits. We have found similar results for both basis sets, so we only discuss the results of the DZP basis here. A PBE exchange–correlation functional is used for the electron–electron interactions and norm-conserving Troullier–Martins pseudopotentials are employed for the ion–electron interactions [28,29]. The Brillouin Zone is sampled using a $10 \times 10 \times 1$ Monkhorst–Pack k-point grid for single-layer and bilayer BP and a $10 \times 10 \times 4$ for bulk BP [30]. For single-layer and bilayer BP, a vacuum distance of 20 Å is used in order to isolate the slabs from their periodic images.

Since experimental values for single-layer and bilayer BP are not yet available and theoretical predictions present variations depending on the choice of basis, exchange–correlation functional and inclusion of van–der–Waals interactions [13,19–21], we fix all structural parameters to the experimental values of bulk BP in all cases [31]. Finally, since DFT underestimates energy gaps, we perform a rigid shift of all conduction bands in order to reproduce the quasiparticle gaps obtained from GW calculations (a procedure also known as scissors shift) [18]. It is found in many cases that such a shift is the main effect of the quasiparticle corrections in semiconductors, so it is enough for the purposes of this work [32].

2.2. Tight-binding calculations: Slater-Koster model

In our TB model, we use an atomic basis with $3s$, $3p_x$, $3p_y$ and $3p_z$ orbitals for each atom, resulting in a 16×16 hamiltonian in k-space. Following the prescription of the Slater-Koster model within the two-center approximation, any hopping or overlap integral between orbitals centered at different atomic sites can be expressed in terms of their relative orientations and four integrals related to σ and π bonding [33].

The simplest case is the hopping between two equivalent s orbitals separated by a displacement vector \vec{r} pointing from one to another. It is given simply by $V_{ss}(\vec{r}) = V_{ss}(r)$ and does not depend on the orientation of the bond. The hopping between a s orbital and a p_i ($i = x, y, z$) orbital separated by a displacement vector \vec{r} from s to p is given by:

$$V_{sp_i}(\vec{r}) = l_i V_{sp\sigma}(r), \quad (1)$$

where $l_i = \vec{r} \cdot \hat{x}_i / r$ is the direction cosine of \vec{r} with respect to the corresponding cartesian direction and $V_{sp\sigma}(r)$ is the σ hopping between a s orbital and a p orbital directed along the bond. Similarly, the hopping between p_i and p_j orbitals ($i \neq j$) is given by:

$$V_{p_i p_j}(\vec{r}) = l_i l_j [V_{pp\sigma}(r) - V_{pp\pi}(r)], \quad (2)$$

where $V_{pp\sigma}(r)$ is the σ hopping between p orbitals directed along the bond and $V_{pp\pi}(r)$ is the π hopping between p orbitals directed perpendicular to the bond and parallel to each other. For two equivalent p orbitals centered at different sites, the expression is:

$$V_{p_i p_i}(\vec{r}) = l_i^2 V_{pp\sigma}(r) + (1 - l_i^2) V_{pp\pi}(r). \quad (3)$$

Therefore, all hoppings can be expressed in terms of direction cosines and the amplitudes $V_{ss}(r)$, $V_{sp\sigma}(r)$, $V_{pp\sigma}(r)$ and $V_{pp\pi}(r)$ calculated at the bond length. These amplitudes decrease as the distance

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