An Improved Tight-Binding Model for Phosphorene

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AN IMPROVED TIGHT-BINDING MODEL FOR PHOSPHORENE

by

KURSTI DELELLO

A thesis submitted in partial fulfillment of the requirements
for the Honors in the Major Program in Physics
in the College of Sciences
and in The Burnett Honors College
at the University of Central Florida
Orlando, Florida

Spring Term, 2016

Thesis Chair: Dr. Eduardo Mucciolo
Abstract

The intent of this thesis is to improve upon previously proposed tight-binding models for one dimensional black phosphorus, or phosphorene. Previous models offer only a qualitative analysis of the band structure of phosphorene, and fail to fully realize critical elements in the electronic band structure necessary for transport calculations. In this work we propose an improved tight-binding model for phosphorene by including up to eight nearest-neighbor interactions. The efficacy of the model is verified by comparison with DFT-HSE06 calculations, and the anisotropy of the effective masses in the armchair and zigzag directions is considered.
Dedication

For my mother.
Acknowledgments

I would like to thank everyone who made this work possible, especially my thesis chair and mentor, Dr. Eduardo Mucciolo. Your guidance over the past couple of years has been invaluable and sent me on the path I am today. Thank you to Carlos Páez for his tireless work and patient explanations. To my committee members, thank you for your support. A big thank you to Sean Wiggins; without your love and support these past months I’m not sure where I would be.
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1 Introduction

Black phosphorus was initially discovered by P. W. Bridgman in 1914 in an attempt to convert white phosphorus to red phosphorus using high hydrostatic pressure [1]. This was achieved using a 200°C oil bath and 1.2 GPa of pressure. Bridgman found that black phosphorus was more dense than either white or red phosphorus, and also the most stable allotrope of the three in air. Studies into its bulk conductivity revealed that it is a semiconductor, while both the red and white allotropes are "nearly perfect insulators". With black phosphorus also being the most dense of the three allotropes, Bridgman originally theorized that the reason behind its conductivity was due to the atoms being packed more closely together in black phosphorus, causing the electrons to be "squeezed out" of the atoms, enabling them to travel freely throughout the bulk of the material. This explanation predates quantum mechanics and cannot be taken completely seriously today.

After this black phosphorus received relatively little attention, until the early 1980s, at which point single-crystal growth of black phosphorus became possible [2]. This sparked a number of theoretical and experimental studies into the optical and electronic properties of black phosphorus [3][4][5], which began to take a look into the electronic structure of the material and the physical properties of its bulk form. In 2004 graphene was first isolated and characterized [6], leading to intense interest and investigation into other two-dimensional (2D) materials, such as transition metal dichalcogenides (TMDs), which have also been studied extensively. It was only as recently as 2014 that 2D black phosphorus, from here on referred to as phosphorene, was fabricated, using the mechanical exfoliation techniques first used by Novoselov et al. on graphene [7],[8].
1.1 Physical Characteristics

Black phosphorus features an orthorhombic crystal structure, whose individual layers feature a puckered, honeycomb lattice structure, as illustrated in Figure 1.

(a) Trilayer black phosphorus.

(b) Unit cell of phosphorene.

Figure 1: Crystal structure of phosphorene.
Each atom is covalently bonded to three of its neighbors, resulting in two bond lengths, \( d_1 \) and \( d_2 \), and two bond angles, \( \alpha_1 \) and \( \alpha_2 \), whose values can be found in Table 1[3]. The two bond lengths are approximately equal, and the angles close to 90°. From Bent’s rule [9] we therefore expect that these bonds be predominantly made of 3p orbitals. Within layers the bonds between the phosphorus atoms are chemically saturated, leading to van der Waals-like interactions between different layers. It is this property of phosphorene that allows it to be mechanically exfoliated down to the monolayer level of thickness.

**Table 1:** List of lattice constants for phosphorene.

<table>
<thead>
<tr>
<th>lattice parameters</th>
<th>a 3.3133Å</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>b 10.473Å</td>
</tr>
<tr>
<td></td>
<td>c 4.374Å</td>
</tr>
<tr>
<td>crystal structural parameters</td>
<td>u 0.0806</td>
</tr>
<tr>
<td></td>
<td>v 0.1034</td>
</tr>
<tr>
<td>bond lengths</td>
<td>( d_1 ) 2.222Å</td>
</tr>
<tr>
<td></td>
<td>( d_2 ) 2.277Å</td>
</tr>
<tr>
<td>bond angles</td>
<td>( \alpha_1 ) 96.5°</td>
</tr>
<tr>
<td></td>
<td>( \alpha_2 ) 101.9°</td>
</tr>
</tbody>
</table>

Although in ambient conditions black phosphorus has an orthorhombic crystal structure, through application of pressure the crystal structure can undergo several reversible phase transitions [10], going from orthorhombic, to rhombohedral at 5 GPa, and then to simple cubic at 10 GPa, although the pressure at which it undergoes these phase transitions can be influenced by temperature [4]. Its rhombohedral structure exhibits semimetallic behavior, whereas the simple cubic structure is metallic.

While black phosphorus is reportedly the most stable allotrope of phosphorus in its bulk form, its 2D counterpart is significantly less stable. Recent theoretical and experimental studies have confirmed the hydrophilic nature of phosphorene [11] [12]. This hydrophilic nature leads to water being absorbed to samples exposed to air, with droplets forming on
the surface after several hours; when returned to vacuum conditions, however, these droplets disappear. After more than a week of exposure to air phosphorene begins to deteriorate irreversibly. While this property can be a major drawback for certain applications, it can also be an advantage for other applications, such as sensors and support for biomolecules, where most other 2D materials are particularly ill-suited to due their hydrophobic nature [13] [14].

1.2 Optoelectronic Characteristics

Phosphorene, and consequently black phosphorus, fall into an interesting range of the optoelectronic spectrum, especially when considered in the context of other 2D materials, such as graphene and the various TMDs. Graphene has generated intense interest since it was first exfoliated in 2004 [6]. While it features no band gap, the material enjoys high carrier concentrations of up to $10^{13}$ cm$^{-2}$, and room temperature mobilities reaching around $10^4$ cm$^2$/V·s. The absence of an intrinsic band gap in graphene, however, gives it a poor on/off ratio, generally less than 10, and makes it a less than ideal candidate for logic and optical devices. TMDs, on the other hand, typically display an indirect to direct band gap transition in the monolayer limit [15]. The band gap for these materials is generally found in the range of 1.5 – 2.5 eV, and they typically exhibit high on/off ratios that can reach as high as $10^{10}$, ideal for fast-switching logic devices. Unfortunately, the carrier mobility of these materials is relatively low, generally lower than 100 cm$^2$/V·s.

Phosphorene, however, exhibits electronic properties which can bridge the gap between graphene and TMDs. With a layer-dependent band gap that spans from 0.3 – 2.0 eV [8], on/off ratios as high as $10^5$, and mobilities ranging from $\sim 200 – 1,000$ cm$^2$/V·s [7] [8] [16], making it an ideal candidate for ultra-low power electronics. The material’s unique, puckered crystal structure lends itself to highly anisotropic properties, which can lead to novel device structures and applications [17]. The effective mass of carriers along the zigzag direction is
up to ten times larger than those in the armchair direction, giving rise to strong in-plane anisotropy in its electrical, optical and phonon properties [16] [18] [19].
2 Literature Review

Current methods for calculating the band structure of phosphorene include density functional theory (DFT), the \( \text{GW}_0 \) approximation, pseudopotentials, and a linear combination of atomic orbitals (LCAO), which can also be referred to as a tight-binding model.

The local density approximation (LDA) is the most commonly applied DFT approximation to the electronic exchange and correlation. While this approach is highly successful in predicting the overall trend of the band structure of various materials, it suffers consistently from inaccuracies when predicting the band gap and can be computationally expensive [20]. For large-gap materials LDA vastly underestimates the band gap, whereas for metals the bandwidth is slightly overestimated. Hybrid Fock DFT functionals have proven to be successful; however, these often result in large computational requirements, owing to the long-range nature of the Fock exchange interaction. Other hybrid DFT functionals have appeared in an attempt to alleviate these issues, such as the one proposed by Heyd \textit{et al.} [21]; while these can also suffer from the over or underestimation of the band gaps of certain materials, they generally have better success in predicting the value, and can also drastically reduce the computational cost as compared to other DFT calculations. Similarly, the \( \text{GW}_0 \) approximation, which is a many-body extension of DFT, typically offers accurate results, especially in regards to the ground state properties, but can suffer problems not unlike those of DFT, such as high computational costs, and poor scalability [22].

Attempts at studying the electronic properties of black phosphorus have also been made using a self-consistent pseudopotential approach [5], which has largely been successful at predicting the behavior of black phosphorus under strain, but fails to resolve the anisotropy in the effective mass along the zigzag and armchair directions.

Finally, a tight-binding model has been developed which includes nearest and next-nearest neighbor interactions [23]. While this model offers only a qualitative view of the behavior of
the band structure, it also provides reasonable predictions in agreement with experimental results, and can serve as a good starting point for future models.
3 Methodology

We propose to develop an effective tight-binding model based on the LCAO methods found in [23], and use DFT calculations as the basis for adjusting the model parameters. The simplified LCAO model, used as a preliminary study, is as follows:

3.1 Preliminary Model

The matrix element (transfer integral) between two adjacent atoms is given as $V_{ll'm'}(d) = \eta_{ll'm'}h^2/m_0d^2$, where $d$ is the inter-atomic distance, $m_0$ is the electron rest mass, $l$ and $l'$ are the orbital azimuthal quantum numbers ($s, p$) of two atoms, and $m$ is the common orbital magnetic quantum number ($\sigma, \pi$) along the axis connecting two atoms. $\eta_{ll'm'}$ is a dimensionless quantity that should be chosen depending on the crystal structure. For the preliminary study, the parameters employed are: $\eta_{ss\sigma} = -1.40, \eta_{sp\sigma} = 1.84, \eta_{pp\sigma} = 3.24, \eta_{pp\pi} = -0.81$, as provided by Harrison [24].

This model is applied to monolayer black phosphorus, whose crystal structure is displayed in Figure 1a, with unit cell shown in Figure 1b, and Brillouin zone shown in Figure 2. Four atoms are contained in the unit cell: A, A’, B, and B’, which are located at $\tau_A = (uc, 0, vb), \tau_{A'} = -\tau_A, \tau_B = ((1/2 - u)c, 0, vb)$, and $\tau_{B'} = -\tau_B$, respectively, where $a$, $b$ and $c$ are lattice constants, and $u$ and $v$ are dimensionless parameters. The lattice parameters used for black phosphorus are: $a = 3.314$ Å, $b = 10.478$ Å, $c = 4.376$ Å, $u = 0.08056, v = 0.10168$. The lattice displacement vectors are: $d^{(1)} = \tau_B - \tau_A, d^{(1)'} = (\tau_B - a) - \tau_A, d^{(2)} = \tau_{A'} - \tau_A, d^{(2)'} = \tau_{B'} - (\tau_B - a - c)$ with $a = (0, a, 0)$, and $c = (c, 0, 0)$. 
When expressed in momentum space, the tight-binding Hamiltonian is a $16 \times 16$ matrix, with the Bloch sum of the wave functions of the orbitals at the A, A’, B, and B’ sites taken as the basis vectors:

$$\begin{bmatrix}
M_0 & M_1 & M_2^+ & 0 \\
M_1^\dagger & M_0 & 0 & M_2^- \\
M_2^{+\dagger} & 0 & M_0 & M_1^\dagger \\
0 & M_2^{-\dagger} & M_1 & M_0
\end{bmatrix}. \quad (1)$$

Here the elements $M_0, M_1, M_2^\pm$, are themselves $4 \times 4$ matrices. The $M_0$ matrix on the diagonal expresses the energies of the four atomic sites:

$$M_0 = \begin{bmatrix}
\epsilon_s & 0 & 0 & 0 \\
0 & \epsilon_p & 0 & 0 \\
0 & 0 & \epsilon_p & 0 \\
0 & 0 & 0 & \epsilon_p
\end{bmatrix}. \quad (2)$$

Here, $\epsilon_s = -17.10$ eV and $\epsilon_p = -8.33$ eV represent the energy levels of the 3s and 3p orbitals of phosphorus, respectively. The nearest and next-nearest neighbor coupling between atoms
are represented by $M_1$ and $M_2^\pm$, respectively:

$$
M_1 = \begin{bmatrix}
E_{ss}^{(1)} g_1^+ & E_{sx}^{(1)} g_1^+ & E_{sy}^{(1)} g_1^- & 0 \\
-E_{sx}^{(1)} g_1^+ & E_{xx}^{(1)} g_1^+ & E_{xy}^{(1)} g_1^- & 0 \\
-E_{sy}^{(1)} g_1^- & E_{xy}^{(1)} g_1^- & E_{yy}^{(1)} g_1^+ & 0 \\
0 & 0 & 0 & E_{zz}^{(1)} g_1^+
\end{bmatrix}
$$

(3)

and,

$$
M_2^\pm = \begin{bmatrix}
E_{ss}^{(2)} g_2^\pm & \pm E_{sx}^{(2)} g_2^\pm & 0 & E_{sz}^{(2)} g_2^\mp \\
\mp E_{sx}^{(2)} g_2^\pm & E_{xx}^{(2)} g_2^\pm & 0 & \pm E_{sz}^{(2)} g_2^\mp \\
0 & 0 & E_{yy}^{(2)} g_2^\pm & 0 \\
- E_{sz}^{(2)} g_2^\pm & \pm E_{sz}^{(2)} g_2^\pm & 0 & E_{xx}^{(2)} g_2^\pm
\end{bmatrix}
$$

(4)

In $M_1$ and $M_2^\pm$: $E_{ss}^{(i)} = V_{ss\sigma}(d(i))$, $E_{sx}^{(i)} = (d(i)/d(i)){V_{sp\sigma}}(d(i))$, and $E_{\alpha\beta}^{(i)} = (d(i)/d(i)/d(i^2))V_{pp\sigma}d(i) + (\delta_{\alpha\beta} - d(i)/d(i)/d(i^2)){V_{pp\sigma}}(d(i))$, with $i = 1, 2$ and $\alpha, \beta = x, y, z$, and the phase factors $g_1^\pm = \exp{ikd(i)} \pm \exp{ik'\cdot d^{(1)}}$ and $g_2^\pm = \exp{ikd^{(2)}}$, $g_2^- = \exp{ikd^{(2)}}$. By diagonalizing $H$ the band dispersion of monolayer phosphorus can be obtained, as shown in Figure 3.
The 16 bands are divided into eight pairs, where the lowest two pairs can be considered as 3s bands, the next three pairs as 3p bonding bands, and the highest three pairs as 3p anti-bonding bands.

Unfortunately this model fails to resolve finer details in the band structure, important for electronic transport calculations. In this case the model can be greatly improved by including more nearest neighbor interactions, covered in the next section.

3.2 Improved Model

The model from the previous section is improved by including more nearest-neighbor interactions, the full extent of which are displayed in Figure 4.
Figure 4: Displacement vectors used in improved tight-binding model.

The updated list of displacement vectors representing these interactions are included in Table 2.

Table 2: Displacement vectors for nearest-neighbor interactions.

<table>
<thead>
<tr>
<th>$d^{(1)}$</th>
<th>$\tau_B - \tau_A$</th>
<th>$d^{(4)}$</th>
<th>$\tau_A - (\tau_B - c - a)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d^{(2)}$</td>
<td>$\tau_{B'} - (\tau_B - a - c)$</td>
<td>$d^{(3)}$</td>
<td>$a$</td>
</tr>
<tr>
<td>$d^{(5)}$</td>
<td>$\tau_A - \tau_{B'}$</td>
<td>$d^{(6)}$</td>
<td>$\tau_A - (\tau_{A'} - a)$</td>
</tr>
<tr>
<td>$d^{(5R)}$</td>
<td>$\tau_{B'} - \tau_A + a + c$</td>
<td>$d^{(5L)}$</td>
<td>$\tau_{B'} - \tau_A + a + c$</td>
</tr>
<tr>
<td>$d^{(6L)}$</td>
<td>$\tau_{B'} - \tau_B + 2a + c$</td>
<td>$d^{(7)}$</td>
<td>$\tau_{A'} - (\tau_A - c)$</td>
</tr>
<tr>
<td>$d^{(8)}$</td>
<td>$c$</td>
<td>$d^{(1)'}$</td>
<td>$\tau_B - a - \tau_A$</td>
</tr>
<tr>
<td>$d^{(2)'}$</td>
<td>$\tau_A - \tau_A$</td>
<td>$d^{(3)'}$</td>
<td>$-a$</td>
</tr>
<tr>
<td>$d^{(4)'}$</td>
<td>$\tau_A - (\tau_B - c)$</td>
<td>$d^{(5)'}$</td>
<td>$\tau_A - \tau_{B'} - a$</td>
</tr>
<tr>
<td>$d^{(5L)'}$</td>
<td>$\tau_{B'} - \tau_A + a + c$</td>
<td>$d^{(6)'}$</td>
<td>$\tau_{B'} - (\tau_A + c)$</td>
</tr>
<tr>
<td>$d^{(6L)'}$</td>
<td>$\tau_{B'} - \tau_B + c$</td>
<td>$d^{(7)'}$</td>
<td>$\tau_{B'} - (\tau_B - a)$</td>
</tr>
<tr>
<td>$d^{(8)'}$</td>
<td>$-c$</td>
<td>$d^{(8)'}$</td>
<td>$-c$</td>
</tr>
</tbody>
</table>

The new tight-binding Hamiltonian is
\[
H = 
\begin{bmatrix}
M_0 + M_3 + M_8 & M_1 + M_4 & M_2^+ + M_6^+ + M_7^+ & M_5^+ + M_5L \\
M_1^+ + M_4 & M_0 + M_3 + M_8 & M_5^+ + M_5L & M_2^+ + M_6L + M_7^+ \\
M_2^- + M_6R + M_7^+ & M_5R + M_5L & M_0 + M_3 + M_8 & M_1^+ + M_4 \\
M_5R + M_5L & M_2^+ + M_6L + M_7^- & M_1 + M_4 & M_0 + M_3 + M_8
\end{bmatrix}
\] \quad (5)

The \(M_0\), \(M_1\), and \(M_2^\pm\) matrices are as before, and the new coupling matrices are as follows:

\[
M_3 = 
\begin{bmatrix}
E_{ss}^{(3)} g_3^+ & 0 & E_{sy}^{(3)} g_3^- & 0 \\
0 & E_{xx}^{(3)} g_3^+ & 0 & 0 \\
-E_{sy}^{(3)} g_3^- & 0 & E_{yy}^{(3)} g_3^+ & 0 \\
0 & 0 & 0 & E_{zz}^{(3)} g_3^+
\end{bmatrix}
\] \quad (6)

\[
M_4 = 
\begin{bmatrix}
E_{ss}^{(4)} g_4^+ & E_{sx}^{(4)} g_4^+ & E_{sy}^{(4)} g_4^- & 0 \\
-E_{sx}^{(4)} g_4^+ & E_{xx}^{(4)} g_4^+ & E_{xy}^{(4)} g_4^- & 0 \\
-E_{sy}^{(4)} g_4^- & E_{xy}^{(4)} g_4^- & E_{yy}^{(4)} g_4^+ & 0 \\
0 & 0 & 0 & E_{zz}^{(4)} g_4^+
\end{bmatrix}
\] \quad (7)

\[
M_5^L = 
\begin{bmatrix}
E_{ss}^{(5)R} g_{5L}^+ & E_{sx}^{(5)R} g_{5L}^+ & E_{sy}^{(5)R} g_{5L}^- & E_{sz}^{(5)R} g_{5L}^+ & E_{ss}^{(5)R} g_{5L}^+ \\
-E_{sx}^{(5)R} g_{5L}^+ & E_{xx}^{(5)R} g_{5L}^+ & E_{xy}^{(5)R} g_{5L}^- & E_{xz}^{(5)R} g_{5L}^+ & E_{ss}^{(5)R} g_{5L}^+ \\
-E_{sy}^{(5)R} g_{5L}^- & E_{xy}^{(5)R} g_{5L}^- & E_{yy}^{(5)R} g_{5L}^+ & E_{yz}^{(5)R} g_{5L}^- & E_{ss}^{(5)R} g_{5L}^+ \\
-E_{sz}^{(5)R} g_{5L}^+ & E_{xz}^{(5)R} g_{5L}^+ & E_{yz}^{(5)R} g_{5L}^- & E_{zz}^{(5)R} g_{5L}^+ & E_{ss}^{(5)R} g_{5L}^+
\end{bmatrix}
\] \quad (8)
\[
M_{6L}^R = \begin{bmatrix}
E_{ss}^{(6)} g_{6L}^+ & E_{sx}^{(6)} g_{6L}^+ & E_{sy}^{(6)} g_{6L}^+ & E_{sz}^{(6)} g_{6L}^+ & \pm E_{sz}^{(6)} g_{6L}^+ \\
-E_{sx}^{(6)} g_{6L}^- & E_{xx}^{(6)} g_{6L}^+ & E_{xy}^{(6)} g_{6L}^+ & E_{xz}^{(6)} g_{6L}^+ & \pm E_{xz}^{(6)} g_{6L}^+ \\
-E_{sy}^{(6)} g_{6L}^- & E_{yx}^{(6)} g_{6L}^+ & E_{yy}^{(6)} g_{6L}^+ & E_{yz}^{(6)} g_{6L}^+ & \pm E_{yz}^{(6)} g_{6L}^+ \\
\mp E_{sz}^{(6)} g_{6L}^- & -E_{xz}^{(6)} g_{6L}^+ & \pm E_{yz}^{(6)} g_{6L}^- & E_{zz}^{(6)} g_{6L}^+ & \pm E_{zz}^{(6)} g_{6L}^+
\end{bmatrix}
\]

(9)

\[
M_{7}^\pm = \begin{bmatrix}
E_{ss}^{(7)} g_7^\pm & \pm E_{sx}^{(7)} g_7^\pm & 0 & E_{sz}^{(7)} g_7^\pm \\
-E_{sx}^{(7)} g_7^\pm & E_{xx}^{(7)} g_7^\pm & 0 & \pm E_{xz}^{(7)} g_7^\pm \\
0 & 0 & E_{yy}^{(7)} g_7^\pm & 0 \\
-E_{sz}^{(7)} g_7^\pm & \pm E_{xz}^{(7)} g_7^\pm & 0 & E_{zz}^{(7)} g_7^\pm
\end{bmatrix}
\]

(10)

\[
M_8 = \begin{bmatrix}
E_{ss}^{(8)} g_8^+ & \pm E_{sx}^{(8)} g_8^- & 0 & 0 \\
-E_{sx}^{(8)} g_8^- & E_{xx}^{(8)} g_8^+ & 0 & 0 \\
0 & 0 & E_{yy}^{(8)} g_8^+ & 0 \\
0 & 0 & 0 & E_{zz}^{(8)} g_8^+
\end{bmatrix}
\]

(11)

In the newly defined matrices, \(E_{ss}^{(i)} = G_{ss} L_{ss}^{(i)} V_{ss\sigma}(d^{(i)})\), \(E_{sa}^{(i)} = G_{sa} L_{sa}^{(i)} (d_{a}^{(i)}/d^{(i)}) V_{sp\sigma}(d^{(i)})\), and \(E_{\alpha\beta}^{(i)} = G_{\alpha\beta} L_{\alpha\beta}^{(i)} [(d_{\alpha}^{(i)} d_{\beta}^{(i)}/d^{(i)})^2 V_{pp\sigma}(d^{(i)}) + (\delta_{\alpha\beta} - d_{\alpha}^{(i)} d_{\beta}^{(i)}/d^{(i)}) V_{pp\sigma}(d^{(i)})]\), with \(i = 1, 2\) and \(\alpha, \beta = x, y, z\), with phase factors equal to \(g_j^\pm = \exp(ik d^{(j)}) \pm \exp(ik d^{(j)})^*\), where \(j = 1, \ldots, 5L, \ldots, 8\), except for \(j = 2, 7\). In these cases \(g_j^\pm = \exp(ik d^{(j)})\), and \(g_j^- = \exp(-ik d^{(j)})\). These definitions are similar to those used in the preliminary model, with the addition of two new parameters, \(G_{\alpha\beta}\), and \(L_{\alpha\beta}^{(i)}\), which stand for "global parameter" and "local parameter." Similarly, the new transfer integrals are \(V_{ii'\sigma}(d) = \eta_{ii'\sigma} \hbar/m_0 d^2\), where \(i = 1 \ldots 8\). The reasoning for these new parameters is that those provided by Slater-Koster coefficients are not sufficient to accurately describe the data. These must be modified in order to provide an accurate representation of the band gap. A full list of coefficients used in this model and their values can be found in the appendix.
4 Results

4.1 Band Structure

The band structure obtained from these parameters can be seen in Figure 5, along with the DFT band structure used for comparison. It can be noted that the two models are in good agreement, especially around the Γ-point.

![Figure 5: Comparison between reference DFT and tight-binding model for the electronic band structure of phosphorene.](image)

To further confirm the accuracy of the model we look at the relative orbital contributions in Figure 6.
Figure 6: Relative orbital contributions for the conduction and valence bands for tight-binding model.

It can be seen that the majority of the orbital contributions in either band are from the \( p_z \) orbitals, around 98% for the conduction band and 92% for the valence band, with little to no contribution from any other orbital. For comparison, DFT calculations predict approximately 70% contribution for the \( p_z \) orbital in the conduction band, and 90% in the valence band, see Figure 7. The tight-binding model is therefore a reasonable approximation.

Figure 7: Relative orbital contributions for the conduction and valence bands from the reference DFT calculations.
4.2 Effective Mass

![Graph](image)

(a) Valence band

(b) Conduction band

Figure 8: 3D plots of the valence and conduction bands using the improved tight-binding model.

The effective mass of the valence and conduction bands in the armchair and zigzag directions can be used to predict in-plane anisotropy in charge transport, which has been reported numerous times in experiments [16][17][18][19]. To do this the conduction and valence bands in either direction were plotted and fit with a quadratic curve of the form \( y = ax^2 + bx + c \), seen in Figure 9.
Figure 9: Curve fitting for effective mass for the valence and conduction bands in the armchair (positive) and zigzag (negative) directions.

The ratio of the effective masses was found with the following equation,

\[
\frac{m^*}{m_e} = \frac{\hbar^2}{2am_e},
\]  

the results of which are summarized in Table 3.
Table 3: Effective mass for valence and conduction bands in the armchair and zigzag directions.

<table>
<thead>
<tr>
<th></th>
<th>v</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>0.130043</td>
<td>0.144135</td>
</tr>
<tr>
<td>ZZ</td>
<td>2.44532</td>
<td>1.04656</td>
</tr>
</tbody>
</table>

The effective mass in the zigzag direction is significantly heavier than that in the armchair direction, which gives rise to the anisotropic electrical conductance and excitons reported in previous experiments [17][18].
5 Conclusion

We began with a preliminary tight-binding model that has previously been used for a qualitative discussion on the electronic band structure of phosphorene, which included only second nearest-neighbor interactions. To continue, up to eight-neighbor interactions were included to bring the model from a qualitative one to a quantitative one, allowing for more rigorous calculations.

To demonstrate the efficacy of the model, DFT-HSE06 calculations were used as a benchmark. In the band structure the model matched accurately with DFT calculations near the main gap region of the spectrum. The next point to consider was relative orbital contributions of the bands. The tight-binding model accurately predicted that the major contribution to the bands comes from $p_z$ orbitals, although this contribution was overestimated for the conduction band. DFT calculations predict about 70% contribution from $p_z$ orbitals in the conduction band, whereas the tight-binding model predicts 98%. Both calculations predict around 90% contribution from $p_z$ for the valence band.

The effective masses were investigated, and the effective mass in the zigzag direction was found to be around ten times greater than that in the armchair direction, which agrees with experimental results. The next step for this model would be to investigate the effect of the anisotropy of the effective mass on electronic transport, and the effect of disorder in the system.
Appendix: List of Parameters and their Values
Table 4: Table of values for variable $G_{\alpha\beta}$.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G_{ss}$</td>
<td>0.209911963</td>
</tr>
<tr>
<td>$G_{sx}$</td>
<td>1.996392203</td>
</tr>
<tr>
<td>$G_{sy}$</td>
<td>0.999715639</td>
</tr>
<tr>
<td>$G_{sz}$</td>
<td>0.989120306</td>
</tr>
<tr>
<td>$G_{xx}$</td>
<td>1.908096318</td>
</tr>
<tr>
<td>$G_{xy}$</td>
<td>1.013882680</td>
</tr>
<tr>
<td>$G_{xz}$</td>
<td>0.306432200</td>
</tr>
<tr>
<td>$G_{yy}$</td>
<td>3.012483116</td>
</tr>
<tr>
<td>$G_{yz}$</td>
<td>2.003825037</td>
</tr>
<tr>
<td>$G_{zz}$</td>
<td>3.194543177</td>
</tr>
</tbody>
</table>
Table 5: Modified Slater-Koster coefficients. \( \eta_{mci} \) denotes a cross term.

<table>
<thead>
<tr>
<th>( \eta )</th>
<th>Value</th>
<th>( \eta )</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \eta_{ss\sigma 1} )</td>
<td>-1.397197823</td>
<td>( \eta_{ss\sigma 5} )</td>
<td>-1.401372964</td>
</tr>
<tr>
<td>( \eta_{sp\sigma 1} )</td>
<td>0.332639375</td>
<td>( \eta_{sp\sigma 5} )</td>
<td>0.375157776</td>
</tr>
<tr>
<td>( \eta_{pp\sigma 1} )</td>
<td>2.046916423</td>
<td>( \eta_{pp\sigma 5} )</td>
<td>2.031179025</td>
</tr>
<tr>
<td>( \eta_{pp\sigma c 1} )</td>
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<td>( \eta_{pp\sigma c 5} )</td>
<td>-0.678438179</td>
</tr>
<tr>
<td>( \eta_{pp\sigma 2} )</td>
<td>3.049847256</td>
<td>( \eta_{pp\sigma c 6} )</td>
<td>2.032306278</td>
</tr>
<tr>
<td>( \eta_{pp\sigma c 1} )</td>
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<td>-1.396849302</td>
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<td>-1.400606738</td>
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<tr>
<td>( \eta_{sp\sigma 2} )</td>
<td>0.349955726</td>
<td>( \eta_{sp\sigma 6} )</td>
<td>0.356305993</td>
</tr>
<tr>
<td>( \eta_{pp\sigma 2} )</td>
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<td>( \eta_{pp\sigma 6} )</td>
<td>2.020451022</td>
</tr>
<tr>
<td>( \eta_{pp\sigma 3} )</td>
<td>-0.677704845</td>
<td>( \eta_{pp\sigma 6} )</td>
<td>-0.726892550</td>
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<td>( \eta_{ss\sigma 7} )</td>
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</tr>
<tr>
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</tr>
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<tr>
<td>( \eta_{ss\sigma 4} )</td>
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<td>9.797396315</td>
</tr>
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<td>( \eta_{sp\sigma 4} )</td>
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<td>( \eta_{pp\sigma 4} )</td>
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Table 6: Table of values for variable $L_{\alpha\beta}$.

<table>
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<tr>
<th>$L_{xx}$</th>
<th>$L_{yy}$</th>
<th>$L_{zz}$</th>
<th>$L_{xy}$</th>
<th>$L_{xz}$</th>
<th>$L_{yz}$</th>
</tr>
</thead>
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<td>$L_{2\times1}^{(2)}$</td>
<td>$L_{3\times1}^{(3)}$</td>
<td>$L_{4\times1}^{(4)}$</td>
<td>$L_{5\times1}^{(5)}$</td>
<td>$L_{6\times1}^{(6)}$</td>
</tr>
<tr>
<td>0.817928260</td>
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</tr>
<tr>
<td>$L_{1\times2}^{(1)}$</td>
<td>$L_{2\times2}^{(2)}$</td>
<td>$L_{3\times2}^{(3)}$</td>
<td>$L_{4\times2}^{(4)}$</td>
<td>$L_{5\times2}^{(5)}$</td>
<td>$L_{6\times2}^{(6)}$</td>
</tr>
<tr>
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<td>-2.767316320</td>
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</tr>
<tr>
<td>$L_{1\times3}^{(1)}$</td>
<td>$L_{2\times3}^{(2)}$</td>
<td>$L_{3\times3}^{(3)}$</td>
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</tr>
<tr>
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<td>3.758296042</td>
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</tr>
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<td>$L_{3\times5}^{(3)}$</td>
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<td>$L_{1\times6}^{(1)}$</td>
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<td>$L_{3\times6}^{(3)}$</td>
<td>$L_{4\times6}^{(4)}$</td>
<td>$L_{5\times6}^{(5)}$</td>
<td>$L_{6\times6}^{(6)}$</td>
</tr>
</tbody>
</table>
6 References


