

STRAIN-CAUSED BAND GAP MODULATION IN PHOSPHORENE AS A PROMISING 2D MATERIAL FOR NANO-ELECTRONICS

In the Earth's crust, black phosphorus comprises around 0.1% and forms a layered molecular crystal with giant planar monoatomic P layers, known as lamellae, alongside other P allotropes. Our focus is on phosphorene, a single-layer black phosphorus, a relatively new two-dimensional (2D) material discovered separately by different teams in 2014. Unlike graphene's flat structure, phosphorene has a puckered crystal structure (see Fig. 1(a)–1(d)), making it anisotropic, influencing its electronic, optical, thermal, transport, and mechanical properties [1, 2]. Phosphorene's electronic structure involves a direct band gap but reported calculations range widely from 0.76 eV to 2.31 eV, with experimental values spanning 1.45–2.2 eV [3]. As the phosphorene layers increase, the band gap reduces linearly to values akin to bulk black phosphorus, around 0.31–0.36 eV. Mechanically, phosphorene withstands up to 27–30% strain in uniaxial and 10–13% in shear deformations [4]. That is why it acts as a promising material, akin to graphene, for flexible electronics due to its exceptional mechanical flexibility.

The study is also motivated by the literature inconsistencies in deformation-affected band-gap values, which vary significantly even without strain, and the lack of research on the shearing impact on the band-gap behaviour.

In contrast to our previous phosphorene-related work [5], in the present study we use an alternative approach to include the distance dependence of the hopping parameters on the strain in the tight-binding method.

METHODS OF NUMERICAL STUDY

Tight-Binding Model and Strain-Affected Hoppings

The tight-binding (TB) Hamiltonian incorporates p_z -like orbitals for the five nearest neighbour hopping integrals ($\gamma_1, \gamma_2, \gamma_3, \gamma_4, \gamma_5$), as schematically shown in Fig. 1, with summation over phosphorene lattice sites i and j ,

$$\hat{H} = \sum_{i \neq j} \gamma_{ij} c_i^\dagger c_j + \text{H.c.}, \quad (1)$$

where $c_i^\dagger$ and c_j are the electron creation and annihilation operators, respectively. Hamiltonian (1) focuses on a defect-free lattice, assuming equal electron energy across the sites.

The hopping integral values for the strain-free phosphorene can be adopted from the literature. The density of electronic states (DOS) is determined through the Hamiltonian $\hat{H}$ as

$$\rho(E) = \text{Tr}[\delta(E - \hat{H})/S] \quad (1)$$

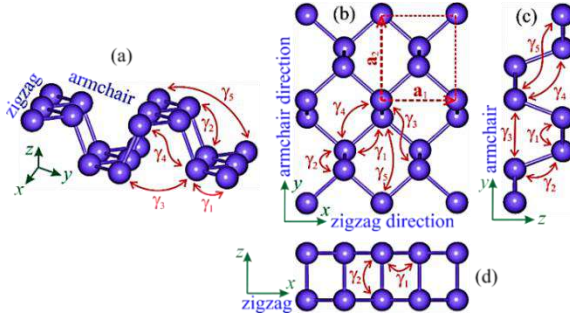


Figure 1 – Black phosphorene crystal lattice: perspective (a), top (b), side (c), (d) views. Dashed rectangle (b) sketches the basic unit cell with the basis translation vectors $\mathbf{a}_1$, $\mathbf{a}_2$. Parameters γ_1 – γ_5 (a)–(d) denote 5 inequivalent hopping integrals for the first 5 nearest neighbour sites. The structure is drawn following the design in [5].

To avoid quadratic computational complexity, we use a numerical method allowing linear scaling. While not delving into the details here, this method is suitable for lattices with millions of atoms. Our model computes a phosphorene lattice of 1300×1000 atoms, approximating a realistic $\approx 450 \times 450 \text{ nm}^2$ sample size that is typical for experiments.

To investigate alterations in the electronic structure of phosphorene due to strain, we examine two deformation types: uniaxial tensile and shear strains, illustrated in Figs. 2(a)–2(b) and 2(c)–2(d), respectively. These strains can be implemented by stretching or shearing along the zigzag direction, as depicted in Figs. 2(a) and 2(c), or the armchair direction, shown in Figs. 2(b) and 2(d). Other directions can be achieved by combining armchair and zigzag orientations.

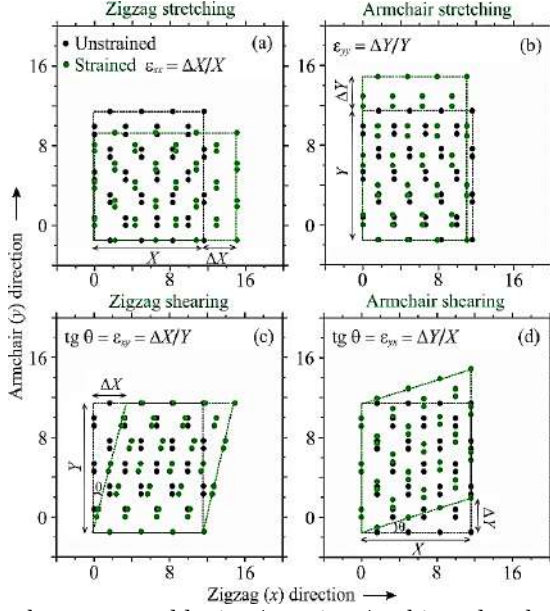


Figure 2 – Phosphorene crystal lattice (top views) subjected to the uniaxial tensile (a)–(b) or shear (c)–(d) strains. To represent the deformation type and direction, we followed the sketch in [5].

To model the strain-induced change in the hopping parameters, we assume the exponential dependence of the hoppings on the P–P bond lengths $l = |\mathbf{R}_{ij}| - |\mathbf{R}_{ij}^0|$:

$$\gamma_{ij}(l) \approx \gamma_{ij}^0 \exp[-\beta(|\mathbf{R}_{ij}|/|\mathbf{R}_{ij}^0| - 1)], \quad (3)$$

where γ_{ij}^0 —hopping of the unstrained lattice, $\mathbf{R}_{ij}^0$ and $\mathbf{R}_{ij}$ —original and modified vectors connecting atoms at i and j sites, and Poisson's ratio can be adopted from the literature; see Table 1 in [5]. Currently, there are no experimental or theoretical data from which the decay rate β can be adopted. Here, we assume $\beta \approx 1.2$, *i.e.* lower than that (≈ 3.37) used for graphene, which is more-less planar in contrast to the buckled phosphorene.

Another, alternative, approach for including the deformation effect on the hopping integrals is based on Harrison's rule definition. The inversely quadratic dependence of the hopping parameters on the bond length, $\gamma(l = |\mathbf{R}_{ij}| - |\mathbf{R}_{ij}^0|) \propto l^{-2}$, acts as an alternative way to model the strain-induced change in the hopping energies. In a linear deformation regime, such an approach leads to

$$\gamma_{ij}(l) \approx \gamma_{ij}^0[(1 - 2/|\mathbf{R}_{ij}^0|)(\alpha_{xx}^{ij}\epsilon_{xx} + \alpha_{yy}^{ij}\epsilon_{yy} + \alpha_{zz}^{ij}\epsilon_{zz} + \alpha_{xy}^{ij}\epsilon_{xy})], \quad (4)$$

where coefficients α depend on the structure of the system at hand. Each of these coefficients corresponds to a certain hopping integral, that certain pair of sites i and j . In our calculations, we adopted values from the literature [5].

First-Principles Calculations

In addition to the previously discussed TB method, we applied an alternative approach to investigate numerically the band gap behaviour of phosphorene: *ab initio* calculations based on density functional theory (DFT). For this purpose, the Quantum Espresso (QE) simulation package [6], an open-source computational framework, was utilized. It employed projector augmented wave (PAW) pseudopotentials within the standard generalized gradient approximations (GGA) for the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional.

Before the calculations, we conducted a geometry optimization procedure to achieve the relaxed state of the atomic structure. After optimizing the unstrained lattice, the resulting lattice parameters were determined as $|\mathbf{a}_1| = 3.344 \text{ \AA}$ and $|\mathbf{a}_2| = 4.588 \text{ \AA}$, as shown in Fig. 1(b). These values are consistent with earlier theoretical predictions and available experimental results [7, 8].

To avoid the layer interaction in the z -direction, a vacuum space of $22 \text{ \AA}$ was introduced, taking into account the periodic boundary condition. The expansion of electron wave functions utilized plane waves with a kinetic energy cut-off of 34.414 Ry , while the energy cut-off for the charge density was set tenfold higher.

To generate a reciprocal $\mathbf{k}$ -space mesh with dimensions of $10 \times 8 \times 1$, the Monkhorst–Pack method was employed. Lattice parameters were adjusted to model stretching or shearing along different edge directions. The strain magnitude ϵ was defined in correlation with the proportional alteration of the sides (parameters), as depicted in Figs. 2(a)–2(d). After each adjustment in the level of strain, taking into account the specific type and direction of deformation, the structure underwent geometric optimization (relaxation).

The outcomes of first-principles calculations based on density functional theory (DFT) in Fig. 3(a) unequivocally demonstrate that monolayer phosphorene is a semiconductor material with an approximate direct band gap of 0.945 eV at the Γ -point, situated at the centre of the Brillouin zone. This gap magnitude aligns well with the findings of several other GGA/PBE–DFT-based first-principles calculations [4, 9, 10].

The total density of electronic states, based on the tight-binding model, shown in Fig. 3(b), reveals a band gap value of approximately 1.5 eV . This value agrees well with previous experimental findings and first-principles results [3, 4, 11] utilising the Heyd–Scuseria–Ernzerhof (HSE)06 hybrid functional.

It is recognized in the literature that standard PBE-pseudopotential-based DFT calculations lead to an underestimated band gap in the electronic structure of

phosphorene. To address this issue, one can either employ the hybrid HSE06 functional [3, 4, 12] instead of PBE or opt for the so-called GW approximation [7] instead of GGA. Despite the underestimation of the band gap, all these pseudopotentials (PBE, HSE06, and GW) lead to similar characteristics and behaviours of the band gap. This includes their responses to applied tensile or shear strain, as demonstrated in the subsequent subsection.

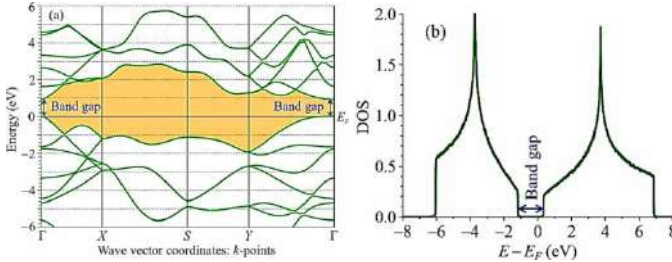


Figure 3 – The phosphorene’s band structure (a) along the high-symmetry points of the 1st Brillouin zone. Total DOS (d) is calculated within the TB model. The shaded region in (a) is an area between the valence band maximum and conduction band minimum with the Fermi level $E_F = 0$.

Figs. 4 and 5 present a comparative analysis of how the band gap evolves under the uniaxial tensile (Fig. 4) and shear (Fig. 5) strains. In these figures, we compare the results of our TB model, which incorporates distant-dependent hoppings (3) or (4), with *ab initio* calculations of other authors using different functionals, primarily PBE or HSE. The TB model demonstrates a linear deformation dependence of the band gap for both types and directions of strain within the considered range (up to 20%, as shown in Figs. 4 and 5). The band gap exhibits a monotonic increase or decrease with the magnitude of stretching (compression), as illustrated in Figs. 4(a) and 4(b). These findings agree with a linear strain-induced variation of the band gap within the multiscale approach at small and moderate strains ($\leq 5\%$), falling within the valid range of the approach. Confirming earlier observations, the band gap experiences a slightly faster linear increase for armchair extension (in Fig. 4(a)) as compared to zigzag extension (in Fig. 4(b)) for both bond-length dependencies of hopping energies (3) and (4).

Figs. 4(a) and 4(b) exhibit a qualitative concurrence between the outcomes derived from our PBE–DFT calculations and those based on either the HSE pseudopotential [3, 11] or GW approximation [7]. Furthermore, there is some quantitative resemblance between our results and the PBE-based findings from other researchers [6, 9]. Regardless of the chosen approximation (GGA or GW) and pseudopotential (PBE or HSE06), the nonmonotonic evolution of the band gap with applied stretching along the zigzag or armchair direction is evident in the first

principles calculations. The presence of this non-monotonic behaviour is consistent with analogous findings in other DFT computations but disagrees with the linearity suggested by TB calculations for both relationships (3) and (4). The nonmonotony is attributed to the contributions of atomic orbitals (s , p_x , p_y , p_z): they overlap and hybridize close to the Fermi level which cannot be observed in the total DOS curves within the TB model.

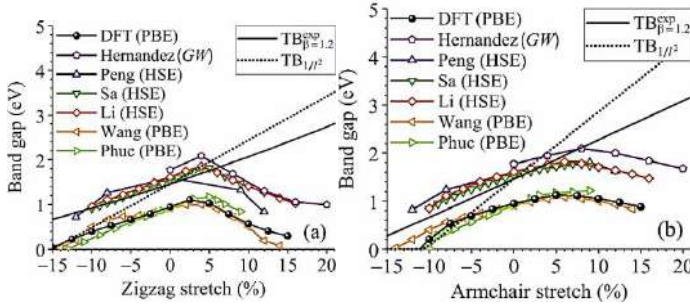


Figure 4 – The band gap vs. the uniaxial tensile strains along the zigzag (a) and armchair (b) directions calculated within the tight-binding (TB) model (black solid and dotted straight lines) and density functional theory (DFT) method (black circle). For comparison, the numerical findings of other authors are adapted and re-plotted in the same sequence as in [5]. Here, open down-pointed triangle ∇ —Sa *et al.* [3]; open right-pointed triangle $\triangleright$ —Phuc *et al.* [7]; pentagon $\square$ —Hernandez *et al.* [8]; open left-pointed triangle $\triangleleft$ —Wang *et al.* [9]; open up-pointed triangle $\triangle$ —Peng *et al.* [11]; rhombus $\diamond$ —Li *et al.* [12]. The solid and dotted lines for TB model refer to different hopping replacements: exponential (3) with $\beta = 1.2$ and inversely quadratic (4) respectively.

In Figs. 5(a) and 5(b), a progressive decrease in the band gap is evident when subjected to shear strain along the same principal edge directions. Quantitative distinctions, rather than qualitative ones, are more or less observed among different models: TB using exponential (3) or inversely quadratic (4) hoping replacement and DFT employing PBE or HSE functionals. As expected, the band gap curves are lower for the PBE approach compared to those within the HSE approach and the TB model.

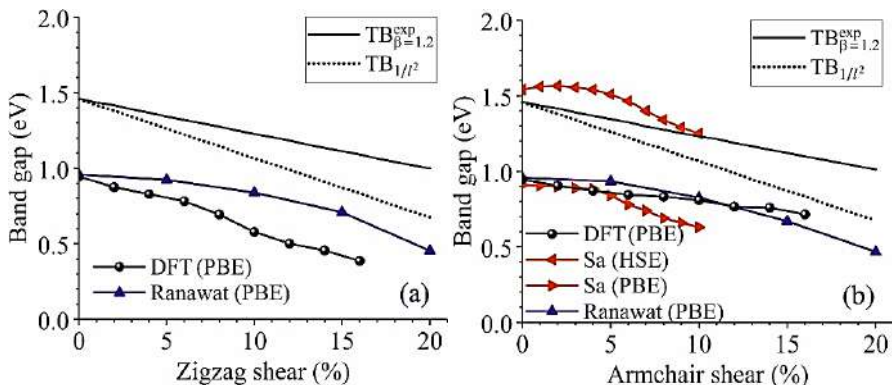


Figure 5 – The same as in the previous figure, but for the shear strains along the zigzag (a) and armchair (b) directions calculated within the TB model (black solid and dotted straight lines) and DFT method (black circle). The adapted numerical findings are replotted in the same sequence as in [5], where the filled left-pointed $\blacktriangleleft$ and right-pointed $\blacktriangleright$ triangles—Sa *et al.* [4]; the filled up-pointed triangle $\blacktriangle$ —Ranawat *et al.* [9]. The solid and dotted lines for the TB model relate to the exponential (3) with $\beta = 1.2$ and inversely quadratic (4) hopping replacements.

Both the TB and DFT methods affirmed the potential conversion of unstrained phosphorene's semiconductor properties into semi-metallic ones. Single-axial extension (compression) resulted in an increased (decreased) band gap in the TB model, while shear deformation gradually diminished the gap over a broad strain range (up to 20%). Notably, there were distinctions in the underestimated gap values for PBE-DFT in comparison to TB and HSE-DFT in both TB and DFT calculations. In contrast to the TB model, including two dependences of the hoppings on the bond length, (3) and (4), the *ab initio* calculations lead to the nonmonotonic single-axial tensile deformation dependence of the band gap. The nonmonotony is attributed to the overlapping and hybridization of atomic orbitals close to the Fermi level and cannot be detected in the total DOS extracted from the TB model. Such results, when the TB calculations are in good agreement with one set of existing experimental results, over a limited strain range, while the DFT calculations are in better agreement with another set of data, require additional analysis and study to address the adequate recommendations on the application of the findings. The decay rate parameter β in (3) may vary and strongly affect the strain-dependent band-gap behaviour. As follows from the literature, the Poisson's ratio is found to vary in different literature sources; moreover, it is not a constant (as we used here for the phosphorene), but can vary (even nonmonotonically) with the applied strain depending on its direction. This can contribute to a clear understanding of some

discrepancies between the TB- and DFT-based results and may even adequately explain them.

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