Multi-scale approach for strain-engineering of phosphorene

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Abstract
A multi-scale approach for the theoretical description of deformed phosphorene is presented. This approach combines a valence-force model to relate macroscopic strain to microscopic displacements of atoms and a tight-binding model with distance-dependent hopping parameters to obtain electronic properties. The resulting self-consistent electromechanical model is suitable for large-scale modeling of phosphorene devices. We demonstrate this for the case of inhomogeneously deformed phosphorene drum, which may be used as an exciton funnel.

Keywords: phosphorene, strain-engineering, tight-binding model

(Some figures may appear in colour only in the online journal)
minimizing the VFM of a strained unit-cell [17], which generalize the standard Cauchy–Born approximation. While the focus of [17] was on the renormalization of the strain induced vector potential of Dirac materials, here we investigate the influence of strain on the band-structure of atomically thin semiconductors and thus establish a connection to the well-known theory of deformation potentials [18].

In this article we develop a theoretical framework that consistently treats both the elastic and electronic degrees of freedom of phosphorene [19–21] and is suitable for large-scale modeling of phosphorene devices. To this end, we put forward a minimal TB model that accurately describes the electronic band-structure of phosphorene in the vicinity of the \( \Gamma \)-point. Introducing distance-dependent hopping parameters and using strain-displacement relations obtained from the VFM, we derive analytical expressions that relate the renormalization of the hopping parameters with the modifications of the band-gap and effective masses caused by strain. Our approach is valid for moderate strain values (<5%), which is the experimentally relevant range for strain-engineering applications (For moderate values of strain we find that the band-gap correction obtained from the Cauchy–Born approximation differs by a factor 3 from our results.).

To demonstrate the versatility of our approach, we study the mechanical and electronic properties of a phosphorene drumhead subjected to uniform pressure. Due to the non-uniform strain distribution of the deformed drumhead, this example requires a consistent treatment of both the mechanical and electronic degrees of freedom on macroscopic scales, which is enabled by the multi-scale approach provided in this paper. For different central deflections values (the ratio between the maximal deformation height and the drum radius) we determine the non-uniform strain both analytically using the elasticity theory and numerically from the VFM. The agreement is remarkable. We calculate the local band-gap and find that it depends very strongly on the deformation profile, and can be easily enhanced by 10 ~ 15%.

The paper is structured as follows. In section 2 we briefly present the lattice structure of phosphorene, introduce a TB model that accurately describes the low energy band structure of phosphorene, and discuss how to account for strain effects on the electronic properties. Section 3 begins with the study of the uniform strain case, from which we determine the parameters of the TB model. Next, we analyze the situation of non-uniform strain arising in a pressurized phosphorene drum. Finally, in section 4 we present our conclusions and outlook.

2. Model

The crystal structure of phosphorene consists of an orthorhombic lattice with lattice vectors \( \mathbf{a}_i \) and \( \mathbf{a}_i \) and four basis atoms arranged in a puckered structure, as depicted in figure 1(a). We denote the atomic positions by \( \mathbf{R}_i \), with subindex \( i \) running from 1 to \( N \), where \( N \) is the number of atoms in the phosphorene sheet. The interatomic bond vectors are \( \mathbf{b}_{ij} = \mathbf{R}_j - \mathbf{R}_i \), and the angle between \( \mathbf{b}_{ij} \) and \( \mathbf{b}_{ik} \) is denoted by \( \theta_{ijk} \). The equilibrium structure is characterized by the interatomic spacing \( d \approx 2.22 \, \text{Å} \) and intra- and inter-pucker angles \( \theta_1 \approx 96.5^\circ \) and \( \theta_2 \approx 101.9^\circ \) [22]. The primitive lattice vectors are thus \( \mathbf{a}_1 = 2d(\cos(\theta_1/2) - \cos(\theta_2)/\cos(\theta_2)/2, 0, 0) \) and \( \mathbf{a}_2 = 2d(0, \sin(\theta_2)/2, 0) \), whereas the equilibrium bond vectors are \( \mathbf{b}_{12} = d(\cos(\theta_2)/2, -\sin(\theta_2)/2, 0) \), \( \mathbf{b}_{23} = d\left(-\cos(\theta_2)/\cos(\theta_1)/2, 0, \sqrt{1 - \cos(\theta_2)/\cos(\theta_2)/2^2}\right) \) and \( \mathbf{b}_{34} = d(\cos(\theta_2)/2, \sin(\theta_2)/2, 0) \).

2.1. Tight-binding model

To calculate the electronic structure we consider an effective four-band TB Hamiltonian [20, 21], containing four \( p_z \) like orbitals per unit cell (one per atom), namely

\[
\mathcal{H}_{el} = \sum_{i<j} t_{ij} c_i^\dagger c_j,
\]

where indices \( i \) and \( j \) run over all sites of the phosphorene sheet and \( t_{ij} = t_{ji} \) are the hopping parameters. Our aim is to develop a simple TB model that accurately describes the strain-induced reconstruction of the electronic bands close to the \( \Gamma \)-point.

Let us start by putting forward a minimal model that captures the energy dispersion close to the \( \Gamma \)-point in the absence of strain, as schematically shown in figure 1(b). To describe the electron-hole asymmetry and the anisotropy of the electronic dispersion relation around the \( \Gamma \)-point [5, 7, 23, 24], we consider both nearest and next-nearest neighbor couplings within a cutoff radius of 4 Å to obtain the five-parameter TB model put forward in [20]. The hopping parameters are denoted by \( t_1, \ldots, t_5 \). Figure 1(a) shows the correspondence between the hopping parameters and interatomic matrix elements connecting orbitals centered at the \( i \) and \( j \) lattice atoms. We note that \( t_5 \) does not affect the dispersion of the valence and conduction bands and, hence, set \( t_5 = 0 \) to simplify the model. The agreement between the resulting four-parameter model and DFT band-structure calculations at the \( \Gamma \)-point with respect to the corresponding effective electron and hole masses [23] is not very good. We find that the accuracy of the TB model is significantly improved by introducing a single additional hopping parameter \( t_6 \), see figure 1(a). Finally, we introduce another hopping parameter \( t_6 \) in figure 1(a) to allow for reproducing the strain-dependence of the electronic band-gap reported in recent \textit{ab initio} calculations [24]. At the \( \Gamma \)-point our six-parameter TB Hamiltonian has the following eigenenergies

\[
E_1 = 2t_1 - t_2 - 2t_4 + t_6 + 2t_8, \quad (2a)
\]
\[
E_2 = -2t_1 - t_2 - 2t_4 - t_6 - 2t_8, \quad (2b)
\]
\[
E_3 = 2t_1 + t_2 + 2t_4 + t_6 + 2t_8, \quad (2c)
\]
\[
E_4 = -2t_1 + t_2 - 2t_4 + t_6 - 2t_8. \quad (2d)
\]

where we have subtracted a common energy shift \( E_0 = 2t_1 \) from all eigenvalues. The band gap is given by the difference of the energy of the conduction band \( (E_3) \) and the valence band \( (E_1) \).
whereas for the other two bands we obtain

\[ E_4 + E_5 = 0, \quad E_4 - E_5 \equiv \Delta E = 4(t_2 + t_6) - E_g. \tag{4} \]

Hence, using the band-gap and \( \Delta E \) as inputs one can only determine two hopping parameters.

Additionally, close to the \( \Gamma \)-point we find that

\[
E_3(k_x, 0) \approx -\frac{E_g}{2} - \frac{1}{16} \left( E_g - 8t_2 + 16t_4 \right)^2 (a_k c_k)^2, \tag{5a}
\]

\[
E_3(k_x, 0) \approx +\frac{E_g}{2} + \frac{1}{16} \left( E_g - 8t_2 + 16t_4 \right)^2 (a_k c_k)^2 \tag{5b}
\]

along the armchair direction and

\[
E_2(0, k_y) \approx -\frac{E_g}{2} - \frac{1}{4} \left( t_1 - 4t_3 + t_4 + 9t_6 \right) (a_k c_k)^2, \tag{6a}
\]

\[
E_2(0, k_y) \approx +\frac{E_g}{2} - \frac{1}{4} \left( t_1 + 4t_3 + t_4 + 9t_6 \right) (a_k c_k)^2 \tag{6b}
\]

in the zigzag direction.

Our results are conveniently cast in terms of the energy-band curvatures (or inverse effective masses), namely, \( c_{i,\alpha} = \partial^2 E_i / \partial k_\alpha^2 \) with \( i = 2,3 \) and \( \alpha = x,y \). Using \( E_g, \Delta E, c_{2,y} \) and \( c_{3,y} \) as input parameters, we obtain the following simple analytical relations

\[
t_1 + t_4 = \frac{9}{64} (E_g - \Delta E) - \frac{1}{8} a_2^2 (c_{3,y} + c_{2,y}), \tag{7a}
\]

\[
t_2 + t_6 = \frac{1}{4} (E_g + \Delta E), \tag{7b}
\]

\[
t_3 = \frac{1}{4} a_2^2 (c_{3,y} - c_{2,y}), \tag{7c}
\]

\[
t_8 = \frac{1}{64} (\Delta E - E_g) + \frac{1}{8} a_2^2 (c_{3,y} + c_{2,y}). \tag{7d}
\]

These relations show that one needs more input information to uniquely determine the model parameters. We choose to use the curvature in armchair direction and the strain-dependence of the band-gap energy, a quantity that we address in the following section.

### 2.2. Strained phosphorene

The application of strain to a phosphorene sheet induces a shift in the interatomic distances, which also changes the material band-structure. In the TB model, the modifications of the electronic properties can be accounted for by hopping parameters \( t_{ij} \) which depend on the interatomic distances. Here, we assume that after a deformation the hopping parameters become

\[
t_{ij}' = t_{ij} \exp \left[ -\beta (|\mathbf{R}_{ij}'|/|\mathbf{R}_{ij}| - 1) \right], \tag{8}
\]

where \( \mathbf{R}_{ij}' \) (\( \mathbf{R}_{ij} \)) is the modified (original) vector connecting atoms at sites \( i \) and \( j \) and \( \beta \) quantifies the decay.

Next, we need to establish a relation between the applied strain, which is a macroscopic quantity, and the resulting microscopic shift in atomic positions. As already mentioned, since phosphorene has four atoms in the unit cell, the Cauchy–Born rule does not apply [16, 17]. Instead, the positions of the atoms within the unit cells of a strained sample is obtained by minimizing the microscopic elastic energy with the constraint \( \mathbf{a}_{ij} = \mathbf{a}_i + \mathbf{u} \cdot \mathbf{a}_j \), where \( \mathbf{a}_i \) is the unstrained primitive lattice vector, \( \mathbf{a}_j \) is the strained one, and \( \mathbf{u} \) is the strain tensor. The latter has three independent elements and is given by...
applied shear cancel to linear order, leaving the band structure unchanged for small shear [25].

The band structure of strained phosphorene is obtained by using the modified hopping terms $t_{ij}^\prime$ from equation (8) in the TB Hamiltonian. In particular, the band-gap of strained phosphorene is given by

$$E_g^\prime = 4t_1 + 2t_2 + 4t_4 + 2t_6 + 4t_8.$$  (14)

To lowest order in strain, the modified effective masses are obtained by inserting $t_{ij}^\prime$ into equations (5) and (6), which describe the electronic dispersion close to the Γ-point.

3. Results

3.1. Parameter estimation

We have described the general procedure for obtaining a TB model to calculate strain-induced changes on the electronic structure of phosphorene. Let us now determine the model parameters introduced in the previous section.

We obtain the strain-displacement parameters $v_i$ by minimizing the VFM put forward in [19]. The results are given in table 1. Next, with the help of equation (14) we write the strain-induced modification of the band-gap, $\Delta E_g = E_g^\prime - E_g$, as

$$\Delta E_g \approx \beta u_{x1}(0.11t_1 + 0.10t_2 - 4.63t_4 - 0.65t_6 + 0.02t_8)$$
$$+ \beta u_{xy}(-1.50t_1 + 0.13t_2 - 1.64t_4 + 0.33t_6 - 3.54t_8).$$  (15)

The hopping parameters are estimated by fitting the main features of the low energy band structure [21], namely, $E_g = 1.84$ eV and the effective masses $m_X(X) \approx 0.2m_e$, $m_Y(X) \approx 0.2m_e$, $m_X(Y) \approx 1.2m_e$, and $m_Y(Y) \approx 3.9m_e$. Further, we set $E_4 = -E_1 = 6.9$ eV. As explained in section 2.1, these inputs are not sufficient to determine all six hopping parameters and $\beta$. To remedy this, we compare the strain-induced modification of the band-gap predicted by equation (15) with ab initio results [24]. The latter show that the band-gap increases linearly by approximately 0.1 eV with strains up to \(\approx 4\%\). The increase is larger for strain in armchair direction. By using $\beta = 2$ and the hopping parameters given in table 1 our TB model nicely reproduces this behavior, as shown in figure 2(b). The model is also in good quantitative agreement with the electronic dispersion of [21] at zero strain, see figure 2(a), and with recent DFT calculations [26].

We verify the accuracy of our analytical results by comparing the band gaps predicted by equation (15) with those obtained from numerical calculations. For that, we consider a system with periodic boundary conditions, consisting of supercells containing $15 \times 15$ unit cells. For a given strain, the system is allowed to relax using the VFM developed in [19]. The band-gaps obtained by diagonalization of the TB

| Table 1. Hopping parameters and strain-displacement parameters used in this study. |
|---|
| $t_1$ (eV) | $t_2$ (eV) | $t_3$ (eV) | $t_4$ (eV) | $t_5$ (eV) | $t_6$ (eV) |
| 1.25 | 4.38 | -0.106 | -0.34 | -0.47 | 0.09 |
| $\beta$ | $\kappa_1$ | $\kappa_2$ | $\kappa_3$ | $\kappa_4$ | $\kappa_5$ |
| 2 | 0.71 | 0.27 | 1.26 | -0.39 | -0.16 |

and $v_i$ is the projection of $v$ onto the plane of the monolayer. The parameters $\kappa_i$ are obtained by minimizing the elastic energy per unit cell with the constraints imposed by equations (10). Note that the component $v_x$, accounts for a transversal Poisson effect, i.e. a change of thickness due to strain in the $x-y$ plane. In phosphorene, this effect has recently been addressed by using an ad hoc ‘3D Cauchy–Born’ relation, where the strain-tensor has a non-zero component $u_{xz}$ [11]. In effect, this procedure correctly accounts for the component $v_x$, but neglects the components $v_y$ and $v_z$.

To estimate the modification of the hopping terms due to an applied strain, equation (8), it is convenient to write $R_k$ as a linear combination of the lattice vectors and the bond vectors in the unit cell, namely

$$R_k = na_1 + ma_2 + \sum_i C^i_k b_i.$$  (12)

where the index $k$ runs over the pair of sites (1,2), (2,3) and (3,4). $C^i_k$ is a matrix of integers, which is explicitly given in appendix A. After a little algebra, we write $R_k$ as

$$R_k = |R_k| + R_k \cdot u \cdot R_k = \left[ C^i_{k(2,3)} v - (C^i_{k(1,2)} + C^i_{k(1,3)} v) \cdot R_k \right] / |R_k|.$$  (13)

We comment at this point on the implications of equation (13) for the modification of the dispersion due to an applied shear. Since the component $v_x$ is proportional to the shear, the last term in equation (13) implies that shear, in contrast to what one expects from the Cauchy–Born rule, does not preserve the lengths of bond vectors with a non-vanishing $y$-component. On the other hand, the inversion symmetry of phosphorene implies that shear cannot contribute to the electronic structure to linear order. Consistent with this, we find that the contributions to the electronic structure from an
Hamiltonian for the resulting atomic configurations agrees very well with equation (15), as shown by figure 2(b). The 2D and 3D Cauchy–Born relations (dotted and dashed lines) lead to significant deviations from the numerical results, with the latter giving rise to the largest errors.

Interestingly, we find that the magnitude of $t_4$ (or $t_6$ depending on which parameter is undetermined) is crucial to correctly describe the behavior of the band gap versus strain. Maintaining the constraints for the band-gap and the effective masses, we use equation (15) to calculate the ratio of $\Delta E_g$ for stretching along the armchair and zigzag directions. Figure 2(c) shows that if $t_4 \geq -0.24$ eV, the ratio becomes smaller than one, which disagrees with the findings of [24].

In the present case, $t_4 = -0.34$ eV leads to a ratio of $\approx 1.64$. Further investigations and, in particular, experimental results are needed to better assess $\Delta E_g$.

3.2. Nonuniform strain

Now we turn to an example of practical interest: a suspended phosphorene drum and the influence of nonuniform strain. If the drumhead is subjected to uniform pressure, it will be statically deformed, which leads to a nonuniform strain distribution. This system is conveniently described by continuum elasticity [19]. The phosphorene monolayer is effectively modeled as a thin anisotropic plate. Its macroscopic elastic properties are characterized by two bending rigidities and four stiffness constants. We find the shape of the deformed drum and the strain distribution by solving the equations corresponding to the out-of-plane displacement-field $w(r)$ and for the Airy stress function $\chi(r)$ [19]. In following we focus our discussion on approximate analytic solutions (details are given in appendix B) and compare them with numerical results.

For sufficiently small pressure the bending contribution to the elastic energy of the drum dominates and its shape is well approximated by $w(x, y) = w_0[1 - (x/R)^2 - (y/R)^2]$, where $w_0$ is the deflection at the center and $R$ is the radius of the drum. In contrast, for large pressures stretching plays a major role and the shape is approximately given by $w(x, y) = w_0[1 - (x/R)^2 - (y/R)^2]$. As shown in appendix B, the strain distribution in both regimes becomes

$$u_{xx}(r) = (w_0/R)^2 \frac{P_1(r)}{C_{11}} - \frac{C_{12}}{C_{11}C_{22}} P_2(r), \quad (16a)$$

$$u_{yy}(r) = (w_0/R)^2 \frac{P_2(r)}{C_{22}} - \frac{C_{12}}{C_{11}C_{22}} P_1(r), \quad (16b)$$

$$u_{xy}(r) = (w_0/R)^2 \frac{P_3(r)}{R^2} \frac{x y}{C_{66}}, \quad (16c)$$

where $P_1$, $P_2$ and $P_3$ are polynomials containing even powers of $x/R$ and $y/R$ (see appendix B). The tensile strains are maximal and the shear vanishes at the center of the drum. From equation (15) we find that the corresponding change in band-gap is maximal and proportional to $(w_0/R)^2$, with a factor of proportionality of approximately 6.4 eV for both deformation regimes.

In order to verify the analytical results, we use the VFM of [19] to numerically calculate the shape of a pressurized drum. To validate our approach in the continuum limit while maintaining computational convenience we simulate a drum of radius 103.16 Å. The out-of-plane deformation field $w(r)$ is obtained by considering the midpoints of each primitive unit cell. In figures 3(a) and (b) the deformation field is plotted along $x = 0$ and $y = 0$, respectively, for three central deflections $w_0/R$, together with the analytical expressions for the deformation in the bending and stretching regimes. We find that the drum shape is indeed very close to being radially symmetric and shows the expected crossover from the bending to the stretching dominated regime as $w_0/R$ increases.

Further, we consider the vectors connecting the midpoints of adjacent primitive unit cells to estimate the local strain distribution. We test the accuracy of our strain-displacement relations, by calculating the expected lengths of the bond vectors using equation (10), and comparing them to the numerically obtained ones. The maximal error of the strain-displacement relations occurs at the center of the drum, where the strain is maximal. Figure 3(c) shows the relative errors as a function of central deflection together with the relative error given by the 3D Cauchy–Born rule, ignoring $v_8$. At the largest deflection, the accuracy of the Cauchy–Born approximation is about 3% at the largest deflection, whereas our method leads to bond
length relative errors of less than 0.5%. These differences have a significant impact on the hopping matrix elements $t_{ij}$ and, hence, on the tight-binding electronic structure calculations.

For each unit cell we also calculate the (local) electronic band-structure using the TB model and a $3 \times 3$ super-cell centered at the unit cell of interest and using periodic boundary conditions. This allows us to obtain the local band-gap $E_g$. In figure 4(a) we show maps of the band-gap for three different central deflections, indicating the transition from a bending-dominated regime at low deflections to a stretching dominated regime at high deflections. Figure 4(b) shows a comparison between the numerically calculated band-gap at the center of the drum with our analytical result. The agreement is excellent, suggesting that the model can be used to give qualitative predictions of local electronic properties in complex geometries.

4. Conclusions

In summary, we have presented a multi-scale approach to calculate electronic properties of deformed phosphorene. To this end, we developed a TB model to describe the electronic structure. We found that six hopping parameters are required to get a good quantitative description of the electronic bands, which includes the band-gap and the (anisotropic) effective masses at the $\Gamma$-point. The influence of deformations is described by considering distance-dependent hopping-parameters. The crucial point of our approach is the fact that in almost all cases of interest, the macroscopic strain-distribution can be inferred, but the microscopic positions of the atoms after deformation are not known. Thus a relation between strain and atomic displacements is required to make use of the TB model. As we have shown, the simple Cauchy–Born relation—often employed in this context—is not a good approximation as it tends to overestimate the strain. Instead, we propose to use strain-displacement relations, which are obtained by minimizing the elastic energy [17]. This approach is easily combined with the microscopic TB model and yields good quantitative agreement. The central result is given by equation (15), which gives an expression for the strain-induced modification of the band-gap for a given (homogeneous) strain.

We demonstrate our method for the relevant case of a phosphorene drum. The deformation due to pressure leads to inhomogeneous strain distributions. Introducing a local band-gap, one then finds a spatially changing strain-induced contribution, which is essential for the so-called inverse funneling effect [14]. We obtain a very good agreement between fully numerical results (TB and VFM) with analytical estimates resulting from continuum elasticity [19] combined with the derived strain-induced modification of the band-gap given by equation (15). In contrast, we find that using only the TB
model together with the Cauchy–Born rule greatly overestimates the shift in electronic band-gap. Further, the renormalization of the interatomic distances differ significantly from the numerical result already at moderate deformations. This error will be reflected in the local renormalization of the hopping parameters, and thus it will influence the electronic structure calculations. This shows that a consistent treatment of both mechanical and electronic degrees of freedom via the approach presented in this paper is crucial for predicting the electronic properties in complex geometries.

The multi-scale approach presented in this article can also be used for other 2D materials, provided suitable TB and VF models are known. It offers a quantitative and efficient procedure to study the structural and electronic properties of single-layered materials with arbitrary deformation landscapes.

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Appendix A. Strain-displacement relation for phosphorene

A detailed description of the procedure to obtain strain-displacement relations, equations (10), from a VF is given in [17]. Here we revisit the theory to explain and provide further insight on some of the expressions used in section 2.2.

For a homogeneous strain the primitive lattice-vectors change according to

\[ a'_i = a_i + u \cdot a_i, \quad (A.1) \]

The position \( \mathbf{R}_i \) of any arbitrary lattice site can be expressed in terms of the primitive lattice-vectors and the \( N_{bb} \) bond-vectors of the basis,

\[ \mathbf{R}_i = m_i \mathbf{a}_i + n_i \mathbf{a}_2 + \sum_{k=1}^{N_{bb}} C^k_{ij} \mathbf{b}_k, \quad (A.2) \]

where \( m_i, n_i, \) and the entries of the matrix \( C^k_{ij} \) are integers. The vector \( \mathbf{R}_j \) connecting the atoms \( i \) and \( j \) is then given by

\[ \mathbf{R}_j = m_j \mathbf{a}_i + n_j \mathbf{a}_2 + \sum_{k=1}^{N_{bb}} C^k_{ij} \mathbf{b}_k, \quad (A.3) \]

where for all variables \( X_j = X_i - X_j \) holds. Since we assume that the deformation preserves the lattice structure, \( m_{ij}, n_{ij}, \) and \( C^k_{ij} \) remain unchanged, upon strain

\[ \mathbf{R}'_{ij} = \mathbf{R}_{ij} + u \cdot \mathbf{R}_{ij} + \sum_{k=1}^{N_{bb}} C^k_{ij} \mathbf{b}_k, \quad (A.4) \]

which implies that the basis bond-vectors transform as

\[ \mathbf{b}'_k = \mathbf{b}_k + u \cdot \mathbf{b}_k + \delta \mathbf{b}_k, \quad (A.5) \]

For a monoatomic basis, where \( N_{bb} = 0 \), equation (A.4) is reduced to the standard Cauchy–Born relation. The lattice symmetries relate the vectors \( \delta \mathbf{b}_k \) to each other and thus reduce the number of unknown components [17]. In the case of phosphorene, one has \( \delta \mathbf{b}_{23} = \mathbf{v} \) and \( \delta \mathbf{b}_{12} = \delta \mathbf{b}_{13} = \mathbf{v}_b \) which are explicitly given by equation (11). The nearest neighbors of the atoms within a unit cell are shown in figure A1. The corresponding values of \( m_{ij}, n_{ij} \) and \( C^k_{ij} \) are given in table A1.

In general, the vectors \( \delta \mathbf{b}_k \) can be determined by minimizing the elastic energy of the deformed structure, that for small deformations reads [27]

\[ E_{VF} = \frac{1}{2} \sum_{(i,j), (i',j')} (\mathbf{R}'_{ij} - \mathbf{R}_{ij}) \cdot \mathbf{R}'_{ij} - \mathbf{R}'_{ij}, \quad (A.6) \]

where the sum runs over all pairs of atoms and \( \mathbf{R}'_{ij} \) denotes the matrix of force-field parameters. The latter is typically restricted to neighboring bonds. Using equation (A.4) one finds that \( E_{VF} \) is a second order polynomial in \( u \) and \( \delta \mathbf{b}_k \). By requiring that \( \delta E_{VF}/\delta \mathbf{b}_k = 0 \) one obtains a set of linear relations between \( \delta \mathbf{b}_k \) and \( u \), which constitutes the strain-displacement relations.

Table A1. Decomposition of the nine nearest-neighbor vectors within the unit cell and connecting to the neighboring unit cells according to equation (A.4).

| \((i,j)\) | \(m_{ij}\) | \(n_{ij}\) | \(C^{1,2}_{ij}\) | \(C^{2,3}_{ij}\) | \(C^{3,4}_{ij}\) |
|---|---|---|---|---|---|
| (1, 2) | 0 | 0 | 1 | 0 | 0 |
| (2, 3) | 0 | 0 | 0 | 1 | 0 |
| (3, 4) | 0 | 0 | 0 | 0 | 1 |
| (1, 5) | -1 | 0 | 1 | 1 | 1 |
| (2, 6) | 0 | -1 | -1 | 0 | 0 |
| (3, 7) | 0 | -1 | 0 | 0 | 1 |
| (4, 8) | -1 | 0 | 1 | 1 | 1 |
| (4, 9) | 1 | 0 | -1 | -1 | -1 |
| (1, 10) | 0 | 1 | 1 | 0 | 0 |

Figure A1. Sketch of phosphorene structure indicating the nearest neighbors (5 to 10) of the atoms in the unit cell (1 to 4).
Appendix B. Strain distribution for a drum

Denoting the displacement field by \( u = (u(r), v(r), w(r)) \) and the Airy stress function by \( \chi(r) \), the shape of the deformed drum is determined by the following equations [19]

\[
\frac{1}{Y_x} \partial_x^2 \chi + \frac{1}{Y_y} \partial_y^2 \chi + \left( \frac{1}{Y_y} + \frac{2}{Y_x} \frac{\nu Y_x}{Y_y} \right) \partial_x \partial_y \partial_y \partial_x \chi = (\partial_x \partial_x w)^2 - (\partial_y \partial_y w)(\partial_x \partial_y w) \tag{B.1}
\]

and

\[
(\partial_x^2 \chi)(\partial_y^2 \chi) - 2(\partial_x \partial_y \chi)(\partial_x \partial_y w) = \left( \kappa_x \partial_x^2 w + \kappa_y \partial_y^2 w + 2\sqrt{\kappa_x \kappa_y} \partial_x \partial_y \partial_y \partial_x w \right) - P_z \tag{B.2}
\]

Here, \( Y_{xy} \) and \( \kappa_x \) are the Young’s modulus and the bending rigidity in \( x \) and \( y \) direction, \( G_{xy} \) is the shear modulus and \( \nu_{xy} \) and \( \kappa_y \) are the Poisson ratios.

In the following, we solve these equations for a drum of radius \( R \) with vanishing prestrain under a spatially constant external pressure for the limit cases of small and large deformations. Taking into account the boundary conditions for the in-plane displacement fields, namely, \( u(\bar{x} = 0, \bar{y} = 0) = 0, v(\bar{x} = 0, \bar{y} = 0) = 0, v(\bar{x} = 0, \bar{y} = 1) = 0, v(\bar{x} = 1, \bar{y} = 1) = 0 \), we find the Airy stress function and, hence, the strain fields.

For sufficiently small deformations one can ignore the left hand side in (B.2) which is cubic in the deformation. The deformation is then given by \( w(x, y) = w_0(1 - \bar{x}^2 - \bar{y}^2)^2 \) where \( \bar{x} = x/R \) and \( \bar{y} = y/R \). The maximal deflection \( w_0 \) is related to the applied pressure by

\[
w_0 = \frac{P R^3}{64 \kappa_{\text{eff}}}, \tag{B.3}
\]

where \( \kappa_{\text{eff}} = (3\kappa_x + 3\kappa_y + 2\sqrt{\kappa_x \kappa_y})/8 \approx 3.9 \text{ eV} \) for phosphorene [19].

We consider a generic 8th order polynomial as Ansatz for the Airy stress function and solve equation (B.1) together with the boundary conditions for the drum in-plane displacement fields by coefficient matching. The resulting strain distributions are sixth order polynomials in \( \bar{x} \) and \( \bar{y} \) with coefficients that depend on intricate combinations of the elastic constants. Taking the explicit values for the elastic constants given in [19], we find

\[
u_{xx} = \frac{w_0^2}{R^2} [0.73 + 0.12\bar{x}^6 - 3.18\bar{y}^2 + 3.69\bar{y}^4 - 1.24\bar{y}^6 + \bar{x}^2(-0.07 - 1.99\bar{y}^2) + \bar{x}^2(-0.37 + 4.94\bar{y}^2 - 3.14\bar{y}^4)]
\]

\[
u_{yy} = \frac{w_0^2}{R^2} [0.63 - 0.84\bar{x}^6 + 0.04\bar{y}^2 - 0.22\bar{y}^4 + 0.09\bar{y}^6 + \bar{x}^2(2.35 - 0.80\bar{y}^2) + \bar{x}^2(-2.14 + 0.88\bar{y}^2 - 0.11\bar{y}^4)]
\]

\[
u_{xy} = \frac{w_0^2}{R^2} [\bar{x}\bar{y}(2.68 + 1.88\bar{x}^4 - 2.99\bar{y}^4 + 1.06\bar{y}^4 + \bar{x}^2(-4.32 + 2.71\bar{y}^2)]. \tag{B.4}
\]

To gain insight into the interpretation of these expressions, we solve the Airy stress function for an isotropic material with hexagonal symmetry and small Poisson ratio \( \nu \ll 1 \), such as graphene. In that case, we find a simpler expression for the strain fields that is independent of the elastic constants, namely

\[
u_{xx} = \frac{w_0^2}{6R^2} [5 - 6(\bar{x}^2 + 3\bar{y}^2) + 4(\bar{x}^2 + \bar{y}^2)(\bar{x}^2 + 5\bar{y}^2) - (\bar{x}^2 + \bar{y}^2)^2(\bar{x}^2 + 7\bar{y}^2)],
\]

\[
u_{yy} = \frac{w_0^2}{6R^2} [5 - 6(\bar{y}^2 + 3\bar{x}^2) + 4(\bar{x}^2 + \bar{y}^2)(\bar{x}^2 + 5\bar{x}^2) - (\bar{x}^2 + \bar{y}^2)^2(\bar{y}^2 + 7\bar{x}^2)],
\]

\[
u_{xy} = \frac{\bar{x}\bar{y}}{3} [6 - 8(\bar{x}^2 + \bar{y}^2) + 3(\bar{x}^2 + \bar{y}^2)^2]. \tag{B.5}
\]

Comparing the leading order coefficients of the polynomials in equations (B.5) and (B.4) we find that despite the anisotropy of phosphorene, the strain distribution close to the center of the drum, \( \bar{x} \ll 1 \) and \( \bar{y} \ll 1 \), deviates only by about 30% from what one would expect for an isotropic material.

In the opposite limit of large deformations, we ignore the bending related terms in (B.2) and consider the Ansatz \( w(x, y) = w_0(1 - \bar{x}^2 - \bar{y}^2)^2 \), \( \bar{x} = x/R \) and \( \bar{y} = y/R \) for the drum deformation. Inserting this Ansatz into (B.1) we find that the right-hand-side of the equation becomes spatially constant, namely, \( (\partial_x \partial_x w)^2 - (\partial_y \partial_y w)(\partial_x \partial_y w) = -(4w_0^2/R^4) \). By inspection of (B.1), this implies that the Airy function is given by a fourth order polynomial whose coefficients are obtained by matching the boundary conditions at the rim of the drum. We find the strain distribution

\[
u_{xx} = (2/3 - \gamma_x)(w_0/R)^2(1 - \bar{y}^2) + \gamma_y(w_0/R)^2\bar{x}^2, \tag{B.6}
\]

\[
u_{yy} = (2/3 + \gamma_x + \gamma_y)(w_0/R)^2\bar{y}^2, \tag{B.7}
\]

\[
u_{xy} = (2/3 - \gamma_x)(w_0/R)^2(1 - \bar{x}^2) + \gamma_y(w_0/R)^2\bar{y}^2, \tag{B.8}
\]

where \( \gamma_x \) and \( \gamma_y \) are functions of the elastic parameters. For phosphorene one has \( \nu_{xy} \ll 1 \), for which one finds \( \gamma_x \approx 0 \) and \( \gamma_y \approx (2/3)\nu_{xy}(C_{66} - 2C_{12}^2)/(6C_{12} + C_{66}\nu_{xy}) \). Using the values for the elastic constants provided in [19] we find that \( C_{66} \approx 2C_{12} \), and therefore \( \gamma_y \approx 0 \). Interestingly, despite phosphorene being anisotropic, this result coincides with the case of isotropic materials with small Poisson ratio \( \nu \ll 1 \), where \( \gamma_x = \gamma_y = 0 \).

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