

# Phosphorene and Graphene Nanoribbons with Vacancies in Magnetic Field

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**Abstract** - The electronic spectra of the nanostructured materials show an interesting behaviour under the influence of the uniform magnetic field: the dependence of the energy levels on the magnetic field shows a fractal structure. This feature follows from the procedure of the calculation in which the matrix form of the Schrödinger equation is replaced by a system of the Harper equations, where the exponentials with the magnetic factors are supplied to all of the terms. We show the electronic spectra for the case of the narrow phosphorene and graphene zigzag nanoribbons with atomic vacancies and for the nanoribbons equipped with the so-called Stone-Wales defects.

**Keywords:** graphene nanoribbons, phosphorene, electronic spectrum, magnetic field, density of states, edge states, Stone-Wales defects

## 1. Introduction

The nanostructures are in the center of the physical research for more than 10 years. In the last 5 years, the development has been enhanced with an additional research on the nanostructures based on phosphor, stannum, molybdenum, boron, silicon [1,2] etc. In this paper, we will be concerned with the carbon and phosphor planar nanostructures and their electronic properties.

The atoms in the carbon nanostructures contain 4 valence electrons and at the same time, they are  $sp^2$ -hybridized. It means that one electron does not participate in the chemical bonding. It is localized in the  $p_z$ -orbital and depending on the concrete molecular structure, it can improve the metallic properties. The hexagonal planar structure (graphene) can be modified by placing the pentagonal or the heptagonal defects. In this way, fullerenes, nanocones, wormholes, nanotoroids, nanotubes [3,4] etc. can be created. The graphene nanoribbons are created by cutting parts of the planar graphene [5].

The nanostructures based on the phosphor atoms are called phosphorenes. Their chemical structure is analogous to the structure of the graphene materials, but the atoms are  $sp^3$ -hybridized. So, due to spacial orientation of the chemical bonds, the phosphorene layers are not smooth, they have the semi-planar structure (puckered honeycomb lattice). Nevertheless, each atom in the monolayer has 3 neighbors again, i.e. one bond remains without any exploitation. However, the phosphor atoms have 5 valence electrons. They are divided into 3 hybridized  $\sigma$ -orbitals and 1 lone pair orbital [6]. The electrons located in this orbital play the same role as the 4th electron of the carbon atom in the graphene (graphitic) plain.

Here, we investigated the influence of the magnetic field in the cases of the phosphorene and graphene zigzag nanoribbons with vacancies and with a combination of the pentagonal and heptagonal defects – the Stone-Wales defects. This results in the shift, changes of the width and a creation of new gaps in the electronic spectrum. Furthermore, new edge states could be created in this way.

First, we explain the procedure of the calculation of the electronic spectrum using the Schrödinger equation and the Harper equations in which the influence of the magnetic field is included. After that, we calculate the electronic structure of different kinds of the zigzag nanoribbons.

## 2. Schrödinger Equation and Harper Equations

For the planar structures, the calculation of the electronic spectrum starts on solving the Schrödinger equation for the electron bounded on the molecular surface

$$\hat{H}\psi = E\psi. \quad (1)$$

Here,  $E$  is the energy of electron. The wave function can be expressed as [7]

$$\psi = C_{A_1}\psi_{A_1} + C_{A_2}\psi_{A_2} + \dots + C_{A_n}\psi_{A_n}, \quad (2)$$

where the components  $\psi_{A_1}, \psi_{A_2}, \dots, \psi_{A_n}$  correspond to the particular sublattices,  $n$  is the number of the atoms in the elementary cell. By the substitution of this expression into the Schrödinger equation, multiplying it by  $\psi^\dagger$  and by performing the integration over  $\vec{r}$ , we create the expressions

$$H_{ab} = \int \psi_a^* H \psi_b d\vec{r}, \quad S = \int \psi_{A_i}^* \psi_{A_i} d\vec{r}, \quad a, b, A_i \in \{A_1, \dots, A_n\}, \quad (3)$$

and the Schrödinger equation is transformed into the matrix form

$$\begin{pmatrix} H_{A_1A_1} & H_{A_1A_2} & \dots & \dots & H_{A_1A_n} \\ H_{A_2A_1} & H_{A_2A_2} & \dots & \dots & H_{A_2A_n} \\ \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots \\ H_{A_nA_1} & H_{A_nA_2} & \dots & \dots & H_{A_nA_n} \end{pmatrix} \begin{pmatrix} C_{A_1} \\ C_{A_2} \\ \dots \\ \dots \\ C_{A_n} \end{pmatrix} = ES \begin{pmatrix} C_{A_1} \\ C_{A_2} \\ \dots \\ \dots \\ C_{A_n} \end{pmatrix}, \quad (4)$$

where  $H_{A_1A_1} = \dots = H_{A_nA_n}$ . The nonzero matrix elements can be written in the form

$$H_{A_mA_n} = t_i S \Omega_{\vec{k}, m, n}^{N(i)} \quad (5)$$

where  $N(i)$  denotes the neighbouring interactions of the  $i$ -th order,  $t_i$  denotes the corresponding hopping integral and  $\vec{k}$  represents the wave vector. Then, the  $j$ -th equation of the system has the form

$$EC_j = \sum_{i,m} t_i \Omega_{\vec{k}, j, m}^{N(i)} C_m. \quad (6)$$

The indices  $m, n$  denote the corresponding atomic sites.

The electronic spectrum is given by the eigenvalues of the matrix in (5). The density of states is calculated from the expression

$$DOS(E) = \int_0^{2\pi} \delta(E - E(\vec{k})) d\vec{k}. \quad (7)$$

For the cases of plain phosphorene and graphene, the elementary cells of the molecular surface we see in Fig. 1. It contains 4 atoms in the case of phosphorene, while in the case of graphene, it contains 2 atoms. The phosphorene structure includes 5 kinds of hoppings between atoms, while in the case of graphene, they are 2 hoppings only. Moreover, in the case of the nearest-neighbor approximation, it is one hopping only. In Figs. 2 and 3, we see the 3D graph of the electronic spectrum and the density of states for both phosphorene and graphene. It is interesting that the shape of the elementary cell in the reciprocal space (Brillouin zone) differs for both cases: it is rectangular in the case of phosphorene and hexagonal in the case of graphene. The density of states also shows main difference between the electronic properties – the nonzero gap around zero energy for phosphorene and zero gap for graphene. It means that the first material is semiconductor which makes it more perspective for the applications. The second material is semimetal.

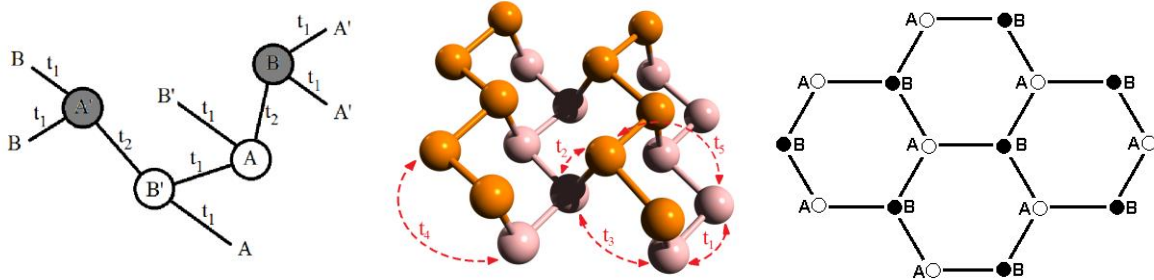


Fig. 1: Elementary cell of phosphorene (left), 5 hoppings in the phosphorene honeycomb lattice (middle) and the elementary cell of graphene (right).

In the case of the zigzag nanoribbons which are in the center of our interest, the electronic spectrum and the density of states have the form sketched in Fig. 4 for both phosphorene and graphene allotropes [8]. We see that in both cases, the properties of both materials are changed to metallic.

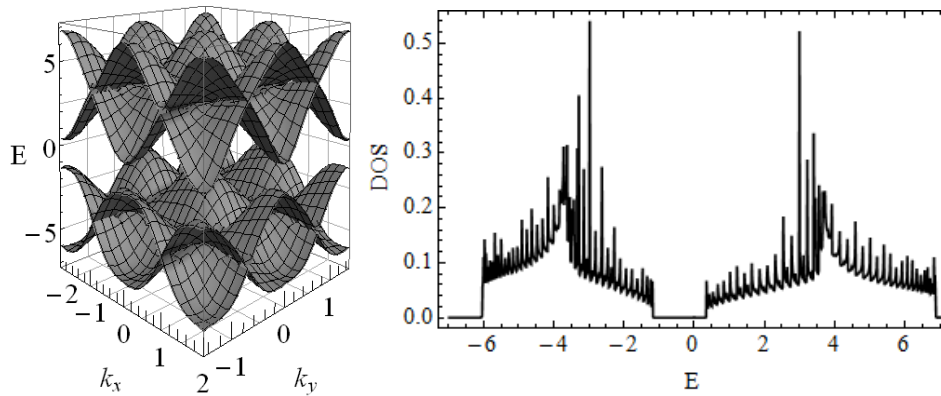


Fig. 2: Electronic spectrum depending on the  $x$  and  $y$  components of the wave vector and the density of states of planar phosphorene.

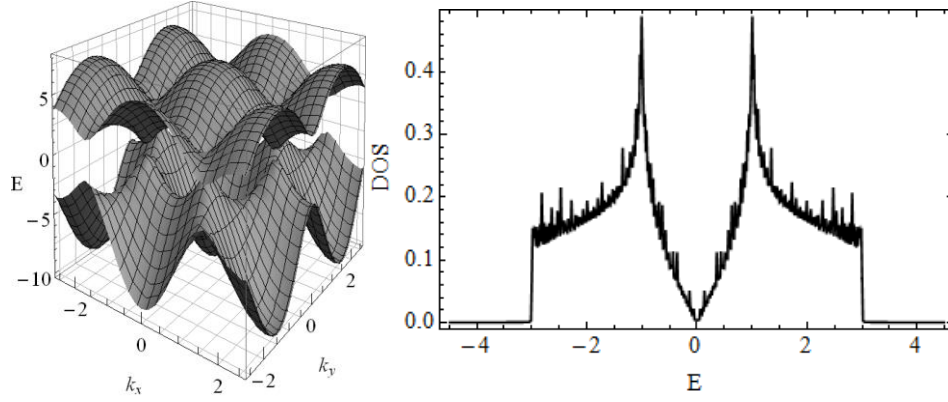


Fig. 3: Electronic spectrum depending on the  $x$  and  $y$  components of the wave vector and the density of states of planar graphene.

### 2.1. Influence of the Magnetic Field

Now, we consider the influence of a uniform magnetic field whose direction is perpendicular to the molecular surface. In this case, the terms of the matrix in (4) are multiplied by the exponentials depending on the magnetic flux, so, the system of equations (6) can be rewritten into the form

$$EC_j = \sum_{i,m,n} t_i \Omega_{\vec{k},j,m}^{N(i)} C_m \rightarrow EC_j = \sum_{i,m,n} t_i \exp(i\gamma_{jm}) \Omega_{\vec{k},j,m}^{N(i)} C_m. \quad (8)$$

The resulting system of equations is called the Harper equations [9]. Here,  $\gamma_{jm}$  is the magnetic phase factor. Its value is

$$\gamma_{ij} = -2\pi i \frac{e}{\hbar} \int_i^j \vec{A} d\vec{l}, \quad (9)$$

where the integration goes over the line from  $i$ -th to  $j$ -th atomic site.  $\vec{A}$  is the vector potential, for which  $\text{rot} \vec{A} = \vec{B}$ .

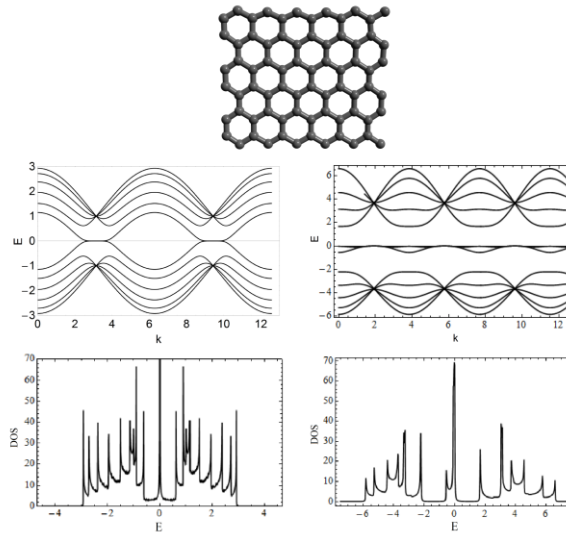


Fig. 4: Schematic sketch of the zigzag nanoribbon (up), electronic spectrum (middle) and the density of states (bottom) for the graphitic and phosphorene cases.

There is a lot of possibilities, how to satisfy this relation, we chose  $\vec{A} = (0, Bx, 0)$ . Next, we denote  $\hbar/e = \Phi_0$ , then

$$\gamma_{ij} = -\frac{2\pi i}{\Phi_0} \int_i^j Bx dy = -\frac{\pi i B}{\Phi_0} (x_j + x_i)(y_j - y_i). \quad (10)$$

Let us suppose that we investigate a structure which contains no defects (pentagonal or heptagonal), then

$$x_\beta + x_\alpha = 2m_a + s_1 \frac{a}{2} \sqrt{3}, \quad y_\beta - y_\alpha = s_2 \frac{a}{2} \quad (11)$$

with  $s_1, s_2$  integers, so,

$$\gamma_{ij} = -\frac{\pi i}{2\Phi_0} 4nB \cdot \frac{3}{2} a^2 \sqrt{3} \left( \frac{s_2 m_a}{3na\sqrt{3}} + \frac{s_1 s_2}{12n} \right) = -\frac{\pi i}{2\Phi_0} 4nB \cdot S \left( \frac{s_2 m_a}{3na\sqrt{3}} + \frac{s_1 s_2}{12n} \right) = -\frac{\pi i}{2\Phi_0} \Phi \left( \frac{s_2 m_a}{3na\sqrt{3}} + \frac{s_1 s_2}{12n} \right). \quad (12)$$

Here,  $a$  is the length of the atomic bond,  $\Phi = 4nB \cdot S = 4nB \cdot \frac{3}{2} a^2 \sqrt{3}$  is the magnetic flow through  $4n$  hexagons and the choice of  $n$  is such that  $3na\sqrt{3}$  is the translation vector in the  $x$ -direction. If  $\Phi/\Phi_0 = p/q$  with  $p, q$  mutually primes, we can easily find that for  $s_2 = 1$ ,  $\gamma_{ij}$  as a function of  $\frac{m_a}{3na\sqrt{3}}$  has the period  $4q$ . As the consequence, the size of the elementary cell is enlarged  $4q$ -times (Fig. 4) and in the same way, the size of the matrix (4) is changed.

## 2.2. Dependence of the Spectra on the Magnetic Field

In Figs. 5 and 6, we compare the dependence of the electronic spectrum on the magnetic flux for the graphene and the phosphorene monolayers and the corresponding narrow nanoribbons. We see that while the case of the monolayers shows a big similarity in the appropriate spectra, this similarity violates in the case of the appropriate nanoribbons.

In the agreement with [10,11], the graphs in Fig. 5 show a fractal structure. This kind of the fractal structure was called the Hofstadter butterfly [12]. The appearance of the fractal structure is connected with the self-similarity of the electronic spectrum for different values of the magnetic field [10,13] and with the periodicity following from the previous subsection. In the case of graphene, the period depends on the chosen kind of the approximation: it is 1 for the presented case of the nearest-neighbor approximation (Fig. 7 left), however, it would be 6 for the case of the next-nearest-neighbor approximation. In the case of phosphorene, where the 3rd nearest neighbors are considered, the period is 8 and because of the complicated puckered honeycomb lattice structure of phosphorene, we don't consider different kinds of the approach here.

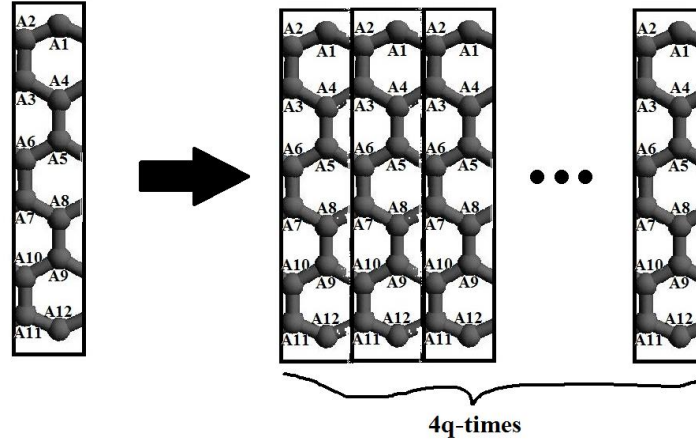


Fig. 4: Enlargement of the elementary cell in the presence of an uniform magnetic field.

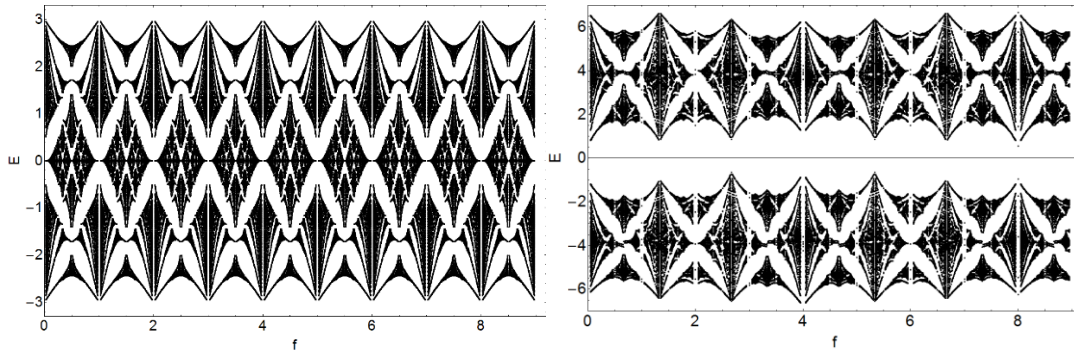


Fig. 5: Electronic spectrum of the graphene (left) and the phosphorene monolayers (right) depending on the magnetic flux.

In the case of the nanoribbons, the fractal structure of the magnetic dependence of the electronic spectrum is disrupted (Fig. 6). Here, we do the calculations for the narrow nanoribbons which we will investigate in the next section as well. In this case of the narrow nanoribbons, the disruption of the spectrum is more significant. In the graphitic case, new small gaps appear. On the other hand, some of the main features of the graph (in comparison with the case of the plain graphene) remain. In the phosphorene case, a significant shift of the gaps occurs. As we will see, the addition of the atomic vacancies into the molecular structure increases the number of the gaps in the electronic spectrum and its character will be changed significantly for both the graphitic and phosphorene cases.

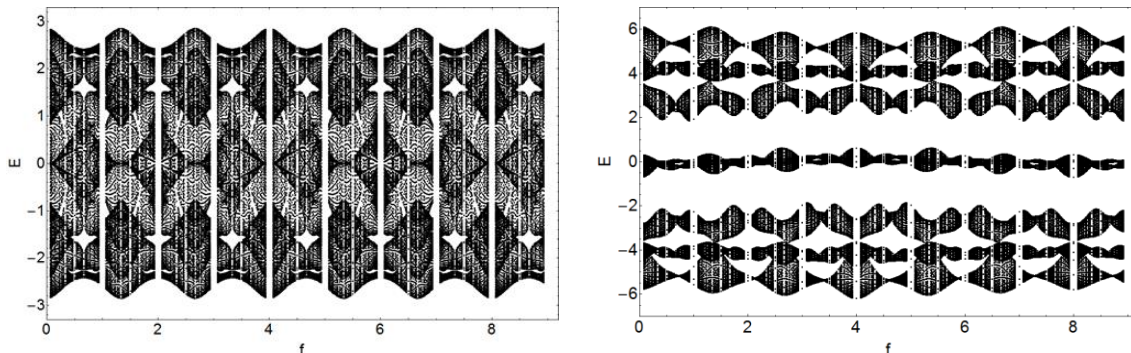


Fig. 6: Electronic spectrum of the graphene (left) and the phosphorene (right) nanoribbons depending on the magnetic flux.

### 3. Zigzag Nanoribbons with Atomic Vacancies Influenced by the Magnetic Field

Now, we investigate the modifications of the narrow zigzag nanoribbons which contain atomic vacancies in the edge structure. These vacancies can have a significant impact on the thermal properties [14]. We investigate the influence of the magnetic field on the electronic spectrum for some simple cases of a periodic placement of the vacancies in the edge structure.

In Fig. 7, the dependence of the electronic spectrum on the magnetic field is plotted for different distances between 2 vacancies in the molecular structure. We see that the magnetic field influences the width of the gaps in the electronic spectrum. Moreover, some new gaps can be created (and other can violate). For the purpose of the simplification, we don't consider the influence of the next-nearest neighbors in the case of the graphene nanoribbons. Except the periodicity, this does not affect the results. We see that - neglecting the length of the period - for the case of the phosphorene nanoribbons, the resulting spectrum does not differ very much from the case without vacancies in Fig. 6: some new gaps in the electronic spectrum arise in addition to the existing gaps, but their size is quite small. On the other hand, in the case of the graphene nanoribbons, a lot of new gaps is created which in fact suppresses the structure of the Hofstadter butterfly which is still visible in the case without vacancies (Fig. 6). Furthermore, for each distance between the vacancies, the placement of the gaps in the electronic spectrum is characteristic and for the higher distances between the vacancies, the density of the gaps is so high that it results in the creation of new edge states. This effect of the creation of the edge states occurs (with a smaller intensity) in the case of the phosphorene nanoribbons as well. It is interesting to compare this feature with the results in [15], where the addition of an impurity into the structure of the planar graphene causes the creation of the localized states.

### 4. Nanoribbons with Stone-Wales defects

In the case when in the investigated structure some defects are present, the equations (11) and (12) are changed in this way:

$$x_\beta + x_\alpha = 2m_a + s_1a, \quad y_\beta - y_\alpha = s_2a, \quad (13)$$

where  $s_1, s_2$  are real numbers. Next, if  $S = k_1a^2$  denotes the area of the elementary cell and  $\Delta = k_2a$  is the translation vector, then

$$\gamma_{ij} = -\frac{\pi i B}{\Phi_0} (2m_a + s_1a)s_2a = -\frac{\pi i}{2\Phi_0} BS \frac{2(2m_a + s_1a)s_2a}{k_1a^2} = -\frac{\pi i}{2\Phi_0} BS \frac{2k_2}{k_1} \left( 2s_2 \frac{m_a}{k_2a} + \frac{s_1s_2}{k_2} \right). \quad (14)$$

Here, we denote  $\Phi = \frac{2k_2}{k_1} S \cdot B$  and the next procedure is similar as in the previous case, it means we require that

$\Phi / \Phi_0 = p / q$  with  $p, q$  the mutually primes. Then, the magnetic factor as a function of  $2s_2 \frac{m_a}{k_2a}$  has the period  $4q$ , so it

has the period  $2q / s_2$  as a function of  $\frac{m_a}{k_2a}$ . But a problem appears here: generally,  $2q / s_2$  is a real multiple of  $q$  and the

number of the magnetic factors (with real periods) is higher than 1. It means that they have not a common period, so, the magnetic elementary cell is infinite and we can do only an estimate of the solution. This is also the case of the structure containing the Stone-Wales defects [14] (periodically repeating combination of the pentagons and the heptagons - Fig. 8).

### 5. Conclusion

We studied the behavior of the phosphorene and graphene zigzag nanoribbons with atomic vacancies and Stone-Wales defects under the influence of an uniform magnetic field, perpendicular to the molecular surface. It follows from the plots in Figs. 7 and 8 that if we vary the values of the magnetic field, it would have a strong influence on the electronic structure and connected metallic and semiconducting properties: a lot of new gaps in the electronic spectrum appear and other disappear.



This variability is much higher in the case of the graphene nanoribbons. In the case of the phosphorene nanoribbons, the dependence of the electronic spectrum on the magnetic field has nearly the same character for an arbitrary length of the unit cell (Fig. 7). The electronic spectrum shows self-similar properties [10], i.e. it has a similar character for all the values of the magnetic field, but the size of the curves in the graphs changes. Furthermore, next edge states appear.

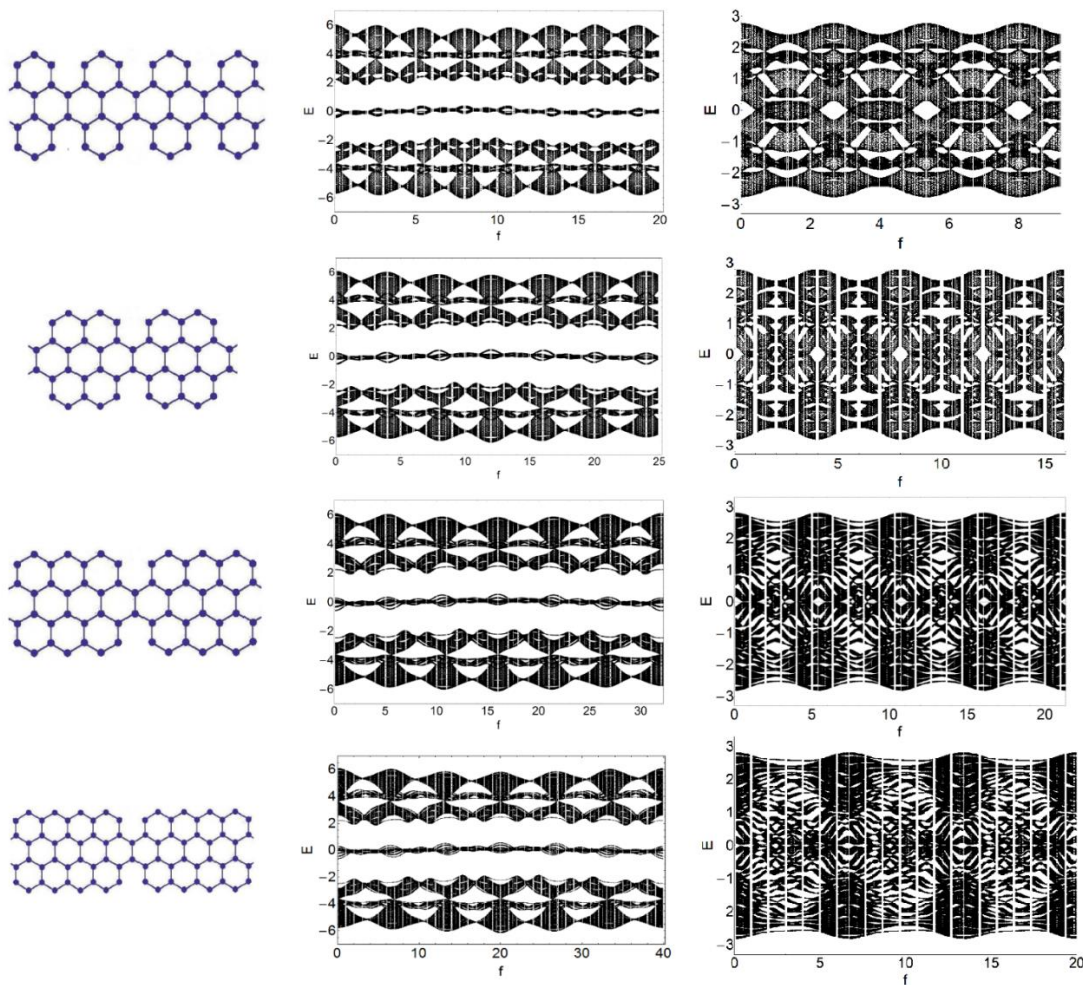


Fig. 7: Electronic spectra depending on the magnetic flux for different kinds of the phosphorene and graphene zigzag nanoribbons. The corresponding molecular surfaces are sketched in the left part.

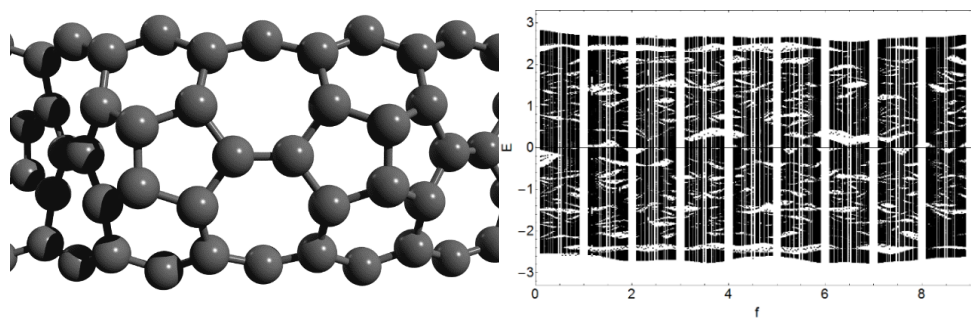


Fig. 8: Electronic spectrum of the nanoribbon containing the Stone-Wales defects. The periods of the magnetic factors are approximately  $2.081q, 12.658q, 2.472q, 2.328q, 6.472q$  and  $2q$ , so we chose the size of the magnetic elementary cell to be  $13q$ -times larger than the usual elementary cell (i.e. we chose the smallest integer multiple of  $q$  higher than arbitrary of the periods). But it can only approximate the real solution.



In the case of the atomic vacancies, the dependence on the magnetic field is periodic, i.e. it can be characterized by a dependence on the values on a minimal interval. Another situation happens in the case of the Stone-Wales defects: the sizes of these defects and hexagons have not common multiples; so, we have to do an estimate of the size of the matrix of the Hamiltonian to get an acceptable approach of the electronic spectrum which has not periodic dependence on the magnetic field (Fig. 8).

In summary, the phosphorene nanostructures are characteristic by their energy band gap and high hole mobility [16]. This makes them good candidates for the field effect transistors. As we demonstrated, the corresponding zigzag nanoribbons are metallic. In the same way, we can show the semiconducting properties of the armchair nanoribbons. By the hydrogenization of the edges, both forms would become semiconducting and their thermal properties would improve significantly. This makes them good candidates for the thermoelectric applications [17]. Our calculations showed a considerable influence of the magnetic field on the gaps in the electronic spectrum. This could have an important significance for both areas of the field effect transistors as well as the thermoelectric applications.

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