ISSN 1063-7826, Semiconductors, 2020, Vol. 54, No. 12, pp. 1678–1681. © Pleiades Publishing, Ltd., 2020.

XXVIII INTERNATIONAL SYMPOSIUM
"NANOSTRUCTURES: PHYSICS AND TECHNOLOGY",
MINSK, REPUBLIC OF BELARUS, SEPTEMBER, 2020.
GRAPHENE

Quantum Chemical Calculations of Carbon Nanoscroll Energy Rolled from Zigzag Graphene Nanoribbon

A. I. Siahlo[a], S. A. Vyrko[a], S. V. Ratkevich[a], N. A. Poklonski[a,*], A. T. Vlassov[a], N. N. Hieu[b,c], and Yu. E. Lozovik[d,e]

[a] *Physics Department, Belarusian State University, Minsk, 220030 Belarus*
[b] *Institute of Research and Development, Duy Tan University, Da Nang, Vietnam*
[c] *Faculty of Natural Sciences, Duy Tan University, Da Nang, Vietnam*
[d] *Institute for Spectroscopy of Russian Academy of Sciences, Troitsk, Moscow, 108840 Russia*
[e] *Moscow Institute of Electronics and Mathematics, National Research University Higher School of Economics, Moscow, 101000 Russia*
**e-mail: poklonski@bsu.by*

Received June 27, 2020; revised July 23, 2020; accepted July 27, 2020

Abstract—Using the semi-empirical quantum chemical PM3 method the energies of carbon nanoscrolls formed from flat zigzag graphene nanoribbons 46zGNR and 70zGNR are calculated. For this purpose a simple algorithm to define the Cartesian coordinates of the atoms of a carbon nanoscroll is proposed. The dependences of the energy of the nanoscrolls relative to the energy of the corresponding flat nanoribbon on the inner radius of nanoscroll obtained using both the quantum chemical calculations and the semi-classical analytical model shows the bistability of the system. This shows promise for nanoscroll-based nanoelectromechanical systems.

Keywords: carbon nanoscroll, graphene nanoribbon, Archimedean spiral, Cartesian coordinates
DOI: 10.1134/S1063782620120350

1. INTRODUCTION

Carbon nanoscroll is a single graphene layer rolled into a scroll [1, 2]. It is known that the structure and energetics of a system which contain up to a few hundred atoms can be calculated using the quantum chemical methods [3]. For example, the calculations of the electronic band structure and the magnetic states of zigzag graphene nanoribbons using the semiempirical method of molecular orbitals PM3 [4], implemented in the MOPAC2016 program [5], were provided in [6]. The atom coordinates in [6] were initially set using translation algorithms and then refined by the full geometry optimization of nanoribbons. In the present work we propose a simple algorithm to define the Cartesian coordinates of the atoms of a carbon nanoscroll to use them in quantum chemical calculations.

The purpose of the work is to define the atomic structure of nanoscrolls for quantum chemical calculations using the analytical expressions and to compare the change of nanoscroll energy at process of the nanoscroll rolling from flat graphene nanoribbon obtained by the semi-classical analytical model and by the quantum chemical method.

2. RESULTS AND DISCUSSION

The length L of a zigzag graphene nanoribbon nzGNR, that forms a nanoscroll, is equal to $L = (3n/2 - 1)a_{CC}$, where n is the number of zigzag chains along the length of the nanoribbon (along the x axis in Fig. 1a) and $a_{CC} = 0.142$ nm is the C–C bond length of graphene. For 46zGNR ($n = 46$) the length $L = 9.66$ nm and for 70zGNR ($n = 70$) the length $L = 14.77$ nm.

The coordinates of carbon atom of a zigzag nanoribbon, which is rolled into a nanoscroll, are determined by the three indices: the first index q corresponds to two atoms in graphene unit cell and takes the values A or B, the second index i is the number of the graphene unit cell along the length L of the nanoribbon, and the third index j is the number of the graphene unit cell along the width W of the nanoribbon, see Fig. 1a. The coordinates of the carbon atoms of the nanoribbon are given by the formulae:

$$x_{Aij} = (3/2)(i-1)a_{CC}, \quad x_{Bij} = x_{Aij} + a_{CC},$$
$$y_{qij} = (j-1)a + a/2 \text{ for odd } i,$$
$$y_{qij} = (j-1)a \text{ for even } i,$$

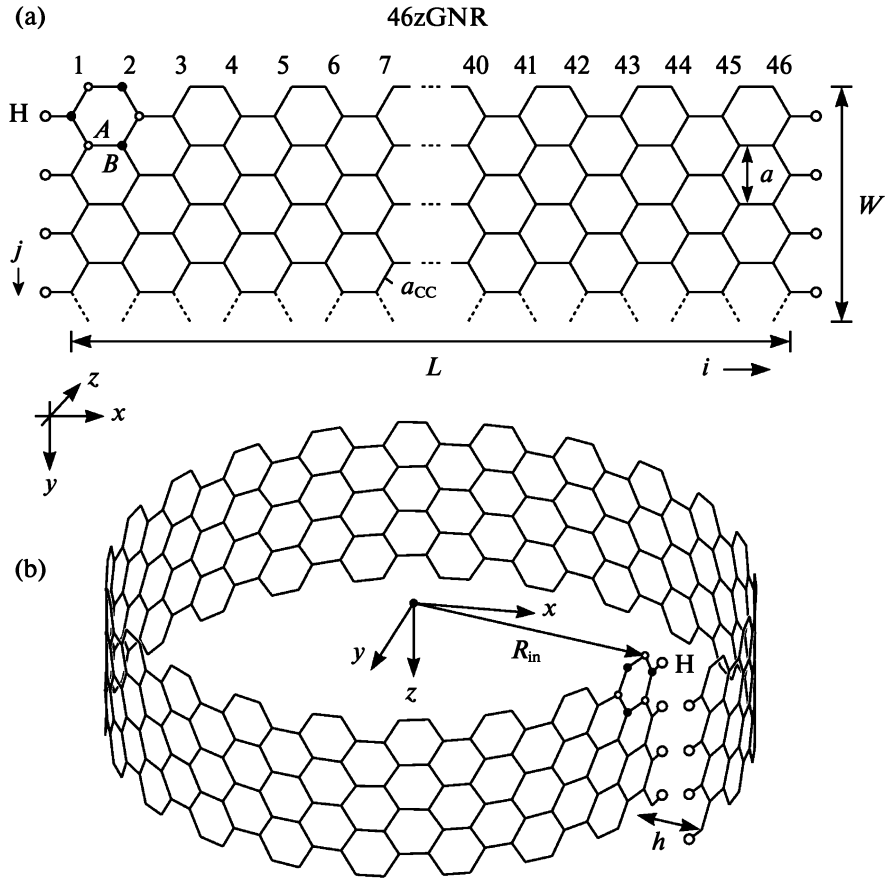

Fig. 1. Structure of a computational cell of width W for 46zGNR nanoribbon of length L (a) and for a nanoscroll formed from the nanoribbon with the inner radius $R_{in} = 1.35$ nm (b). Here $n = 46$ zigzag chains of carbon atoms constituting the 46zGNR are enumerated; a_{CC} is the C–C bond length of graphene, a is the graphene translation period, and h is the distance between the layers of the nanoscroll.

$$z_{qij} = 0, \tag{1}$$

where $a = \sqrt{3}a_{CC} = 0.246$ nm is the graphene translation period (along the y axis).

The free zigzag edges of the nanoribbon are passivated by hydrogen atoms, which are positioned at the distances of $a_{CH} = 0.1091$ nm from the carbon atoms along the x axis.

A nanoribbon rolled up around the axis that is perpendicular to the nanoribbon length (around the y axis in Fig. 1a) forms a carbon nanoscroll shown in Fig. 1b. The cross-section of the nanoscroll is the Archimedean spiral with the distance between the turns $h = 0.335$ nm (this equals to the distance between graphite layers). Note that in the proposed model of the nanoscroll geometry the distance between carbon atoms is not equal to a_{CC} (Fig. 1b). The coordinates $(x_{qij}, y_{qij}, z_{qij})$ for carbon atoms of the nanoscroll are given by the following expressions:

$$x_{qij} = R_{qij}\cos(\varphi_{qij}), \quad y_{qij} = R_{qij}\sin(\varphi_{qij}),$$

$$z_{qij} = (j-1)a + a/2 \text{ for odd } i,$$

$$z_{qij} = (j-1)a \text{ for even } i, \tag{2}$$

where $R_{qij} = h\varphi_{qij}/2\pi$ is the curvature radius of the nanoscroll surface at the point corresponding to the angle φ_{qij} in radians, which is found from the equation $X_{qij} = \Lambda(\varphi_{in}, \varphi_{qij})$, here $X_{Aij} = (3/2)(i-1)a_{CC}$ and $X_{Bij} = X_{Aij} + a_{CC}$ are the coordinates of carbon atoms along x axis of the corresponding nanoribbon, and

$$\Lambda(\varphi_{in}, \varphi_{qij}) = \int_{\varphi_{in}}^{\varphi_{qij}} \frac{h}{2\pi}\sqrt{1+\varphi^2}d\varphi$$

$$= \frac{h}{4\pi}[\varphi_{qij}\sqrt{1+\varphi_{qij}^2} - \varphi_{in}\sqrt{1+\varphi_{in}^2}$$

$$+ \ln(\varphi_{qij} + \sqrt{1+\varphi_{qij}^2}) - \ln(\varphi_{in} + \sqrt{1+\varphi_{in}^2})] \tag{3}$$

is the length of an Archimedean spiral with the distance between the adjacent nanoscroll turns h, the inner angle φ_{in}, and the outer angle φ_{qij}. The inner angle φ_{in} of the nanoscroll is expressed via the inner radius R_{in} as $\varphi_{in} = 2\pi R_{in}/h$. Note that we used the different systems of coordinates for the carbon nanoscroll

and for the carbon nanoribbon. For the nanoribbon the x axis is directed along the nanoribbon length L, while for the nanoscroll the xy plane is perpendicular to the axis of the nanoscroll.

In the quantum chemical calculations the periodic boundary conditions along the axis of the nanoscroll (z axis in Fig. 1b) were used. The width W of the computational cell was set to four graphene translation periods along the axis of the nanoscroll, $W = 4\sqrt{3}a_{CC} = 0.984$ nm, for both nanoribbon and nanoscroll.

Figure 2 shows the total energy of the nanoscrolls formed from the carbon nanoribbons 46zGNR (points a) and 70zGNR (points b) with the coordinates of carbon atoms defined by Eq. (2) relative to the total energy E_{flat} of the corresponding flat nanoribbon with coordinates defined by Eq. (1), calculated in MOPAC2016 program, as the function of the nanoscroll inner radius R_{in}. The PM3 method was used; the optimization of the structures was not carried out.

A semi-classical analytical model for calculating of the structure and energetics of a carbon nanoscroll formed from a rectangular graphene nanoribbon has been proposed [2]. The model includes following parameters of the nanoscroll: the length L of the nanoribbon, which forms the nanoscroll, the nanoscroll width W, the distance $h = 0.335$ nm between the layers of the nanoscroll, the inner radius R_{in}, the area $S_a = 3\sqrt{3}a_{CC}^2/4 = 0.0262$ nm^2 per atom in graphene, the elastic constant $C = 20.1$ meV nm^2/atom relating elastic energy with the radius R of curvature of the graphene layer ($E_{el} = C/R^2$), and van der Waals interaction energy between graphene layers $\varepsilon = -35$ meV/atom. The dependences of the nanoscroll energy on the geometric parameters of nanoscrolls in [2] are presented and the conclusions about the stability of the nanoscroll are made.

According to [2], the total energy of a nanoscroll rolled up in the form of an Archimedean spiral ($R = h\varphi/2\pi$) with a distance between turns of h from a nanoribbon of width W and length $L = \Lambda(\varphi_{in},\varphi_{out})$ is the sum of the energy of van der Waals interaction E_W between layers of a nanoscroll and bending elastic energy E_{el} of a nanoscroll:

$$E = E_W + E_{el}; \quad E_W = \frac{1}{2}\frac{\varepsilon W}{S_a} \times [\Lambda(\varphi_{in},\varphi_{out} - 2\pi) + \Lambda(\varphi_{in} + 2\pi,\varphi_{out})],$$

$$E_{el} = \frac{2\pi CW}{hS_a}\int_{\varphi_{in}}^{\varphi_{out}} \frac{\sqrt{1+\varphi^2}}{\varphi^2}d\varphi = \frac{2\pi CW}{hS_a}\left[\frac{\sqrt{1+\varphi_{in}^2}}{\varphi_{in}} - \frac{\sqrt{1+\varphi_{out}^2}}{\varphi_{out}} + \ln(\varphi_{out} + \sqrt{1+\varphi_{out}^2}) - \ln(\varphi_{in} + \sqrt{1+\varphi_{in}^2})\right]. \quad (4)$$

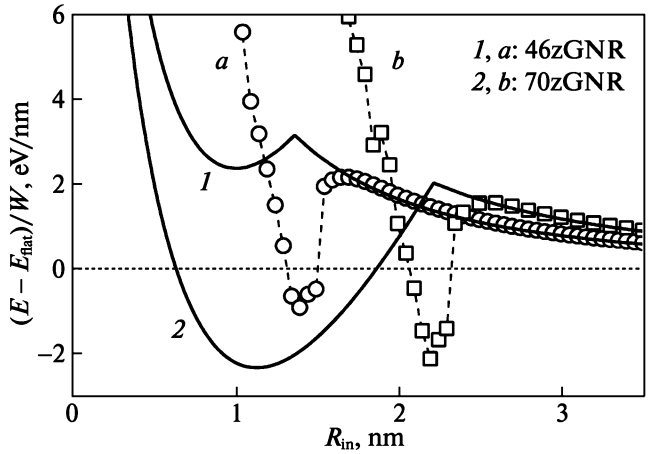

Fig. 2. The total energy of nanoscroll E with respect to the energy E_{flat} of the corresponding flat nanoribbon of length $L = 9.66$ nm (46zGNR: *1*, *a*) and 15 nm (70zGNR: *2*, *b*), as a function of the inner radius R_{in} of the nanoscroll. Calculations are performed using the PM3 quantum chemical method (points *a* and *b*) and using the semi-classical analytical model [2] (curves *1* and *2*). The energies are shown per width W of the computational cell.

For comparison, the calculations of the total energy of the nanoscrolls according to the semi-classical analytical model [2] are also presented in Fig. 2 (curves *1* and *2*).

The semi-classical analytical and quantum chemical calculations show a similar behavior of the nanoscroll energy as a function of R_{in}. For both calculation methods, at large R_{in} the nanoscroll energy converges to the energy of the flat nanoribbon. During nanoscroll rolling (moving along the horizontal axis in Fig. 2 from right to left) the energy increases, can have a maximum value, can have a minimum value and then increases at further decreasing of R_{in}. The calculations by the PM3 method show that the nanoscrolls have a minimum energy at the specific inner radius $R_{in} \approx 1.35$ nm for 46zGNR and $R_{in} \approx 2.2$ nm for 70zGNR. The calculations by the semi-classical analytical model give the minimum energy at the inner radius $R_{in} \approx 1$ nm for $L = 9.66$ nm and $R_{in} \approx 1.2$ nm for $L = 15$ nm. Both the quantum chemical calculations and the semi-classical analytical model show that there is a barrier for the nanoscroll unrolling, i.e. the bistability of the system (see Fig. 2). Such a bistability allows us to consider the possible application of the nanoscroll in nanoelectromechanical systems.

3. CONCLUSIONS

A simple algorithm to define the Cartesian coordinates of the atoms of a carbon nanoscroll for using in quantum chemical calculations is proposed. Using the semi-empirical quantum chemical method PM3 and the semi-classical analytical model, the energy of the

graphene nanoribbon rolled into the carbon nanoscroll is calculated. Both the quantum chemical and analytical calculations show that there is a barrier between the stable nanoscroll and the flat nanoribbon, i.e. the bistability of the system. Such a bistability makes possible application of the nanoscroll in nanoelectromechanical systems such as nanorelay and memory cells.

FUNDING

The work has been supported by the Belarusian Republican Foundation for Fundamental Research (grant no. F20R-301) and the Research Program "Convergence-2020"; Y.E.L. acknowledges support by the Russian Foundation of Basic Research (grant no. 20-52-00035) and Program for Basic Research of the National Research University Higher School of Economics.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

REFERENCES

1. H. Liu, T. Le, L. Zhang, and M. Xu, J. Mater. Sci.: Mater. Electron. **29**, 18891 (2018).
2. A. I. Siahlo, N. A. Poklonski, A. V. Lebedev, I. V. Lebedeva, A. M. Popov, S. A. Vyrko, A. A. Knizhnik, and Yu. E. Lozovik, Phys. Rev. Mater. **2**, 036001 (2018).
3. N. A. Poklonski, S. A. Vyrko, A. I. Siahlo, O. N. Poklonskaya, S. V. Ratkevich, N. N. Hieu, and A. A. Kocherzhenko, Mater. Res. Express **6**, 042002 (2019).
4. J. J. P. Stewart, J. Comput. Chem. **10**, 209 (1989).
5. J. J. P. Stewart, *MOPAC2016* (Stewart Comput. Chemistry, Colorado Springs, CO, USA, 2012). http://openmopac.net.
6. N. A. Poklonski, E. F. Kislyakov, S. A. Vyrko, O. N. Bubel', and S. V. Ratkevich, J. Nanophoton. **6**, 061712 (2012).