ACTA PHYSICA POLONICA A No. 1 Vol. **142** (2022)

Papers submitted to the Conference "Applications of Physics in Mechanical and Material Engineering"

Geometric Isomers of the (3,1) Carbon Nanotube: A Theoretical Study

B. Brzostowski[a], A.P. Durajski[b],
K.M. Gruszka[c] and J. Wojtkiewicz[d,*]

[a] *Faculty of Physics and Astronomy, University of Wrocław,*
pl. M. Borna 9, 50-204 Wrocław, Poland
[b] *Institute of Physics, Częstochowa University of Technology,*
19 Armii Krajowej Av., 42-200 Czestochowa, Poland
[c] *Institute of Physics, Częstochowa University of Technology,*
19 Armii Krajowej Av., 42-200 Czestochowa, Poland
[d] *Faculty of Physics, Warsaw University, Pasteura 5, 02-093 Warszawa, Poland*

Doi: 10.12693/APhysPolA.142.21 *e-mail: wjacek@fuw.edu.pl

This paper presents the results of density functional theory calculations for the (3,1) carbon nanotube ensuing in two structural configurations, representing two local energy minima. To be sure in this conclusion, we used two distinct density functional theory implementations and three different structure optimization algorithms. The interatomic distances of the two kinds of (3,1) carbon nanotubes do not differ too much, but the other properties are more pronounced. We found that the HOMO–LUMO energy gap of the lower energy configuration is 0.69 eV, whereas the second configuration possesses the 0.36 eV HOMO–LUMO gap. Both isomers have been obtained by optimization because the calculations started either with a different initial configuration or with different starting parameters critical for convergence, efficiency and/or accuracy.

topics: carbon nanotubes, electronic properties, DFT calculations

1. Introduction

Carbon nanotubes (CNTs) — quasi-one-dimensional allotropes of carbon, constructed as cylindrical tubes with nanometers in diameter and up to several millimeters in length — have attracted significant research interest ever since their discovery due to their outstanding properties. It is well known that the physical properties and the electronic structure of CNTs are closely related to their chirality (n, m) [1]. In achiral nanotubes, $n = m$, when n is a multiple of three, CNTs become zero-gap semiconductors. Otherwise they become semiconducting nanotubes with a finite size of the band gap. The band gap decreases with the increasing diameter of the tube, approaching zero at infinite diameter. In the case of chiral nanotubes, $n \neq m$, where $n - m = 3k$ with an integer k, CNTs become metallic. Otherwise, they become semiconducting nanotubes [2, 3].

Due to the wide applicability of different CNTs, many papers explore their various properties, such as semiconducting and metallicity features [4–6], and mechanical, magnetic [1], and optical properties [7, 8], to name just a few. Those papers are devoted to the study of CNTs' various properties according to their configuration described using (n, m) notation [9]. In all of them, however, it is implicitly assumed that the chirality parameter (n, m) uniquely determines the whole structure of the CNT.

Here, we want to report detected geometric isomers of the (3,1) CNT. More precisely, we have found two configurations of non-equal energy, i.e., ground state configuration and configuration with higher energy. The identified second configuration has local energy minima and, when compared to the ground state, possesses the identical structure of chemical interatomic bonds, however, distances between atoms are different in both of them. More importantly, both possess different electronic properties, e.g., the energy gap being equal to 0.69 eV for the first one, whereas, for the second one, the gap is 0.37 eV. We have tested carefully to ensure that both of these structures are equilibrium ones, i.e., both correspond to local energy minima.

2. Computational methods

To study the electronic properties of investigated materials, first-principles calculations are performed within the framework of the density-functional theory (DFT) [10] as implemented in the Quantum Espresso (QE) [11, 12] and Siesta [13]

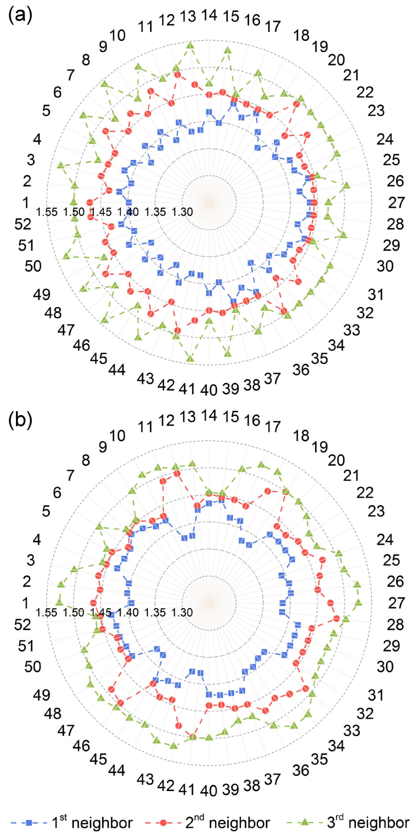

Fig. 1. Histogram of the distance between neighbor C–C atoms for (a) structure#1 and (b) structure#2.

packages. The exchange and correlation effects were accounted for by the generalized gradient approximation (GGA) with PBE exchange-correlation potential. In Quantum Espresso, the optimized atomic structures were obtained by fully relaxing both atomic positions as well as cell parameters by using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) quasi-Newton algorithm. For comparison, in Siesta, two optimization methods were used, i.e., conjugate gradients (CG) and fast inertial relaxation engine (FIRE) [14]. For all the above three methods, the optimization algorithm varied the atomic structure of the system until all forces were smaller than 10^{-6} eV/Å. All parameters critical for convergence, such as the $\boldsymbol{k}$-points mesh and the energy cutoff, were carefully tested to ensure the most accurate results.

3. Results and discussion

We used various generally available generators to obtain the initial structure of the (3,1) nanotube. As a result of optimization, we reach two slightly different atomic configurations.

After performing geometry optimization, we found that the structures are very similar for both CNTs. For structure#2, the cell length along the periodic axis (conventionally named the z-axis) is slightly longer (0.06 Å). In Fig. 1, the relative distances between first three neighbors are presented, i.e., the distance between each CNT's atom (numbered at outline) and its three closest neighbors. The observed differences between both structures are easily noticeable, although the absolute differences in distances are rather small. As can be seen, the distances present some oscillatory behavior for both structures. In the case of structure#1, however, it seems that neighbor positions vary more regularly compared to structure#2. It is also worth noting that when the distance to the first neighbor is shorter, then in most cases, the distance to neighbor 2 and 3 is more similar.

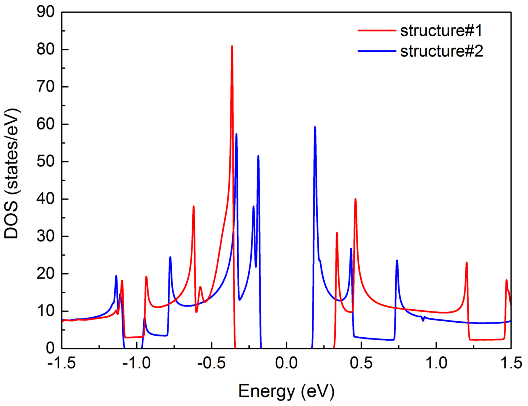

Fig. 2. Total density of states for both investigated CNT structures.

For the CG method in Siesta, regardless of the input structure, the optimization always led to the ground state, i.e., structure#1. However, if we used as input the optimized structure#2, then the system remained in this state even for rigorous optimization parameters. The second optimization method in Siesta, i.e., FIRE, leads to structure#1 or structure#2, depending on the initial time step. For smaller values of this parameter, we get the ground state configuration, and for larger values — the second structure.

In QE, to obtain structure#2, we employed a special two-step procedure, in which the first and second steps differ in tightness in force convergence criteria. First, we generated ideal atomic positions with a fixed 1.41 Å in C–C distance and relaxed, thus obtaining a structure with loose force convergence set to 10^{-4} eV/Å. Then we again relaxed the structure from the previous step, this time setting the convergence threshold to 10^{-6} eV/Å. For the ground state CNT (structure#1), we started from the same ideal structure this time, however, we fixed the convergence threshold to 10^{-6} eV/Å from the very beginning. In general, we found that reproduction of structure#2 is rather hard, especially when starting from randomized atomic orbitals. In that case, several trial runs had to be performed.

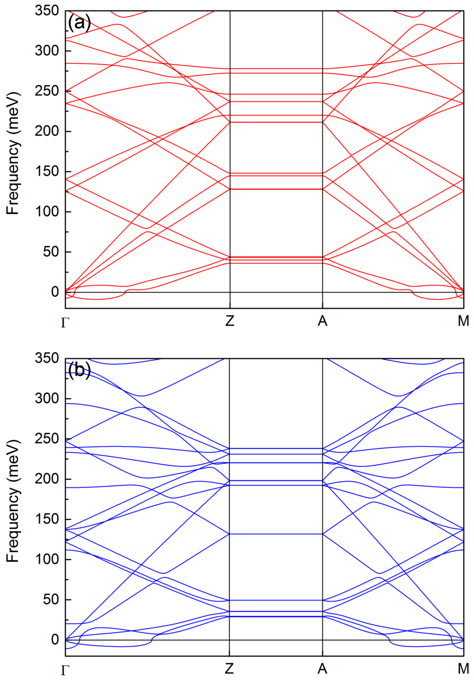

Fig. 3. Phonon frequency dispersion for structure#1 (a) and structure#2 (b) along Γ–Z–A–M high-symmetry line in the Brillouin zone.

From the results presented in Fig. 2, we see that in contrast to semimetal pristine graphene, the (3,1) carbon nanotube systems exhibit an isolation behavior, with HOMO-LUMO (H-L) energy gap of 0.69 eV and 0.37 eV, for structure#1 and structure#2, respectively. Moreover, structure#1 is energetically more favorable, with energy smaller by 0.68 eV compared to structure#2.

The dynamical stability of investigated structures was examined through the calculation of the phonon band structures. The dynamic instability appears as imaginary frequency. Figure 3 shows the obtained results. Both CNTs have imaginary frequencies, however, structure#1 has smaller imaginary frequencies. It means that structure#2 is not only energetically unfavorable — it is also dynamically more unstable.

4. Conclusions

Using different optimization methods in two DFT implementations, we found for (3,1) carbon nanotube two alternative geometric structures with similar total energies and different electronic properties. For a large number of tests and despite the use of various optimization algorithms, it turned out that if the system converges to structure#2, it remains in this state even for very strict convergence parameters such as energy cutoff, $\boldsymbol{k}$-points mesh, and force tolerance. The HOMO–LUMO gap for the ground-state structure (0.69 eV) is more than twice as large as the second structure (0.37 eV). Since the total energy difference between these structures is less than 0.7 eV, the coexistence of both structures is possible. On the base of the phonon dispersion relations, it seems that structure#2 is less dynamically stable. It remains an open question whether the previously reported values of the H-L gap for various carbon nanotubes were for sure obtained for the ground state. We hope that our results will provide useful guidance for future experimental and theoretical studies on CNTs and will allow verification of whether a similar effect occurs for other nanotubes.

Acknowledgments

We acknowledge the access to the PSNC supercomputing resources.

References

[1] A. Jorio, G. Dresselhaus, M.S. Dresselhaus, *Carbon Nanotubes*, Springer Verlag, 2008.

[2] M.S. Dresselhaus, G. Dresselhaus, R. Saito, *Phys. Rev. B* **45**, 6234 (1992).

[3] K.S. Kim, K.A. Park, H.J. Kim, D.J. Bae, S.C. Lim, Y.H. Lee, J.R. Kim, J.J. Kim, W.B. Choi, *J. Korean Phys. Soc.* **42**, S137 (2003).

[4] M.K. Niranjan, *J. Phys. Commun.* **4**, 015004 (2020).

[5] C. Kamal, A. Chakrabarti, *Phys. Rev. B* **76**, 075113 (2007).

[6] J. Yuan, Y. Huang, *J. Mol. Struct. THEOCHEM* **942**, 88 (2010).

[7] C.D. Spataru, S. Ismail-Beigi, L.X. Benedict, S.G. Louie, *Phys. Rev. Lett.* **92**, 077402 (2004).

[8] J. Wojtkiewicz, B. Brzostowski, M. Pilch, in: *Parallel Processing and Applied Mathematics*, Eds. R. Wyrzykowski, E. Deelman, J. Dongarra, K. Karczewski, 2020, p. 341.

[9] S.B. Sinnott, R. Andrews, *Crit. Rev. Solid State Mater. Sci.* **26**, 145 (2001).

[10] R. Parr, W. Yang, *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, New York 1989.

[11] P. Giannozzi, S. Baroni, N. Bonini et al., *J. Phys. Condens. Matter* **21**, 395502 (2009).

[12] P. Giannozzi, O. Andreussi, T. Brumme et al., *J. Phys. Condens. Matter* **29**, 465901 (2017).

[13] J.M. Soler, E. Artacho, J.D. Gale, A. García, J. Junquera, P. Ordejón, D. Sánchez-Portal, *J. Phys. Condens. Matter* **14**, 2745 (2002).

[14] E. Bitzek, P. Koskinen, F. Gähler, M. Moseler, P. Gumbsch, *Phys. Rev. Lett.* **97**, 170201 (2006).