Structural and Electronic Properties of Small-Diameter Carbon NanoTubes: A DFT Study

Bartosz Brzostowski[1(✉)], Artur P. Durajski[2], Konrad M. Gruszka[2], and Jacek Wojtkiewicz[3]

[1] Faculty of Physics and Astronomy, University of Wrocław, pl. M. Borna 9, 50-204 Wrocław, Poland
`bartosz.brzostowski@uwr.edu.pl`
[2] Institute of Physics, Częstochowa University of Technology, Avenue Armii Krajowej 19, 42-200 Częstochowa, Poland
`{artur.durajski,konrad.gruszka}@pcz.pl`
[3] Faculty of Physics, Warsaw University, Pasteura 5, 02-093 Warszawa, Poland
`wjacek@fuw.edu.pl`

Abstract. One of the crucial properties of Carbon NanoTubes (CNTs) is their *conductivity*. They can be metallic, semiconducting or insulating in nature [6]. Therefore, their conducting properties are closely related to the existence and width of *CNTs energy band gap* – quantity which is (relatively) easily calculable. From a theoretical point of view, CNTs have been studied by various methods. Many results have been obtained; however, their status is quite diverse. The widespread rule claims that (n,m) CNT is metallic if $n-m = 0$ mod 3 [2,6]. This rule was based on 'gluing' of graphene sheets into tubes (or the 'zone folding' method). Moreover, the geometry of all hexagons has been assumed to be identical – the structure optimization hasn't been performed. Such an approach can be reliable for large-diameter CNTs, where curvature effects are small. However, it is at least disputable for its applicability to small-diameter CNTs. For these reasons, we undertook a systematic exploration of small-diameter CNTs to examine the significance of the 'deviation' effects (i.e. the deviation from planar regular hexagon geometry) on properties of CNTs. In particular, we wanted to check explicitly the validity of the claim that 'CNTs (n,m), where $n - m = 0$ mod 3, possess zero energy gap'.

In our paper, we present the results of calculations for $(2, m)$ and $(3, m)$ series of CNTs. These are optimized geometries, densities of states, energy gaps, and electronic band structures. The general conclusion is that the 'zone-folding' based rule predicting metallicity for those CNTs where $n-m = 0$ mod 3 is fulfilled, besides the find that hexagons forming CNTs are not planar and possess non-equal bond lengths. So this 'zone-folding' based law describes conductivity aspects of CNTs amazingly well.

Keywords: Carbon nanotubes · Band structure · Energy gap

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1 Introduction

Carbon NanoTubes – one of the allotropic forms of carbon – beginning from its discovery, still are among the most intensively studied quasi-one-dimensional systems. It is due to its exceptional mechanical, electronic, and optical properties, which turns scientific interests in CNTs to this day. Due to the wide applicability of CNTs, many papers explore their diverse properties such as semiconduction/metallicity features [7,13,20], mechanical, magnetic [6], and optical properties [17,18] to name a few.

One of the crucial properties of Carbon NanoTubes (CNTs) is their *conductivity*. Their character can be metallic, semiconducting, or insulating [6] in nature. Conducting properties are closely related to *energy gap* of CNTs – quantity (relatively) easily calculable. From a theoretical point of view, CNTs have been studied by various methods; the most popular are semiempirical and ab-initio ones. Many results have been obtained; however, their status is quite diverse. The broad 'folk knowledge' claims that (n, m) CNT is metallic if $n - m = 0$ mod 3 [2,6]. This rule was derived from simple calculations based on 'cutting and gluing' of the graphene sheets into tubes [8]. However, in such studies the geometry of all hexagons has been assumed to be identical – the structure optimization hasn't been performed. Such an approach can be reliable for large-diameter CNTs, where curvature effects are small. However, it is at least disputable for its applicability to small-diameter CNTs.

For these reasons, we undertook a systematic exploration of small-diameter CNTs to examine the significance of the curvature effects. In particular, we wanted to check explicitly the validity of the rule claiming that 'CNTs (n, m), where $n - m = 0$ mod 3, possess zero energy gap'. In our paper, we present the results of calculations for $(2, m)$ and $(3, m)$ series of CNTs. We have calculated: optimized geometries, densities of states, energy gaps, and band structures. In our study, we have also paid attention to the technical aspect of computations. One of them was a comparison between two popular packages: SIESTA and Quantum Espresso. The second one was the examination of parameters crucial for computations such as density of $k-$points in the grid, and the number of carbon atoms in an elementary cell.

2 Computational Methods

2.1 Quantum Software Packages

To the study electronic properties of investigated materials, we have performed first-principles calculations within the framework of the density-functional theory (DFT) [14] as implemented in the Quantum Espresso [4,5] and SIESTA [16] packages. We performed also calculations for finite CNTs using Gaussian09 package [3].

Quantum Espresso (opEn-Source Package for Research in Electronic Structure, Simulation, and Optimization) is an integrated suite of software for atomistic calculations based on electronic structure, using density functional theory, a plane-wave basis set, and pseudopotentials. Quantum Espresso is free software, released under the GNU General Public License. The compiling of Quantum Espresso packages (7.0 version) was realized by using the open-source gfortran (11.2.0 version) compiler from the GCC distribution with mpi-parallel execution provided by OpenMPI (4.1.2 version). Moreover, external libraries like BLAS and LAPACK for linear algebra and FFTW for fast Fourier transformation were used. In the case of Quantum Espresso, (GGA-PBE) approximation was used for the exchange-correlation functional together with the projector-augmented wave (PAW) method.

In the case of SIESTA, the exchange and correlation effects were accounted for by the generalized gradient approximation (GGA) with exchange-correlation potential proposed by Pedrew, Burke and Ernzerhof (PBE) [15]. SIESTA is density functional method using standard norm-conserving pseudopotentials and numerical linear combination of atomic orbitals basis set, which includes multiple-zeta and polarization orbitals. Also in the case of Gaussian09 the PBE [15] functional was used.

2.2 Computational Parameters

The optimized atomic structures were obtained by fully relaxing of both atomic positions as well as cell parameters until all forces were smaller than 10^{-6} eV/Å. All parameters critical for convergence, such as the k-points mesh and the energy cutoff were carefully tested to ensure the most accurate results. In the case of Quantum Espresso after proper convergence tests, we obtained well-converged values for the kinetic energy cutoff of the wavefunction equal to 80 Ry and the kinetic energy cutoff for charge density equal to 400 Ry. For the Siesta package, the parameters of the calculations were systematically tested also in terms of further calculations of phononic properties. Since unit cells were used for calculations, which for some nanotubes are small and contain few atoms, it was necessary to use larger values of parameters such as plane-wave cutoff (MeshCutoff) and Brillouin zone sampling (k-grid Monkhorst Pack). The unit cells were constructed so that in the z direction the axis of the nanotube was oriented, while in the x and y directions they had a size of 15 Å increased by the diameter of the nanotube. Tests have shown that the 1x1xM Monkhorst-Pack grid [11] is good enough and only the M value is significant for convergence. For the smallest unit cells, the value of this parameter was tested up to 3000. To investigate the electronic properties such as the main energy gap, a sufficiently good value of this parameter is M equal to 1200, but for the phonon properties, it may not be enough. For nanotubes with a clearly non-zero energy gap, a convergence is obtained for smaller values of the M parameter. On the other hand, nanotubes with a gap of zero or close to zero make convergence difficult. As part of the tests, MeshCutoff from 1000 to 2000 Ry was checked. For the study of electronic properties, the value of 1000 Ry is large enough, but even 2000 Ry may not be enough for phonon properties. In the case of Gaussian, all calculations have been performed with the use of 6-31G(d) basis.

2.3 Relaxation Methodology

The ideal atomic positions in cells with a fixed distance of 1.41 Å between C atoms have been generated by the TubeASP applet [12]. The optimized atomic structures were obtained using different methods for maximum atomic force smaller than 10^{-6} eV/Å. In the case of Quantum Espresso, the Broyden-Fletcher-Goldfarb-Shanno (BFGS) quasi-Newton algorithm was used, whereas for the Siesta package the optimization of the coordinates was obtained using the conjugate gradients method.

The change in the initial distance between the carbon atoms given in the nanotube generator did not affect the optimization of the structure. However, choosing a value other than 1.41 Å typically resulted in the need for more molecular dynamics steps to obtain an optimized structure.

In the use of Gaussian for finite CNTs, the option 'Optimization and Frequency' has been used, i.e. after optimization, eigenfrequencies have been calculated and their positivity has been checked.

3 Results

3.1 Calculation Procedure, Energy Gaps, Band Structure

We have calculated all the CNTs of kind $(2, m)$ and $(3, m)$, i.e.: $(2, 0)$, $(2, 1)$, $(2, 2)$; $(3, 0)$, $(3, 1)$, $(3, 2)$, $(3, 3)$. Each of CNTs, were structure-optimized and for each one, we have calculated their electronic properties in terms of the band structure and density of states.

CNTs are *periodic* systems. In Fig. 1 we present structures of elementary cells for all studied seven CNTs. As can be seen, elementary cells of armchair and zig-zag CNTs are much smaller than cells for chiral CNTs. For every optimized structure, we have calculated the band structure and density of states. Plots of these results are presented in Fig. 4 for CNTs $(2, m)$ and Fig. 5 for CNTs $(3, m)$. It is seen that the band structures are much more complicated for chiral CNTs than for armchair and zig-zag ones. It can be attributed to the sizes of elementary cells. For every CNT, structural optimization has been performed. As a rule, the geometry corresponding to the optimized and non-optimized ones are quite different. We illustrate this diversity in the Fig. 2.

It is also seen that all CNTs, for which the 'zone-folding' based rule predicts metallicity (i.e. $(2, 2)$, $(3, 0)$ and $(3, 3)$) are in fact conductive, i.e. possess a non-zero density of states at the Fermi energy. Apparently, the conductivity holds also for optimized structures, which are not regular hexagons. On the other hand, the CNTs $(2, 0)$ and $(3, 2)$ are gapped with gaps 0.65 eV and 0.29 eV, respectively – as 'zone-folding' based rule predicts. Interestingly enough, we have found *two* isomers of the CNT $(3, 1)$. They differ in structure and also energy gap: One isomer with lower energy possesses a gap 0.69 eV and the second one 0.36 eV. We have described these two structures elsewhere [1]. In any case, both structures are gapped, as the 'zone-folding' based rule predicts. And last, interestingly enough, the $(2, 1)$ CNT is gapless, although it should be gapped along the 'zone-folding' based rule.

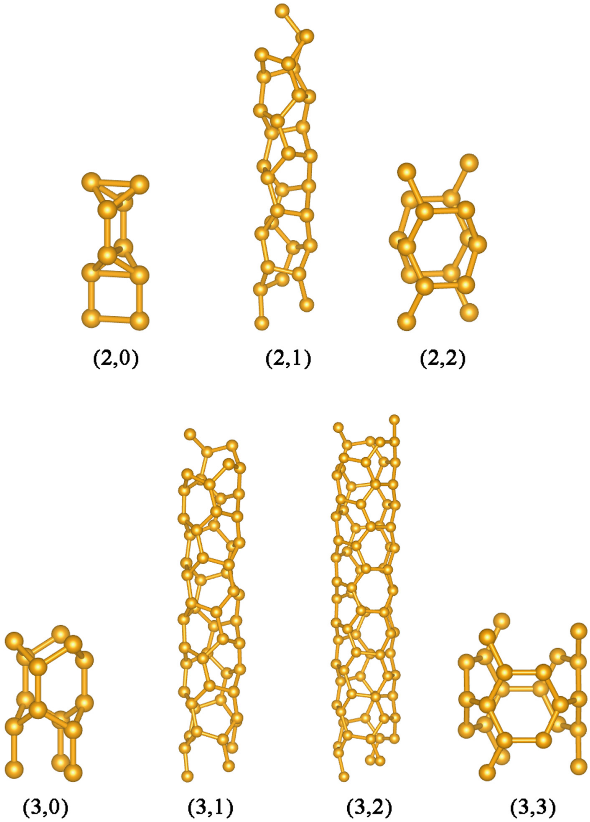

Fig. 1. Elementary cells of all calculated CNTs.

3.2 Comparison with Existing Results

Wherever possible, we also made comparison with literature data. We have found results for the (2, 2) CNT: [20], [9] and [10]. In all papers, authors have obtained small gaps (0.1 up to 0.2 eV, implying that (2, 2) CNT is an indirect semiconductor) - so, their results are similar to ours. The difference can be attributed to the fact that they used functionals other than ones used by us.

We have also carefully inspected results for the $(3, 1)$ CNT in [9]. The authors found, that examined CNT possesses a gap of 0.4 eV, which is consistent with our result for one of the isomers of $(3, 1)$ CNT.

Summarizing our calculations for infinite CNTs, our calculations show that (2,0), (3,1) and (3,2) CNTs are gapped, whereas (2,1), (2,2), (3,0) and (3,3) are gapless.

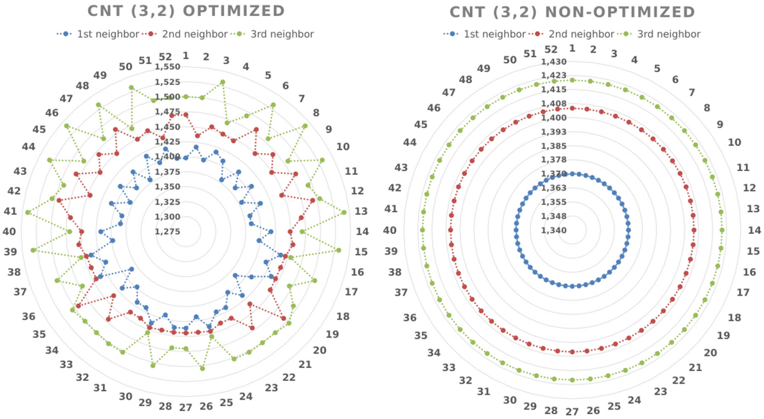

Fig. 2. Histograms of distances of atoms within elementary cell for CNT $(3, 2)$ for non-optimized case (right panel) and optimized one (left panel).

3.3 Finite CNTs

For the sake of comparison, we have also calculated the *finite* CNTs, as real systems are finite ones. We treat these results as preliminary, as the sizes of CNTs calculated were limited by our computational facilities and we were able to calculate systems up to about 150 atoms.

We performed our calculations with the aid of the Gaussian 09 package [3]. The CNT was generated with the use of the same generator as infinite ones. We used the PBE functional as implemented in Gaussian 09. In such systems, we encounter a problem with how to 'end' it, in the order to avoid artifacts coming from unpaired bonds. We decided to take the simplest solution, i.e. to saturate the unpaired bonds by the hydrogen atoms. For an illustration, see Fig. 3 (Table 1).

Table 1. Results of DFT calculations for energy band gaps of finite (upper part) and infinite (lower part) CNTs. All energies are in eV. Energy gaps for infinite CNT (3,1) correspond to two geometric isomers, see [1].

CNT	$(2, 0)$	$(2, 1)$	$(2, 2)$	$(3, 0)$	$(3, 1)$	$(3, 2)$	$(3, 3)$
No. of elementary cells	12	4	12	8	3	2	13
Energy gap [eV]	0.73	0.23	0.08	0.11	0.27	0.49	0.20
Chemical formula	C_{96}	$C_{112}H_6$	$C_{128}H_8$	$C_{96}H_6$	$C_{156}H_8$	$C_{152}H_{10}$	$C_{156}H_{12}$
Gap for infinite system	0.65	0	0	0	0.69/0.36	0.29	0

We see that all finite CNTs have a non-zero energy gap. It is not unexpected, as they are finite systems. Yet, the values of the gap for finite CNTs $(2, 1)$, $(2, 2)$, $(3, 0)$ and $(3, 3)$ (corresponding to zero-gap infinite CNTs) are substantially smaller than $(2, 0)$, $(3, 1)$ and $(3, 2)$ (corresponding to non-zero-gap infinite CNTs). Moreover, gaps of finite CNTs are greater than their infinite counterparts (with one exception of $(3,1)$ CNT). We should note here that it would be especially interesting to see how finite-size data tend to the limit of infinite objects. Preliminary study in this direction has been made in [19]. It is also worth noting, that this behavior is consistent and can be a guide if used properly, to find the finite gap CNT's using only small computational cells.

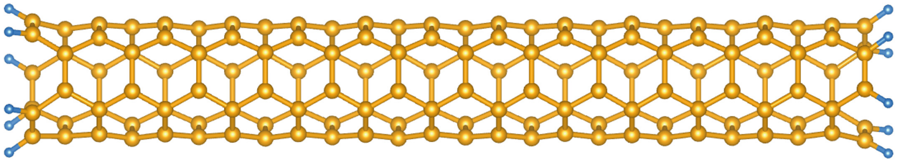

Fig. 3. Finite CNT $(3,3)$ with 13 elementary cells and hydrogen atoms (presented as blue spheres) at the ends.

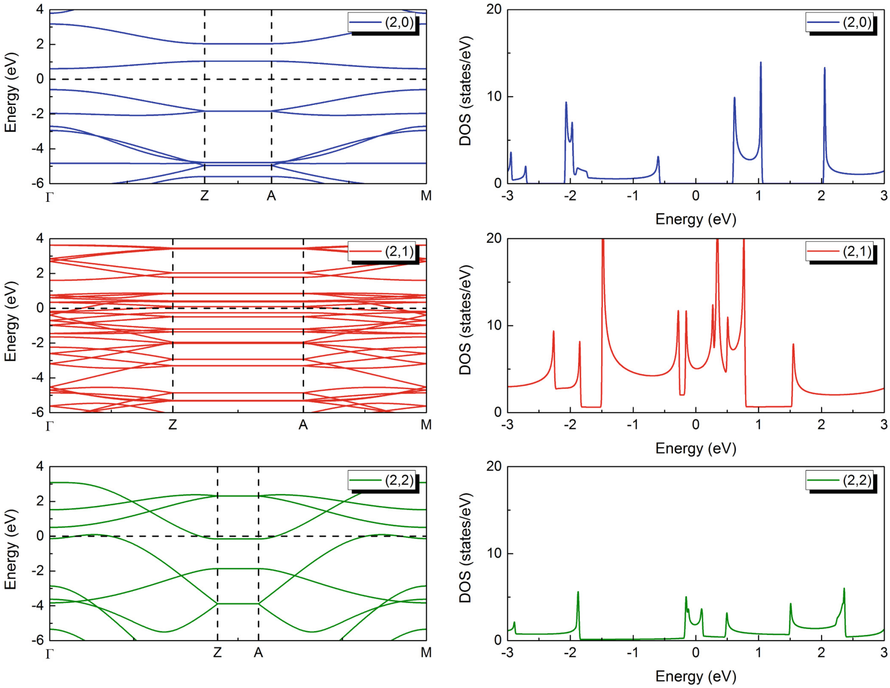

Fig. 4. Band structures (left panels) and densities of states for CNTs $(2,0)$, $(2,1)$ and $(2,2)$. Fermi energy is located at zero.

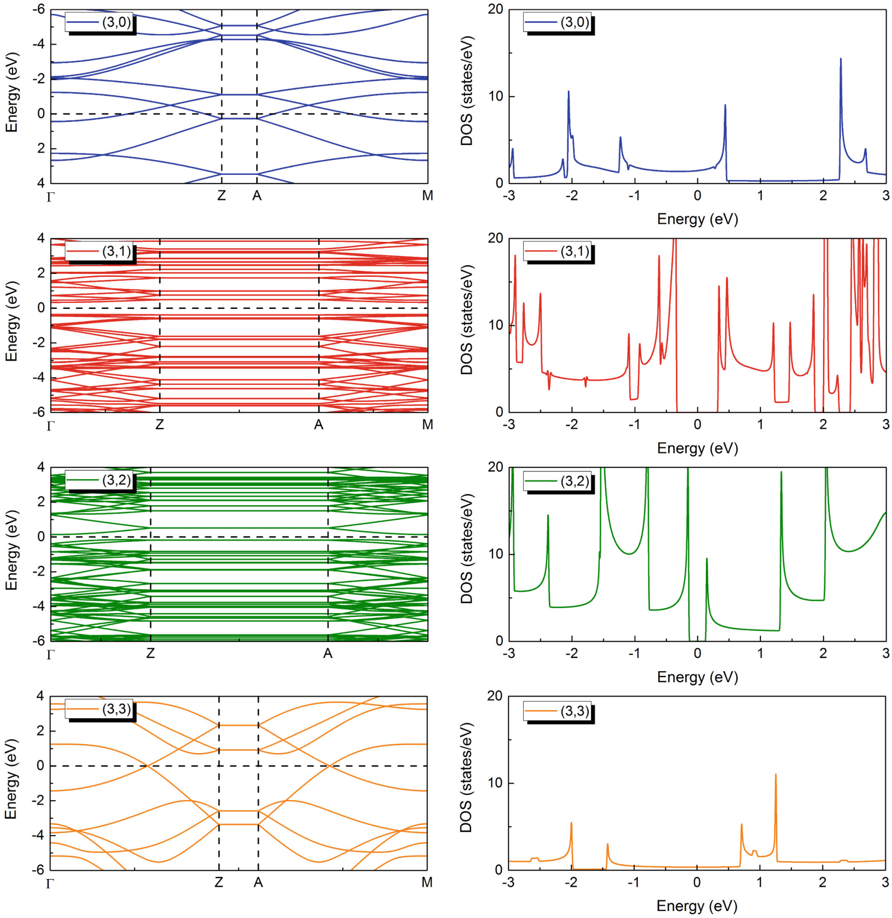

Fig. 5. Band structures (left panels) and densities of states for CNTs (3, 0), (3, 1), (3, 2) and (3, 3). Fermi energy is located at zero.

4 Summary, Conclusions, Outlook

The general conclusion is that the simple ‘zone-folding’ based rule predicting metallicity for those CNTs where $n - m = 0 \bmod 3$ is fulfilled, besides the opportunity that hexagons forming CNTs are not planar and possess non-equal bond lengths. It is a little bit surprising that this simple law describes conductivity aspects of CNTs amazingly well. Apparently, conductivity is not closely related to the regularity of hexagons, but rather to the proliferation of conjugate double bonds parallelly to the CNT axis.

Having developed the methodology and values of parameters of computation, we would like to continue our calculations for subsequent CNTs. However, such an extension of calculations is very demanding from the computational point of view. It is related to the fact that sizes of elementary cells grow fast with n for (n, m) CNTs. For instance, the largest elementary cell for $(3, m)$ CNTs counts 76 atoms (for $(3, 2)$ CNT). For $(4, m)$ series, the elementary cell of CNT $(4, 3)$ counts 148 atoms, and for $(5, m)$ the size of an elementary cell of $(5, 3)$ is 196, and for $(5, 4)$ it is 244. For this reason, the use of supercomputers seems to be inevitable in more systematic studies.

Another problem is the examination of other functionals in calculations. It is well known that PBE functional systematically underestimates the value of the energy gap. For large-gap CNTs, this effect can influence only the value of the gap, but rather not its existence. We observe this for all three gapped CNTs calculated. Another case is CNTs such as $(3, 0)$ and $(3, 3)$, where the bands are crossing and presumably this effect is stable concerning the precision of calculations, resulting in gaplessness of these CNTs. Yet there is also a third group of CNTs, where the existence of gap depends on subtle details of the behavior of their electronic band structure. We encounter this situation in $(2, 2)$ CNT. In our calculations, the Fermi level passes through an upper and lower band and we obtain no gap. But this is a subtle effect – the Fermi level is almost tangent to both minimal and maximal of nearby lying bands. In the paper [20], where another functionals have been used, the upper and lower bands are divided by a small gap. Therefore it would be very interesting to re-examine the presence of gaps by (presumably) more precise calculations using other functionals.

A natural extension of electronic properties examination, is determination of *optical* ones, i.e. calculation of UV-VIS, as well as near-infrared spectra. Such calculations are also of great importance with respect to possible technological applications in new generations of solar cells. Such a study, i.e. calculation of spectra of more than thirty finite CNTs, has been undertaken in [19] in the framework of TDDFT. However, the size of calculated CNTs were limited: only those with elementary cells not exceeding 150 atoms have been calculated. Moreover, is some cases only part of the UV-VIS range was possible to cover. Optical properties are much more demanding from computational point of view than densities of states – in particular, more memory is necessary. To achieve further progress in examination of optical properties of CNTs, it is mandatory to use more advanced computational resources, i.e. multiprocessor stations with parallel processing and large amount of memory. This aspect concerns two routes of calculations, i.e. periodic infinite systems and finite ones. We hope to be able to extend in planned future research the computations reported in [19].

In the case of calculations for infinite nanotubes, the basic problem is the necessity to use a dense set of k-points. This causes a significant increase in computation time and increases the amount of required RAM. For a software whose parallelization limits its use on one node, with a typical 7-day queue walltime it is possible to calculate basic electronic properties, however, the calculation of phonon or optical properties is troublesome or impossible. This problem can be avoided in a way by performing calculations for finite nanotubes. In this case, however, detailed studies of the scalability of the obtained results in terms of the number of unit cells included should be carried out. While for armchair or zig-zag nanotubes it is easy to do, because unit cells consist of a relatively small number of atoms, for chiral nanotubes with a large number of atoms in the unit cell it is difficult, because the calculation time increases significantly with an increase in the number of atoms in the studied structure.

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