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Length Dependence of Band Structure in Carbon Nanotubes of Ultra Small Diameter

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The paper presents results of a study of the band structure and related parameters and also the bond energy of single-walled carbon nanotubes carried out using semiempirical methods and ab initio density functional theory implemented in Gaussian 2003 framework. Much attention is paid to the dependency of the values mentioned on the length and on the chirality of the tubes. Both the infinite and the finite open-ended nanotubes are considered. It was found that the dependency of the band gap on the diameter has oscillating character for infinite zigzag semiconducting tubes. It was also found that finite armchair nanotubes have non-zero band gap which decreases showing oscillations with the length and decreases monotonically with the diameter.

Keywords: Carbon nanotubes, Length, Diameter, Chirality, Band structure, Bond energy.

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1. INTRODUCTION

During the last several years many investigations of the emission properties of carbon nanotubes have been performed. Most of the research efforts in this area are focused on the work function investigation. The latest main theoretical results are the following. The work functions of some small tubes increase dramatically as the diameter of the tube decreases due to the curvature effects; the structure of the tips of CNTs affects their work functions [1]. First principle calculations carried out by Bin Shan et al. from Stanford University [2] show that the tubes may be divided into two groups: with diameter less than 1 nm and with diameter more than 1 nm. For the nanotubes from the first group the work function changes significantly (in range from approximately 4.5 eV to approximately 6.0 eV) with their chirality while for the others it's close to the work function of graphene which they take to be equal 4.66 eV. The work function of carbon nanotubes has also been studied experimentally. Using photoemission spectroscopy the work function was found to be 4.8 eV for single-walled CNTs bundles [3]. Using photoelectron emission spectra the work function was found to be approximately 5.05 eV [4].

Carbon nanotubes are also a promising material for transistors, diodes and other electric circuit elements. One of the important properties for these applications is the materials band structure and ways to modify it. The band structure of single-walled carbon nanotubes (SWCNTs) dependence on their radius in an insufficiently explored issue (especially in the region of very small diameters) and appears to be interesting for carbon-based electronics both theoretically and practically.

Carbon nanotubes are also a promising material for transistors, diodes and other electric circuit elements. One of the important properties for these applications is the materials band structure and ways to modify it. In the nineties of the 20th century the first calculations of the band structure of idealized single-walled carbon nanotubes (SWCNTs) and graphene were carried out within the tight binding model (TBM) [5]. Based on the TBM the analytical expressions for the electrons dispersion were obtained. These expressions allowed determining of the band gap of armchair, zigzag and chiral nanotubes. It was found that if the difference $n - m$ (where n and m are the chirality indices of the nanotube) is a multiple of three than the nanotube has metallic conductivity or zero band gap, otherwise being semiconducting [6] (in the present paper this rule will be referred to as "3k rule"). It was also obtained that the band gap in semiconducting SWCNTs is inversely proportional to their diameter.

Team led by Blasé has found that the theoretical description of the band gap (E_g) of carbon nanotubes in the region of ultra small diameters (less than two nanometers) is strongly affected by the method and the unit cell selected [7]. They performed calculations of the band gap of SWCNTs with small diameters using two methods: the density functional theory (DFT) in local density approximation (LDA) and the TBM. They calculated the values of the band gap for SWCNTs with chirality indices (0, 7) and (0, 8) and diameters 0.55 and 0.63 nm correspondingly. The band gap value for the SWCNT (0, 7) obtained within the tight binding model was found to be 1.04 eV while within the DFT this value was found to be 0.09 eV. As for the nanotube (0, 8) the values are 1.19 eV and 0.62 eV correspondingly. The authors note that with the decrease of curvature radius from the infinity to 2.4 angstroms the band gap changes due to the decrease in the pi states energy.

Using density of states (DOS) spectra (obtained by measuring of the tunneling current from SWCNT to scanning tunneling microscope (STM) probe) Odom et al. [8] (for diameters ranged 0.7 ÷ 1.1 nm) and Wildoer et al. [9] (for diameters ranged 1.0 ÷ 2.0 nm) have experimentally determined E_g. Significant difference between the experimental and calculated values has been found. In the work of Ouyang et al. [10] the following values of E_g for SWCNTs (0, 9), (0, 12) and (0, 15) (which are metallic according to the 3k rule) were experimentally found: 0.080 eV, 0.042 eV and 0.029 eV correspondingly. Calculations carried out by Cabria et

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al. [11] within the DFT LDA have shown that in the region of ultra small diameters band gap dependence on the diameter of SWCNTs loses monotonous character and has a maximum for SWCNT (3, 4) where the band gap equals 1.42 eV.

The band structure of the SWCNTs also depends on their length. The investigation of the impact of length on the band structure of SWCNTs is motivated by the tendency to decrease of the active element sizes in nanoelectronics devices and latest achievements in the technologies of production of short nanotubes [12].

The first ab initio investigations of impact of length on electronic band structure of SWCNTs were carried out in 1999. It was shown that the electronic density of states in finite length tubes is close to that of infinite nanotubes only starting from lengths of about several nanometers. [13] Rocherfort et al. in [14] have studied electronic band structure of open-ended armchair SWCNT (6, 6). Calculations within the Hartree-Fock, DFT, semiempirical MNDO-PM3 and extended Huckel model have shown that additional confinement of electrons along the tube axis leads to non-zero band gap. The value of the gap decreases with the length of the tube. The dependency shows clear oscillations. The authors estimate the length of transition to metallic conductivity to be 10–20 nm. It was shown in 2002 (using B3LYP method and 6-311G* basis) and in 2003 (using semiempirical PM3 method) that the band gap versus length dependency of armchair nanotubes has oscillating character while the same dependency for zigzag tubes shows no oscillations. In both cases the gap value decreases with length. On the other hand the gap for zigzag SWCNTs oscillates depending on their diameter what is not the case for armchair tubes. [15, 16]

Thus, in the region of ultra small diameters (less than 2 nm) the principle of the monotonous change of band gap with diameter is not valid, the dependence acquires signs of nonlinearity and consequently the 3k rule is not always correct. Decrease of the length and the diameter of SWCNTs must lead to qualitative changes in their band structure – discrete levels in the energy spectra. This transition from quantum wires to quantum dots is not sufficiently studied and appears to be interesting both theoretically and practically.

2. METHODOLOGY

We have separately investigated the impact of chirality on the band structure of the infinite and finite length nanotubes. For infinite tubes we used periodic boundary conditions (PBC) and density functional theory within the local spin-density approximation (LSDA) and 6-31G basis. The calculation was performed for 200 points in the Brillouin zone. For finite length nanotubes we used semiempirical Austin model 1 (AM1) method. In order to properly take into account the curvature effects we used a cylindrical unit cell of a nanotube. The length of armchair tubes was measured in segments. A segment here denotes a half of the unit cell of SWCNT (figure 1).

The relevancy of the method and basis was verified in the previous calculations for SWCNTs [17], and also by the comparison of the results obtained with published data of experimental and theoretical investigations.

We used TubeGen 3.4 software for the carbon nanotube (CNT) generation and Gaussian software for the calculation.

In our calculations we used the DFT counterpart of the Koopmans theorem for the ionization energy determination. The modified theorem equates the first (vertical) ionization energy EI of a system of N electrons to the negative of the corresponding Kohn – Sham (KS) highest occupied molecular orbital energy.

The band gap was defined as the difference between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO). The work function was calculated as the energy level corresponding to the middle between the LUMO and HOMO for semiconducting nanotubes and as the energy of HOMO for metallic ones.

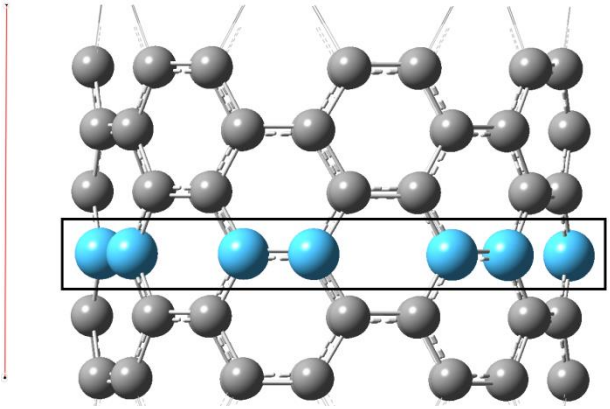

Fig. 1 – Triply replicated unit cell of SWCNT (7, 7) in GaussView preview window. The rectangle denotes a single segment.

We have also performed the bond energy assessment in order to find a general dependence of stability of the tubes of different chiralities. The bond energy was determined as the difference between the energy per atom in the nanotube and energy of a single carbon atom adjusted by the number of bonds per atom in the structure.

The band gap, work function, ionization energy and bond energy were calculated for 23 zigzag and 14 armchair nanotubes. The same parameters except the bond energy were also calculated for all armchair nanotubes with chiralities from (3, 3) to (15, 15) and lengths from 2 to 20 segments (247 SWCNTs).

3. RESULTS AND DISCUSSION

In zigzag SWCNTs one of chirality indices equals zero and in armchair nanotubes both indices are equal. So in these cases it is sufficient to use only one index to denote the nanotube chirality. In the further discussion we are going to use the chirality indices instead of the diameter on all plots which show only zigzag or only armchair tubes. The diameter is linearly proportional to the chirality indices in the armchair and zigzag tubes.

3.1 Infinite nanotubes

For representation purposes we have separated the results of band structure parameters calculation based on the 3k rule. The difference between the two groups is also clearly seen on figure 2.

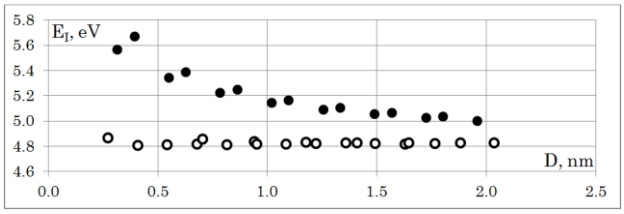

Fig. 2 – Classification of SWCNTs and ionization energy. Solid circles represent semiconducting SWCNTs, open circles represent metallic ones.

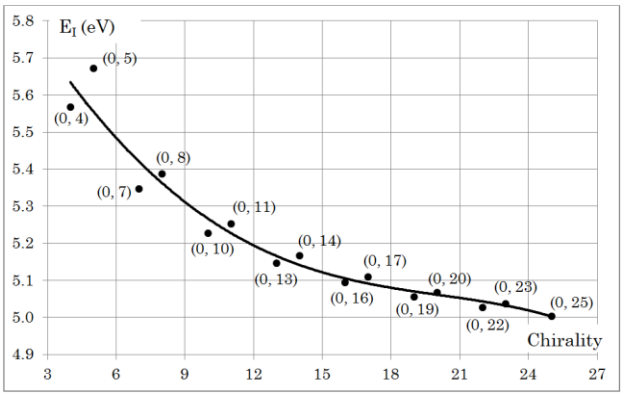

Fig. 3 – Ionization energy dependence on diameter for semiconducting zigzag SWCNTs.

For metallic nanotubes ionization energy was found to have little to none dependence on diameter and chirality with two exceptions for tubes (0, 3) and (0, 6) where ionization energy equals 5.92 and 6.98 eV correspondingly. For all other tubes this value appears to be close to the one in graphene, which is reported to be 4.6 – 5.0 eV (out calculated value is 4.8 eV).

As for the semiconducting tubes (zigzag), ionization energy strongly depends on chirality indices (see figure 3), work function also exhibits similar properties although the dependency becomes rather insignificant for diameters larger than 1 nm (see figure 4).

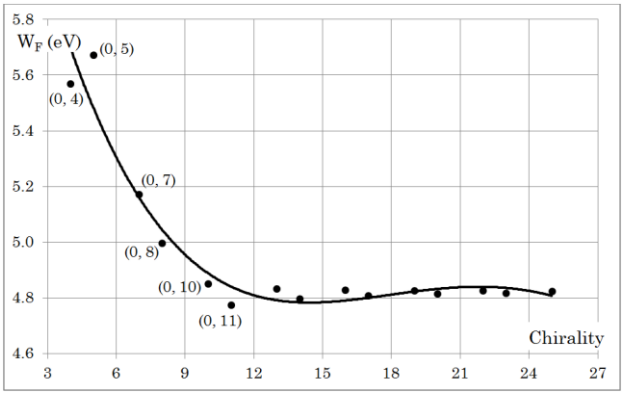

Fig. 4 – Work function dependence on diameter for semiconducting zigzag SWCNTs.

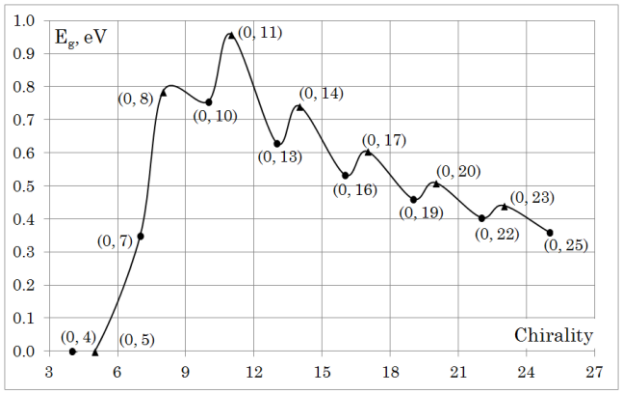

Fig. 5 – Band gap dependence on diameter for semiconducting zigzag SWCNTs.

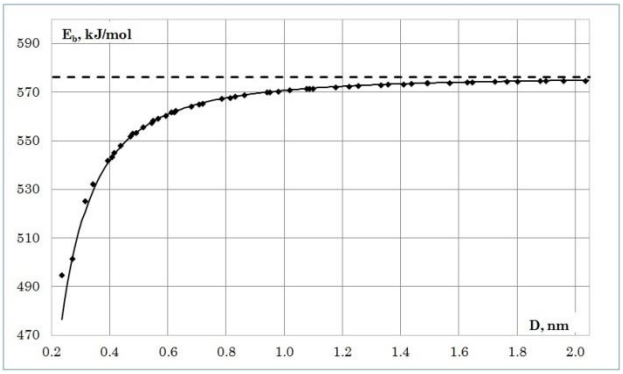

Fig. 6 – SWCNTs bond energy dependence on diameter. Solid line represents fitting formula $E_b = E_b^{Grapehene} - 5/D^2$. Dashed line represents calculated bond energy in graphene 576 kJ/mol.

We have obtained zero or very small value of band gap for tubes that are metallic according to the 3k rule. Band gap dependence on diameter for semiconducting SWCNTs is illustrated on figure 5. We clearly see that 3k rule is not applicable to the tubes (0, 4) and (0, 5) for which we obtain zero band gap while the 3k rule predicts semiconducting behavior. We also see that dependence becomes nonmonotonic and has a global maximum for nanotube (0, 11) with value of 0.96 eV. However, as it was shown earlier [11, 17] this is not the largest band gap possible in carbon nanotubes. We may extend the 3k rule and further separate the results shown on figure 5 into two groups. For the first group we assume that the remainder of the division of chirality indices difference by 3 equals 1 and for the second group this remainder equals 2. Then the minimums on figure 5 correspond to SWCNTs from the first group and maximums correspond to the second group.

The calculation performed also allowed us assessment of bond energy in SWCNTs, although the numeric values do not entirely agree with experiment. The bond energy in carbon nanotubes dependence on their diameter appears to have monotonous character. Following fitting formula can be used $E_b = E_b^{Graphene} - C / D^2$ (see figure 6). Here D is diameter of the tube, C is a coefficient (which we take to be equal 5.5) and $E_b^{Graphene}$ is bond energy of graphene. We consider this formula to be a consequence of the fact that the repulsion of pi electrons becomes smaller inversely proportionally to the cross-sectional area of the nanotube thus increasing stability of the structure and bond energy.

3.2 Finite length nanotubes

Due to computational difficulties we have studied band structure for armchair SWCNTs only.

The figure 7 shows the results of calculation of energy band gap in the finite length armchair single-walled carbon nanotubes. According to the results obtained the finite length armchair nanotubes indeed have non-zero band gap (we still use the term for the latter discussion although in the case of finite length objects it is not correct).

The magnitude of the band gap decreases with the length and the diameter. However the character of the dependency is very different. While the decrease with diameter is monotonic and shows no oscillations the decrease with length exhibits clearly oscillating character. The period of the oscillations is 3 segments (compare to figure 5).

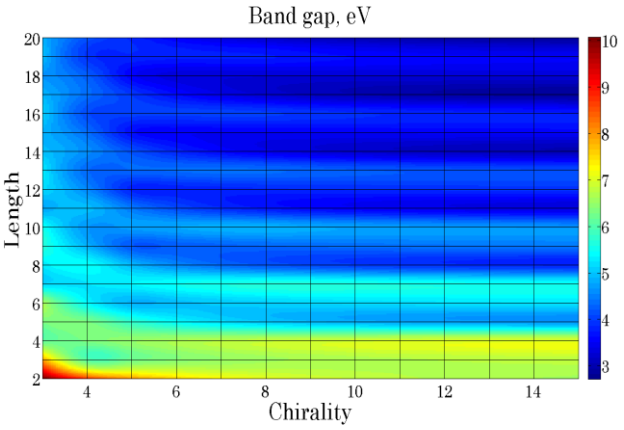

Fig. 7 – Band gap dependency on length and diameter for armchair finite-length nanotubes.

We have also estimated the length which corresponds to transition of armchair tubes to the metallic state (zero band gap) by extrapolating the length dependency of the band gap. According to the extrapolation results the smallest length is about 10 nm but it does strongly increase for very thin tubes.

Work function dependency on length and diameter is shown on fig. 8. According to the results obtained the work function grows with length and decreases with diameter. The values lie in range from 4.2 to 5.2 eV.

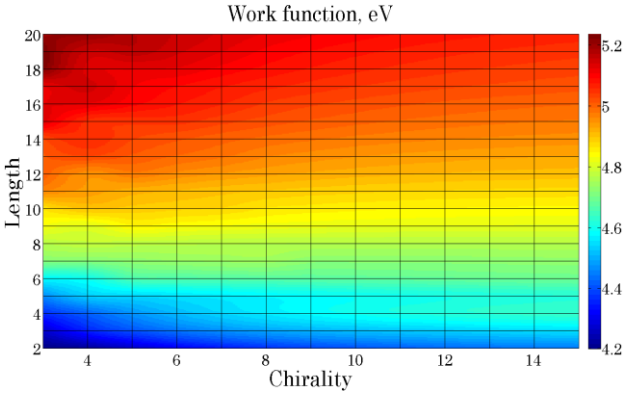

Fig. 8 – Work function dependency on length and diameter for armchair finite-length nanotubes.

4. CONCLUSION

We have studied electronic structure and calculated values for band gap, ionization energy (as the energy of highest occupied molecular orbital) and work function of infinite single-walled carbon nanotubes with diameters ranging from 0.2 to 2.0 nanometers within the density functional theory. We have also investigated band structure parameters in finite length armchair SWCNTs using semiempirical AM1 method. Band gap dependence on diameter of the infinite tubes has non-monotonic oscillating character with a global maximum. For tubes (0, 4) and (0, 5) zero band gap values have been obtained. Work function and ionization energy in metallic tubes do not change much with diameter and corresponding values are close to those in graphene, work function and ionization energy of semiconducting tubes do increase when diameter decreases. The finite length armchair nanotubes do have a non-zero band gap which decreases showing oscillations with length and decreases monotonically with diameter. Average values of work function in finite length armchair nanotubes lie within the range from 4.2 to 5.2 We have also performed assessment of bond energy in carbon nanotubes and found that its dependency on the diameter can be described by a fitting formula $E_b = E_b^{Graphene} - 5.5 / D^2$ eV.

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