

Spin-dependent energy gap oscillations in the ultra-short carbon nanotube (5, 5)

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Abstract. Results of the numerical simulation of an electronic structure of an ultrashort single-walled carbon nanotube (5, 5) at singlet and triplet states were presented. An antiphase energy gap oscillation on the length of the ultrashort nanotube (5, 5) at singlet and triplet states was revealed. It was found that the ground state of the nanotube is singlet, herewith the energy of the singlet-triplet transition corresponds to the energy value of visible and IR-radiation.

1. Introduction

In recent years a significant advance was achieved in the field of the ultra-short single-walled carbon nanotubes (us-SWCNT) synthesis with controlled both chirality and length [1–3]. Sanchez-Valencia et al. [1] synthesized single-chirality and essentially defect-free us-SWCNTs (6, 6) from a flat molecular precursors on a Pt (111). During the surface-catalyzed cyclodehydrogenation process the precursor transforms to the singly capped us-SWCNT (6, 6) seed with the length 4.5 Å. A manage of a concentration of a carbon feedstock gas at the time of an epitaxial elongation allows to control the length of us-SWCNTs up to few Å. The solubility of ultra short nanotubes in organic solvents, acids and water at the level of 2 weight % was revealed [4–6] that is an important achievement for the creation of functional nanomaterials. The experimental success opens up a way for usage of us-SWCNTs for applications such as light detectors, photovoltaics, field-effect transistors and sensors with highly optimized characteristics [1, 3, 7–9]. Lots of theoretical researches of carbon nanotubes demonstrate that the decrease their length less than 10 nm causes of great changes in the electronic structure and fundamental parameters such as the energy gap (E_{LH}) between the lowest unoccupied (LUMO) and the highest occupied (HOMO) molecular orbitals, ionization potential (IP), electron affinity (EA), work function [10–17]. It is known that infinite armchair carbon nanotubes must have zero energy gaps because the difference of chirality indexes equals to zero [18–20]. Rochefort et. al [12], Buonocore et al. [13], Yumura et al. [17], Cioslowski et al. [11] showed that us-SWCNTs (6, 6) and (5, 5) with the length $L < 2.5$ nm have nonzero energy gaps with oscillation dependences on the length of nanotubes. Energy gap oscillations on the length for a range of open-ended armchair us-SWCNTs with the chiral index $n=3–15$ were revealed in works [14, 15]. Numerous investigations of the electronic structure of armchair us-SWCNTs devoted to the singlet state of nanotubes [10–15] however other spin states hitherto not been studied. The investigation of the spin-dependent properties of us-SWCNTs is important for spintronics, optoelectronics and molecular electronics. Electric and magnetic fields can be used for the spin manipulation through the spin-orbit interaction in carbon nanotubes [21, 22]. It is expected that properties and fundamental parameters of us-SWCNTs strongly depend on their spin states. The aim of this work is the theoretical study of the electronic structure of us-SWCNTs (5, 5) at singlet and triplet states.



2. Computational details

The numerical simulations of the electronic structure of the capped armchair us-SWCNT (5, 5) were carried out using hybrid DFT (density functional theory) method of Becke [23] and Lee, Yang, Parr [24] (B3LYP) and 6-31G basis set [25] with the help of the Gaussian09 program package [26] in the Supercomputing center of Voronezh State University. This level of theory widely used for the investigation of the electronic structure of carbon nanomaterials at its ground and excited states and allows to achieve a good agreement of the calculated energy gap, ionization potential, electron affinity with experimental data [11, 27–29].

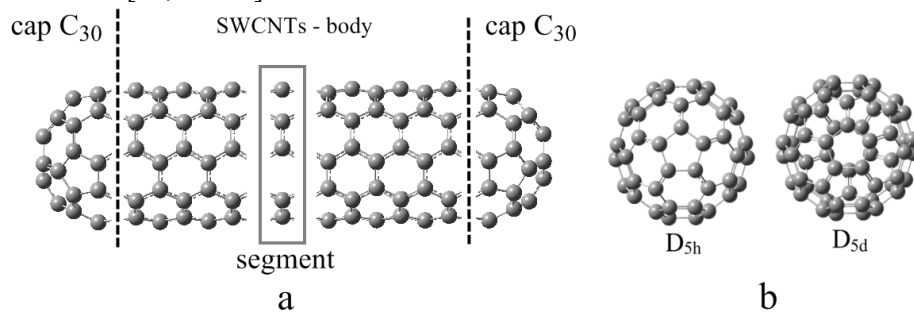


Figure 1. The structure of the ultrashort single-walled carbon nanotube (5, 5) (a) and the mutual orientation of C₃₀ caps of nanotubes D_{5h} and D_{5d} symmetries

A stoichiometric formula of the capped SWCNT (5, 5) is C_{60+10j}, where j denotes the number of segments which forms the body of the nanotube while caps essentially are halves of the fullerene C₆₀ dissected perpendicularly to the C₅ axis (figure 1) [10, 11]. The sequential increment of j causes to the rotation of caps of the us-SWCNT (5, 5) on the $\pi/5$ angle relatively to each other, thus the number of segments j determines symmetry of nanotubes: D_{5h}(i=2m+1) or D_{5d}(i=2m) m=0, 1, 2 ... The increment of j leads to the nanotube length increase on 1.23 Å. The diameter of the us-SWCNT (5, 5) equals to the 7 Å.

3. Results and discussion

3.1. The energy gap oscillation of the capped us-SWCNT (5, 5) in its singlet state

The dependence of the energy gap E_{LH} on the length of the us-SWCNT (5, 5) shows clear oscillations (solid line in the figure 1). The value of E_{LH} significantly exceeds the energy gap of the infinite-length SWCNT (5, 5) $E_g=30\text{meV}$ [15, 30, 31]. The quantum confinement of the electron along the tube axis leads to the non-monotonic change of the energy gap from 2.8 to 0.7 eV in the range of the number of segments j=0–13. Hence, the single nanotube (5, 5) in the range of ultra small lengths forms a whole family of semiconductor nanomaterials. Three types of us-SWCNT (5, 5) with the maximal, intermediate and minimal energy gaps can be distinguished. These include nanotubes with the number of segments j=3m+1, 3m, 3m+2 (m=0, 1, 2...).

The existence of three types of armchair nanotubes is due to the electron density redistribution of LUMO and HOMO [12, 14, 15] and rights for capped, open-ended and single capped us-SWCNTs [32]. Thereby, the electronic structure of us-SWCNTs (5, 5) almost doesn't depend on the boundary condition and primarily determines by the number of segments. That also confirms by the proximity of oscillation amplitudes of us-SWCNT (5, 5) and graphene nanoribbon with the same structure [33].

3.2. The electronic structure of the capped us-SWCNT (5, 5) in its triplet state

At the triplet state of us-SWCNTs (5, 5) the number of electrons with the spin “up” more on two than with the spin “down”. Thereby spins are not compensated and energy gaps for two spin channels $E_{LH}^{\uparrow}$ and $E_{LH}^{\downarrow}$ are different. The dependence of these energy gaps on the length of us-SWCNTs (5, 5) are nonmonotonic (figure 2). In the range of the number of segments j=0–13 energy gaps $E_{LH}^{\uparrow}$ and $E_{LH}^{\downarrow}$ belong to the interval from 0.5 to 2.0 eV. At the triplet state nanotubes of three types with the number of segments j=3m+1, 3m, 3m+2 have minimal, intermediate and maximal energy gaps. Thereby,

dependences of energy gaps on the number of segments of us-SWCNTs(5, 5) at singlet and triplet states are antipase (figure 2).

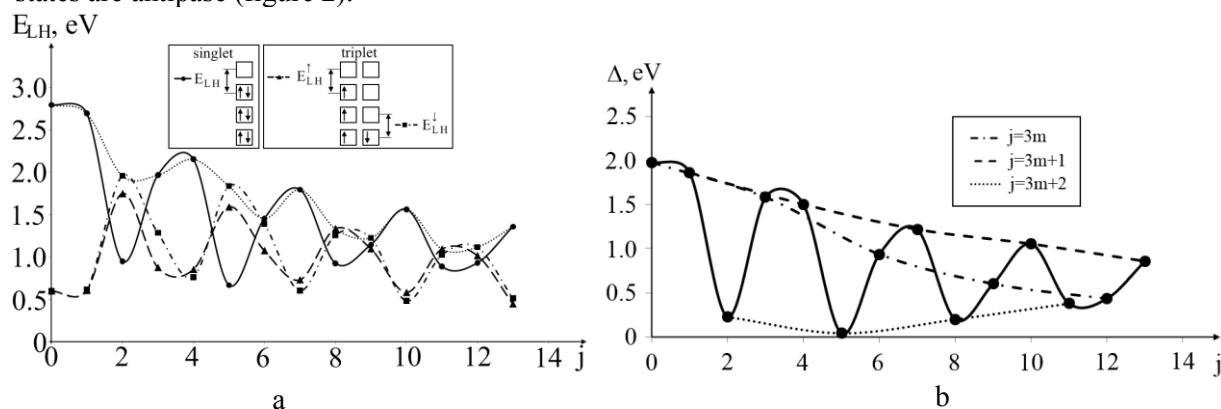


Figure 2. The Energy gap E_{LH} of singlet (solid line) and spin-dependent $E_{LH}^{\uparrow}$ (dash line) and $E_{LH}^{\downarrow}$ (dot-dash line) of triplet states of us-SWCNT(5, 5) versus the number of segments j (a). The maximum gap E_{LH} is shown by the dot line. The energy of the singlet-triplet transition of us-SWCNT (5, 5) (b)

The energy gap is a measure of the stability of molecular systems. At this rate, at the singlet state nanotubes with the number of segments $j=3m+1$ are more stable, than nanotubes of the $(3m+2)$ type and vice versa at the triplet state. The figure 2 shows that energy gaps at the triplet state are more than at the singlet state of us-SWCNTs (5, 5) with the number of segments $j=3m+2$. Hence, the ground state of this type of nanotubes is triplet and singlet for $3m$ and $3+1$ types. This results agrees with Fowler [34, 35] who shows that among isomers of carbon clusters C_n ($n=60+6k$, $k>1$) and clusters with the five-fold symmetry axis C_n ($n=70+30k$ or $n=84+36k$, $k>0$) at least one isomer with the closed electron shells exists. In the case of capped us-SWCNT (5, 5) the first and second type of carbon clusters are nanotubes with the number of segments $j=3m$ and $3m+1$. The third type of clusters at $k=5j+1$ ($j=0, 1, 2, \dots$) are nanotubes of the $3m$ type. Which implies, that nanotubes with $j=3m+2$ have open electron shells at the ground state.

With the aim of the investigation of singlet-triplet transition total energies E_{tot} of us-SWCNTs (5, 5) at two spin states $S=0$ and $S=1$ were compared. Remarkably, the difference of the total energies $\Delta=E_{tot}(S=0)-E_{tot}(S=1)$ is positive in the all over range of the number of segments (figure 2b). Hence, the ground state of us-SWCNTs (5, 5) is singlet, which contradicts to Fowler et al. [34, 35]. The energies of the singlet-triplet transitions of three types of nanotubes correspond to near (for $3m$ and $3m+1$) and far (for $3m+2$) infrared (IR).

4. Conclusions

The size confinement in the capped armchair us-SWCNT (5, 5) causes to the non-zero size-dependent energy gap between lowest unoccupied and the highest occupied molecular orbitals. There are three types of us-SWCNTs (5, 5) with the number of segments $j=3m$, $3m+1$, $3m+2$ that have the intermediate, maximal and minimal energy gap at the singlet state and the intermediate, minimal and maximal energy gap at the triplet state of nanotubes. It was revealed that the ground state of us-SWCNTs (5, 5) is the state with closed electron shells. The energy of the singlet-triplet transition corresponds to the energy value of visible and IR-radiation that makes us-SWCNTs promise materials for optoelectronic and spintronic devices.

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