Spin properties of the ultra–short capped single-walled carbon nanotubes (0, 9)

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Abstract. Results of the numerical simulation of the electronic structure of ultra–short single-walled carbon nanotubes (0, 9) of D_{3h}, D_{3d} and D_3 symmetries at the singlet and triplet spin states were presented. The dependencies of the energy gap, ionization potential, electron affinity and work function on the length of nanotubes at the singlet and triplet spin states were obtained. The analysis of the dimensionally dependent change of the electron density of states and energy gap for electrons with spin up and down allowed to establish the dependence of the spin polarization value on the length and symmetry of nanotubes. It was revealed that the energy required to turn from singlet to triplet is in the IR range that makes ultra-short single-walled carbon nanotubes (0, 9) a promising material for the design of the element base for spintronics and optoelectronics.

1. Introduction

In recent years a signigificant success was achieved in the field of theoretical and experimental studies aimed at the nanosystems characterization. The magnetic properties can be obtained at the nanoscale in materials which are nonmagnetic at the macroscale [1]. The present-day thin metal film ferromagnetic structures are characterized by a high Curie temperature and radiation tolerance. Otherwise, the principal limitation of melal spintronics is the impossibility to design amplifiers. That is why there is a great number of studies devoted to the semiconductor spintronics which is able to combine non-volatility, low leakage currents and rather high operation rates. The main actual task of semiconductor spintronics is a search for new materials which demonstrate a fairly high spin polarization of charge carriers and the construction of devices with a pretty easy registration of the magnetoresistance difference [2]. The relatively low spin-orbit interaction and ballistic transport of charge carriers in carbon nanotubes (CNTs) cause a long spin coherence time [3]. Catalyst particles which are used in CVD- synthesis can act as spin polarizers, however, the technology of doped CNTs controlled synthesis is rather complicated. The theoretical and experimental study of undoped CNTs observes the probability of the intrinsic magnetic moment occurrence [4–7].

The particular emphasis is deserved by the magnetic properties of ultra-short single-walled carbon nanotubes (us-SWCNTs) [5]. The distinctive consideration of us-SWCNTs is caused by a significant achievement in the field of synthesis methods with a narrow distribution in the chirality and length control up to angstroms [8, 9]. Lots of theoretical studies of carbon nanotubes demonstrate that the decrease in their length less than 10 nm causes 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 (W) [10–17]. It is expected that the properties and fundamental parameters of us-SWCNTs

strongly depend on their spin states. Thus, the intrinsic magnetic moment in pure carbon nanotubes makes possible their application as functional nanomaterials for spintronics and optoelectronics.

Literature data describing the origin of intrinsic magnetism in nanotubes are not complete and do not contain the dependencies of main spin-dependent parameters on the tube length. The aim of this work is the theoretical study of the electronic structure of us-SWCNTs (0, 9) at the singlet and triplet states.

2. Computational details

The numerical simulations of the electronic structure of the capped zigzag us-SWCNT (0, 9) were carried out using the DFT (density functional theory) method in the local spin density approximation (LSDA) with 3-21G basis set by means of the Gaussian 09 program package in the Supercomputing center of Voronezh State University.

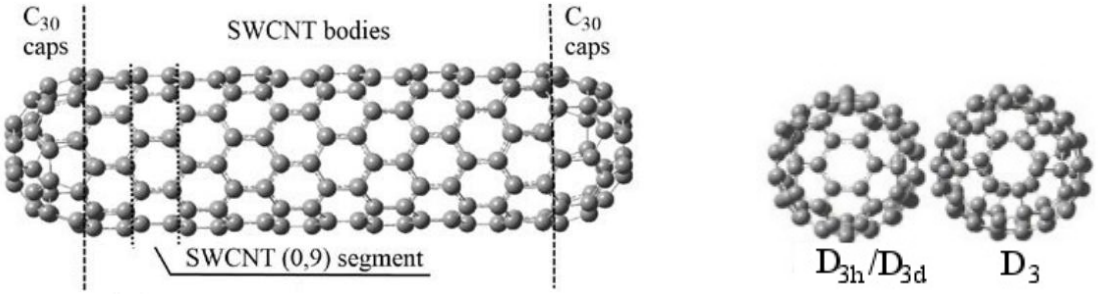

Figure 1. Structural images of capped us–SWCNTs (0, 9) (a). The mutual orientation of two C_{60} hemisphere caps of D_{3h}/D_{3d} and D_3 symmetries (b).

A stoichiometric formula of capped us–SWCNT (0, 9) is C_{60+18i}. Caps are obtained by the dissection of the fullerene molecule perpendicularly to the C_{3v} axis (figure 1). Regardless of number i there may be two orientations of the caps, corresponding to: 1) D_{3h} (when $i = 2p + 1$) and D_{3d} (when $i = 2p$), (where p is an integer) and 2) D_3 symmetries. The nanotube length varied from 1 to 3 nm. According to the Coopmans theorem, the ionization potential IP and electron affinity EA equal to the HOMO and LUMO energy with opposite sign. In case of zero number of segments, the capped us-SWCNT (0, 9) represents fullerene C_{60}. Therefore, fullerene is used as a test object which has been well studied both theoretically and experimentally [18–20]. Our calculated values for fullerene C_{60} IP = 6.69 eV and EA = 4.86 eV differ from the average experimental values IP = 7.56 ± 0.06 eV [21–24] and EA = 2.68 ± 0.02 eV [25, 26]. Using the assumption of Cioslowski et al. [11], the differences between average experimental data and calculated values for fullerene C_{60} and us-SWCNTs (0, 9) are equal. In our research we used the following corrections: ΔIP = 0.87 eV и ΔEA = -2.18 eV.

3. Results and discussion

3.1. The electronic structure of the capped us-SWCNT (0, 9) at the singlet state

The analysis of the all-electron total energy showed that us-SWCNTs with D_3 symmetry are more stable than D_{3h} and D_{3d} ones in all the investigated length range. The exception is the nanotube C_{78} that is in agreement with the calculations of the standard enthalpy formation of us-SWCNT (0, 9), which were carried out in paper [11]. It was found out that the length increase causes the monotonic decrease of the energy gap. The range of the gap E_{LH} energies is from 1.58 eV to 0.59 eV and from 0.81 eV to 0.29 eV for nanotubes of D_{3h}/D_{3d} and D_3 symmetries, respectively. The energy gap is non-zero just in rather close length ranges and seeks to zero at the sizes more than 3 nm. This non-zero gap energy is

caused by the restriction of the electrons motion along the nanotube axis and by the impact of two caps.

This fact together with thermodynamical stability of us-SWCNTs (0, 9) makes it possible to classify them as a whole family of semiconductor nanomaterials. The dependencies of the ionization potential, electron affinity and work function on the tube length are monotonically decreasing. The values belong to the ranges IP = 6.49 – 7.30 eV, EA = 4.67 – 4.97 eV, W = 2.65 – 2.84 eV for us-SWCNTs with D_{3h}/D_{3d} symmetry and IP = 6.37 – 7.29 eV, EA=4.69–5.37 eV, W = 3.02 – 3.44 eV for nanotubes with D_3 symmetry. It is remarkably that in the approximation of the infinite length and flat elementary cell zigzag, CNT (0, 9) has a zero energy gap or Eg = 100 – 140 meV if curvature effects are taken into account [27–30].

3.2. The electronic structure of the capped us-SWCNT (0, 9) at the triplet state

The dependencies of the energy gap between the frontier orbitals on the number of segments for us-SWCNTs (0, 9) at the singlet and triplet states are shown in figure 2. It was found that at the singlet-triplet transition the conductivity of us-SWCNTs (0, 9) of D_3 symmetry decreases that is determined by the increase of the energy gap between frontier orbitals, so $E_{LH}(\uparrow)$ и $E_{LH}(\downarrow)$ changes to 0.1 – 0.5 eV in relation to the energy E_{LH} at the singlet state. In its turn, the decrease of spin-dependent gaps between frontier orbitals to 0.4 – 1.5 eV with respect to the energy E_{LH} of the singlet state of us-SWCNTs of D_{3h}/D_{3d} symmetry points out to the significant increase of their conductivity. The relations between spin-dependent transport properties and the length are qualitatively different for nanotubes of D_{3h}/D_{3d} and D_3 symmetries. The value of the electron spin polarization of the nanotubes D_3 harshly decreases with the increase of the tube length, that is due to the decrease of the difference of energy gaps $E_{LH}(\uparrow) - E_{LH}(\downarrow)$ from 0.231 to 0.011 eV in the range of segments number i = 2 – 8. For us-SWCNTs (0, 9) of D_{3h}/D_{3d} symmetry with the number of segments $i \geq 4$, the value of the spin polarization increases almost linearly with the rise of the nanotubes length. Thus, the difference of gaps between frontier orbitals $E_{LH}(\uparrow) - E_{LH}(\downarrow)$ is 0.056 eV and 0.107 eV at i = 4 and i = 11. The wide length range of the spin polarization existence and the increase of the difference of electron conductivities for two spin channels at the length increase of us-SWCNTs of D_{3h}/D_{3d} symmetry determine the interest in their application in spintronic devices.

At the triplet state of us-SWCNTs (0, 9) the number of electrons with spin up is two more than the number of electrons with spin down. The energies of molecular orbitals with the majority and minority spin for the triplet state of us-SWCNT (0, 9) are shifted up and down relative to energies of the singlet state. This shift of orbital energies is determined by the us-SWCNT symmetry.

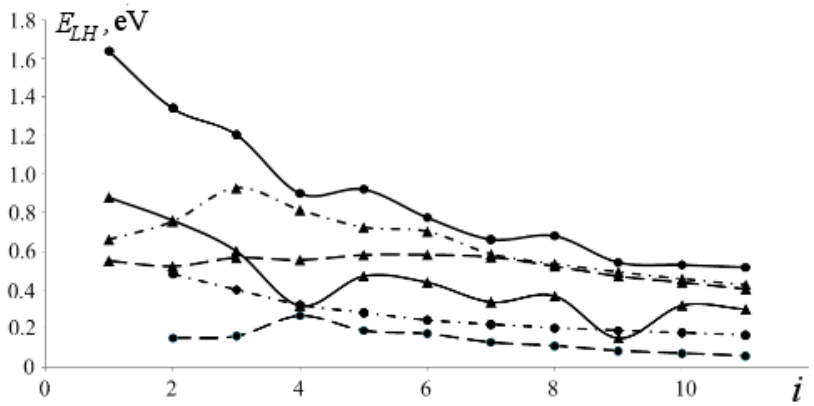

Figure 2. Dependencies of energy gaps E_{LH} at the singlet state (solid lines) and spin-dependent $E_{LH}(\uparrow)$ (dotted line), $E_{LH}(\downarrow)$ (dash-dot line) at the triplet state on the number of segments of the capped us–SWCNTs (0, 9) of D_{3h}/D_{3d} (circles) and D_3 (triangles) symmetries.

In the triplet state of the nanotube of D_3 symmetry, the energies of the LUMO and HOMO for electrons with majority and minority spins are quantitatively shifted almost symmetrically relative to the energies of frontier orbitals at the singlet state. Thus, the dependencies of energy gaps $E_{LH}(\uparrow)$ and $E_{LH}(\downarrow)$ converge to similar values (see figure 2). It follows from the analysis of the electron density of states, that the symmetrical shift of energies of molecular orbitals leads to the intersection of the DOS(↑) and DOS(↓) at the Fermi level. That results in a loss of spin polarization for long us-SWCNTs (0, 9) of D_3 symmetry.

The gaps between frontier orbitals of us-SWCNTs of D_{3h}/D_{3d} symmetries decrease during the singlet-triplet transition that is caused by the unsymmetrical changes of orbital energies. As a result, the energies of the HOMO(↓) and LUMO(↑) are close to HOMO and LUMO levels of the singlet state. That points out to the destabilization of the HOMO and stabilization of the LUMO. As follows from the DOS-spectrum, the asymmetric shift of the electron energies at the singlet-triplet transition defines the spin noncompensation at the Fermi level and, hence, leads to a possibility of spin-dependent transport of charge carriers.

According to the aim of the investigation, the difference of total energies at the singlet and triplet states was analyzed in the relation to the nanotube length. It is remarkably that the singlet-triplet transition energy (the difference $\Delta = E_{tot}(S = 0) - E_{tot}(S = 1)$, where E_{tot} and S are the total energy and total electron spin of the nanotube) is positive in value and inversely proportional to the number of segments (figure 3). The ground state corresponds to the singlet state. The energy of the transition to the triplet state corresponds to the IR – range of spectrum. Since the probability of a direct transition from the singlet to the triplet state is low, switching can be practically realized by a laser radiation through intermediaries or an additional influence on the system, for example, by an external electric field.

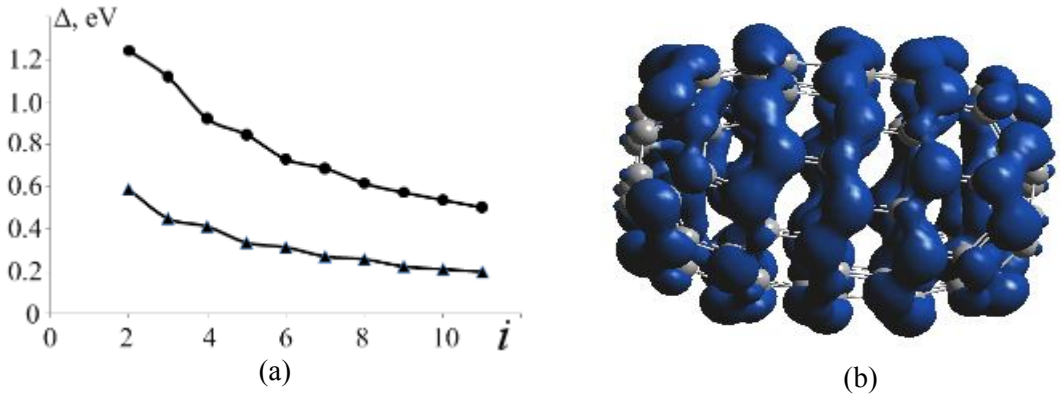

Figure 3. The singlet-triplet transition energy versus the number of segments of the capped us–SWCNTs (0, 9) of D_{3h}/D_{3d} (circles) and D_3 (triangles) symmetries (a) and the visualization of the electron spin density distribution (b)

The electron spin density is localized on the carbon atom segments which form the us-SWCNTs (0, 9) body (figure 1 (a), figure 3 (b)). The segment addition does not lead to the qualitative change of the electron density distribution. Therefore, the ionization potential, electron affinity, energy gap, work function, energy of the singlet-triplet transition and value of the spin polarization depend monotonically on the length of us-SWCNTs (0, 9).

4. Conclusions

The size confinement in the capped zigzag us-SWCNTs (0, 9) causes the size-dependent restructuring of the electronic structure. All main us-SWCNT parameters at the singlet and triplet spin states, such as the energy gap, ionization potential, electron affinity and work function, monotonically decrease

with the increase of the nanotube length. The thermodynamic stability, non-zero energy gap, the energy of the singlet-triplet transition energy lying in the IR-range, the wide length range of the spin polarization existence and the increase of the difference of electroconductivities for two spin channels with the increase of the length of us-SWCNTs (0, 9) of D_{3h}/D_{3d} symmetry determine the promise for their application as materials for design of the element base for spintronics and optoelectronics.

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