A finite-length capped single-walled carbon nanotube (5, 5) under an applied electric field

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Abstract. The paper describes results of a theoretical study of the electronic structure of the capped finite-length single-walled carbon nanotube (5, 5) under an applied electric field in the range from 0 to 0.5 V/Å. Clear oscillations of an ionization potential, electron affinity, gap energy and an effective work function on the length of the nanotube are presented. An applied electric field leads to the energy gap decrease and the work function increase. An estimation of the electron emission current density changes is revealed taking into account the work function dependence both on the nanotube length and the strength of the electric field.

1. Introduction

An electric field affects fullerenes and carbon nanotubes (CNT) in many cases, such as, the arc discharge syntheses, scanning microscopy investigations, in the polymer solar cells, field emission and field effect devises etc. [1-4]. A high curvature and small sizes lead to the high local electric field even if a low voltage is applied [5-6]. The electric field can significantly change the electronic structure of nanotubes [6-8]. Klinovaja at al. [6] showed that electric fields can be used for spin manipulation through spin-orbit interaction in the infinite-length defect-free CNTs. Kim et al. [7] revealed that the linear effective work function of the capped armchair (5, 5) nanotube decreases with the field strength increase. There are many external and internal degrees of freedom, such as field strength, CNT radius, chirality, electronegativity allow an extensive tunability of the electronic structure [6, 8]. From this point of view finite-length single-walled carbon nanotubes (SWCNTs with the length less than 10 nm) are very interesting object with the length as additional internal parameter.

Finite-length SWCNTs are the special class of objects which occupy intermediate position between fullerenes and nanotubes [9, 10]. Buonocore et al. [8], Rocherfort et al. [11] and Wang et al. [12] showed that finite-length open-ended armchair SWCNTs have a non-zero band gap. The energy gap, ionization potential and electron affinity show clear oscillations with the length of tubes. The capped finite-length tube (5, 5) shows oscillations of fundamental parameters and standard enthalpy of the formation with the length [9, 10]. It should be noted, that infinite-length armchair nanotubes must have a zero band gap because their chiral indexes n and m satisfy condition n−m=3k, k= 0, 1, 2... [13-15]. The influence of the electric field on the electronic structure of the capped finite-length SWCNTs is poorly understood. Tuchin et al. [10] showed quadratic decreases of the energy gap of the capped finite-length SWCNT (5, 5) with the field strength increases. The dependences of other fundamental parameters were not discussed.

The aim of the investigation is to reveal the impact of the length and the electric field on the electronic structure of the capped finite-length SWCNT (5, 5).
2. Computational details

All electron simulations of the electronic structure of the capped finite-length SWCNTs were performed using the density functional theory (DFT) computational method with a local spin density approximation (LSDA) and 3-21*G basis set with the help of the Gaussian software in the Supercomputing center of Voronezh State University [16-19]. A stoichiometric formula of the capped SWCNT (5, 5) is \( \text{C}_{60+10i} \), where \( i \) denotes the number of segments which form the body of the tube while caps essentially are halves of the fullerene molecule dissected perpendicularly to the \( C_5 \) axis [9, 10]. The SWCNT has \( D_{5h} \) and \( D_{5d} \) symmetry at odd and even \( i \). A diameter of the tube equals to the 7Å. To take an orientation deformation under the influence of ponderomotive force into account, a geometry optimization of the molecule in the range of electric field \( \epsilon = 0 \)–0.5 V/Å was performed without symmetry retention. The electric field was directed parallel to the tube axis.

There are two approach to calculate the ionization potential (IP) and electron affinity (EA) as \( \text{IP}=E_{\text{vac}}-E_{\text{LUMO}}, \text{EA}=E_{\text{vac}}-E_{\text{HOMO}} \) and \( \text{IP}=E_{\text{tot}}(q=-1)-E_{\text{tot}}(q=0), \text{EA}=E_{\text{tot}}(q=0)-E_{\text{tot}}(q=+1) \), where \( E_{\text{vac}}=0 \) the electrostatic potential energy in the vacuum, far away from system, \( E_{\text{LUMO}}, E_{\text{HOMO}} \) energy of the lowest unoccupied (LUMO) and highest occupied (HOMO) molecular orbitals, \( E_{\text{tot}}(q=0), E_{\text{tot}}(q=-1), E_{\text{tot}}(q=+1) \) total ground-state energies in the neutral and single charged configuration. Buonocore et al. [8] showed that work function of the finite-length SWNTs defined as \( \phi = (\text{EA}+\text{IP})/2 \) not depend on the used approach. In the current work we defined the IP, EA and hence \( \phi \) out of LUMO and HOMO energies because this method requires fewer calculations. The energy gap and an effective work function assigned as \( E_{\text{LUMO-HOMO}}=E_{\text{LUMO}}-E_{\text{HOMO}} \) and \( \phi_{\text{eff}}=(E_{\text{LUMO}}-E_{\text{HOMO}})/2 \) respectively.

3. Results and discussion

3.1. The fundamental parameters oscillation of the finite-length capped SWCNT (5, 5)

Results of the fundamental parameters calculation of the capped finite-length armchair SWCNT (5, 5) are presented in the figure 1. The ionization potential, electron affinity (figure 1a), energy gap, effective work function (figure 1b) show clear oscillations with the tube length. The nature of oscillations discussed in several works for open-ended [8, 12] and capped [9, 10] armchair SWCNTs and can were explained as a quantum confinement effect and an electron density redistribution of the LUMO and HOMO. Rocherfort et al. [11] introduced a division on the number of segments \( i \) of the finite–length open-ended armchair SWCNTs: \( i=3p+1, 3p \) and \( 3p+2 \) with the maximum, average and minimal values. That was further confirmed for capped tubes in the region of ultra-small lengths [9, 10].

![Figure 1](image-url)
Our calculations have revealed that introduced division is true in the studied range i from 0 to 11 (figure 1b). Therefore, properties of finite-length armchair SWCNTs of the ultra-small diameters are primarily determined by the tube length. It is important to consider the influence of curvature effects on the energy gap of the SWCNTs with diameters less than 2 nm [9, 10, 20-23]. Our calculated value for infinite-length open-ended SWCNT (5, 5) is 30 meV. An additional contribution to the nonzero $E_{LUMO-HOMO}$ is the caps influence.

The work function shows low amplitude oscillations because of antiphase dependencies on the length with close amplitudes of the ionization potential and electron affinity (fig.1a). In the range i from 0 to 11 $\phi$ decreases from 5.77 eV to 5.39 eV. The electron field emission current density $j$ is very sensitive to the magnitude of the work function [24]. According to the Fowler-Nordheim model [25] the current density can be expressed as follows:

$$j = \frac{A\beta^2}{\varphi} \exp \left( -\frac{B\varphi^2}{\beta \varepsilon} \right)$$

, where $\varepsilon$ is the applied field (V/nm), $A=1.56 \cdot 10^{-6} (A\cdot eV/V^2)$, $B=6.83 \cdot 10^9 (V\cdot eV^{-3/2}/m)$, $\beta$ is the field enhancement factor. The expression (1), called the Fowler-Nordheim formula, is convenient for treatment of experiments on electron field emission [26-27]. Using (1) we evaluated the relative current density change $j(i=11)/j(i=0) \approx 6$ at $\varepsilon=0.5$ V/Å.

3.2. The finite-length capped SWCNT (5, 5) excited by the electric field

An applied electric field leads to the charge redistribution and polarization of the SWCNT. A dipole moment of capped SWCNT (5, 5) is proportional to the field strength (figure 2a). The absolute change of the dipole moment, relative to the unexcited state, is proportional to the length square. The dependence of a module of a maximum effective charge $|Q_{eff\text{max}}|$ on the field strength is close to linear for tubes with $i>5$ (figure 2b). There is a pronounced threshold field strength $\varepsilon=0.25$ V/Å under which the field-induced charge is less than caps-induced for tubes with $i=1, 2$. It is known that the $|Q_{eff\text{max}}|$ of the unexcited capped SWCNT (5, 5) rapidly converges with the length to the constant value [28] that also markedly in the figure 2b at $\varepsilon=0$. The influence of caps decreases with the tube length. A first low-charged atom ring layer appears at $i=3$. The almost linear dependence of the $|Q_{eff\text{max}}|$ on the field strength can be attributed to the wall polarization of the SWCNTs body. Hence, the rise of the electric field influence on the electronic structure of capped finite-length SWCNT (5, 5) expects with the tube length increase.

![Figure 2. The dipole moment D (a) and the module of the maximum effective charge $|Q_{eff\text{max}}|$ (b) of the capped finite-length SWCNT (5, 5) in the range of the number of segments $i=0$–$11$ under an applied electric field $\varepsilon=0$–$0.5$ V/Å.](image)
Let us present results of the calculation of the energy gap and work function of the capped finite-length SWCNT (5, 5) under an applied electric field. The amplitude of the energy gap oscillation decreases with the increase of the field strength (figure 3a). The quadratic $E_{\text{LUMO-HOMO}}$ decline was previously observed in the fullerene $C_{60}$ as a result of a Stark shift of frontier orbitals [29, 30]. In the case of the capped SWCNT (5, 5) the quadratic energy gap decrease refers to tubes with the number of segments $i=3p$. While tubes of the $3p+2$ group show weak linear dependence $E_{\text{LUMO-HOMO}}(\varepsilon)$. The energy gap of SWCNTs of the $3p+1$ group decreases as a straight line with a low slope coefficient $\sim 0.1$ eV/Å at the field strength less than 3.5, 3.0 and 2.5 V/Å for tubes with $i=4$, 7 and 10 respectively. At the higher field the slope coefficient dramatically increases to 1.0 eV/Å ($i=4$) and 1.8 eV/Å/V ($i=10$). Thus, the field energy gap tuning $\Delta E_{\text{LUMO-HOMO}}=|E_{\text{LUMO-HOMO}}(\varepsilon=0) – E_{\text{LUMO-HOMO}}(\varepsilon)|$ strongly depends on the tube type and its length (figure 3b).

Figure 3. The energy gap LUMO-HOMO (a), energy gap tuning $\Delta E_{\text{LUMO-HOMO}}(\varepsilon=0.5 \text{ V/Å})$ (b), work function $\phi$ (c) and work function tuning $\Delta \phi$ (d) of the capped finite-length SWCNTs (5,5) under an applied electric field in the range from 0 to 0.5 V/Å.

The field-induced energy gap decrease in the fullerene $C_{60}$ occurs due to the $E_{\text{LUMO}}$ drop and the rise of the $E_{\text{HOMO}}$ [29, 30]. This is equivalent to the ionization potential decrease and the electron affinity increase. The response of the EA prevails over IP that is why the work function increases with the strength of the electric field (figure 3c). Taking into account the field-induced work function decrease, the current density reduced in 1.0-1.5 and 1.1-2.6 times at $\varepsilon=0.5$ V/Å for tubes of $3p$, $3p+2$ and $3p+1$ groups respectively. The field effect increases with the length of the SWCNTs especially for tubes of the $3p+1$ group that clearly follows from the dependence of the work function tuning $\Delta \phi=|\phi(\varepsilon=0) – \phi(\varepsilon)|$ on the field strength. Their work function converges to the value 5.6 eV at $i=7$, 10 (figure 3c). Thus, the electron emission current density also saturates.

4. Conclusion
Fundamental parameters and properties of capped finite-length SWCNTs are defined by the quantum confinement effect, curvature effect and influence of capes. There are three groups of the armchair SWCNT (5, 5) with the number of segments $i=3p$, $3p+1$ and $3p+2$ ($p=0, 1, 2, \ldots$) in the region of ultra-small length. These groups behave not only the different set parameters but also response on the electric field. The quantum confinement effect tends to decrease both the energy gap and work function with the tube length increase. The strong electric field leads to the additional drop of the energy gap but the rise of the work function that is more sufficient for longer tubes of the $3p+1$ group.
The evaluation of the electron current density for tubes of these group shows the saturation at the field strength 0.5 V/Å.

5. References

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