

Volume-localized electronic states in charged single-walled carbon nanotubes

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Theoretically and numerically, the presence of a system of short-lived volume-localized electronic states in positively charged nanotubes is shown by the example of a single-wall carbon nanotube (5,5). Unlike electron states that are well studied theoretically and experimentally, localized in a thin surface layer, these electron states are due to the flat part of the Coulomb potential of a positively charged nanotube cylinder. The maximum electron density of such states is located along the axis of the nanotube. The energy width of the system of such discrete body-localized levels depends on the charge and increases with its increase. The published papers show theoretically and experimentally the existence of metastable positively charged nanotubes with a charge of +10 e per 120 atoms or more, which suggests the possibility of experimental observation of the system of volume-localized electronic states under consideration.

(Received February 3, 2021; accepted August 16, 2021)

Keywords: Nanotubes, Carbon, Density of states, Calculation, Charged

1. Introduction

Single-walled carbon nanotubes are nanomaterials with unique properties that attract the attention of researchers [1]. Recently, a significant amount of work has been published on fundamental and practical research of this material [2-6]. In this regard, nanotubes are a well experimentally and theoretically investigated object. The results of studying the electronic states of neutral nanotubes have been published for a long time [1, 7]. Various methods were used to study the stability and decay mechanism of charged nanotubes [8].

In this paper, we concentrated on studying the effect of the positive charge of nanotubes on their electronic structure. Recent articles devoted to the study of discrete states of positively charged fullerenes [9,10,11] theoretically show the existence, along with well-studied electronic states localized on the surface of fullerene, of discrete states with a wave function localized in the volume of fullerene. These states arise as a result of the fact that the potential of the charged fullerene sphere creates a potential well in the center in which they are localized. In this case, it can be noted that the depth of this well depends on the charge. The larger it is, the deeper the well is, which leads to an increase in the number of volumetric-localized states with an increase in the positive charge.

In this paper, using a method based on the density functional theory, we demonstrated that similar states localized at the center of a nanotube are also possible in charged single-walled carbon nanotubes. These states arise as a result of a potential well created by the potential of a positively charged cylinder.

2. Methods and approaches

For numerical calculations, we used a method based on the electron density functional theory (DFT) [12], which was implemented in the QuantumEspresso software package [13]. Electronic wave functions decomposed in the basis of plane waves. To reduce the dimension of the basis, the pseudopotential method was used. In the study of nanomaterials, the supercell method with a translation vector length of 35 a.u. was used to exclude interaction between nanotubes. Norm conserving Perdew-Wang potentials [14] within the local density approximation (LDA) were used as pseudopotential. In the basis, plane waves with energies less than 40 Ry were taken into account. The length of the translation vectors and the plane wave basis energy cutoff were chosen so large that with an increase in these parameters, the total energy changed by less than 10^{-4} Ry. The structure was optimized using a method based on the Broyden-Fletcher-Goldfarb-Shanno algorithm. The position of the ions varied to a state where the interatomic forces became less than 10^{-4} Ry / a.u., and the unit cell parameters varied to values at which the stress in the cell became less than 0.5 Kbar. The calculations were carried out on a high-performance cluster computer K-100 of the Keldysh Institute of Applied Mathematics of the Russian Academy of Sciences.

3. Results and discussion

Similarly to the case of positively charged fullerenes, shown in [9, 11], the potential of a positively charged single-wall carbon nanotube can be represented as the sum of the potential of carbon atoms that make up the wall of the nanotube and the potential of a charged cylinder.

Moreover, the potential component corresponding to the potential of a charged cylinder creates a potential well in the center of the nanotube. The depth of this well increases with increasing positive charge of the nanotube.

To confirm such a simple model, the nanotube potential at various charges was calculated numerically using a method based on the density functional theory. Since such calculations require significant computational resources, we carried out work for a nanotube of type (5,5) with a length of 14.6 angstroms.

Fig. 1 presents the band structure of an infinite nanotube with a charge of $+5e$ on 120 atoms, calculated in our work.

Fig. 3 shows a two-dimensional cross section of the potential of a single-walled carbon nanotube of type (5,5) with a charge of $+5e$ per 120 atoms. The cross section is made in the direction perpendicular to the axis of the nanotube. Fig. 2 presents a one-dimensional cross section of the potentials of nanotubes with different charges. The cross section passes through the center of the nanotube and the carbon atom.

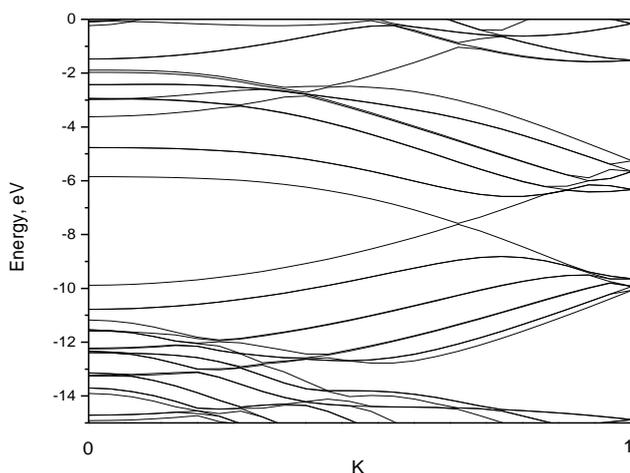


Fig.1. The band structure of a single-wall carbon nanotube with a charge of $+5$

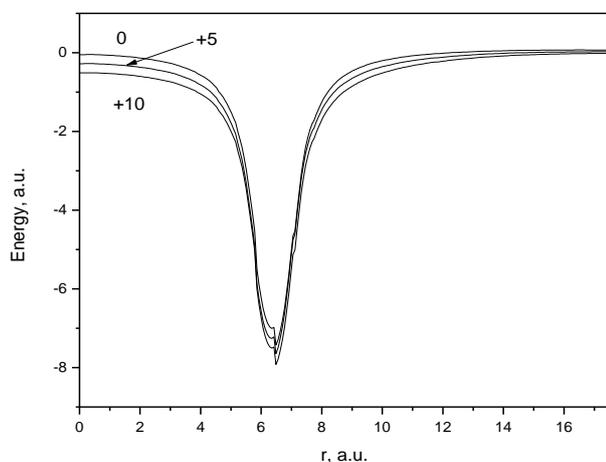


Fig.2. The potential cross section of a single-wall carbon nanotube of type (5,5) passing through a carbon atom at various charges

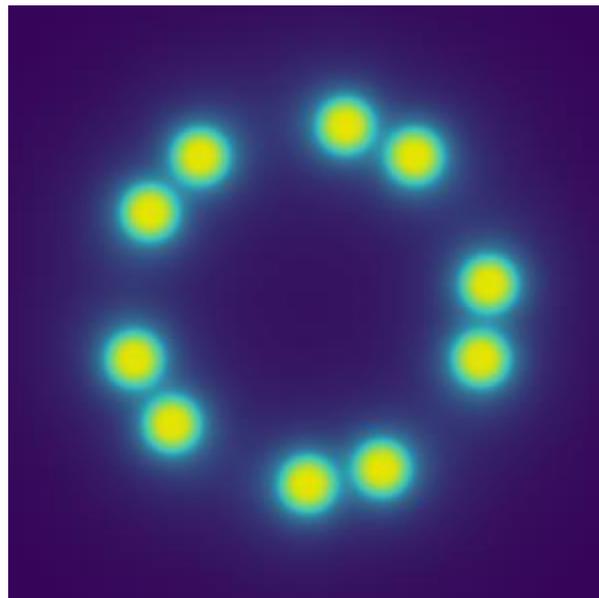


Fig.3. Two-dimensional potential cross section of a single-walled carbon nanotube of type (5,5) with a charge of $+5$ (color online)

As expected, the potential at the center of the nanotube decreases with increasing charge. This leads to the appearance of a potential well in the center of the nanotube with a depth depending on the charge. So, at a charge of $+5e$, the potential in the center of the tube is -0.2784 a.u. (-7.5755 eV). An increase in charge to $+10e$ leads to a decrease in potential to -0.5111 a.u. (-13.9075 eV).

It can be expected that in the energy range above the potential in the center of the nanotube, the appearance of electronic states localized in the volume of the nanotube is possible. That is, the maximum electron density will be on the axis of the tube, and not on the surface. Similar to the results of solving the Schrödinger equation in a potential well. In this case, it should be noted that well-known states localized on the surface of the tube must exist in this range.

The results published in the literature [9,10,11] show a similar case for fullerenes. These states are called volume-localized electronic states in contrast to well-studied surface-localized electronic states. To verify this assumption, we numerically calculated the electron density of various states in a nanotube (5,5). So, Fig. 4 shows one-dimensional cross sections of the electron density of states for a nanotube (5,5). Cross sections pass through the center of the nanotube and one of the carbon atoms. Similar two-dimensional cross sections in a plane perpendicular to the axis of the nanotube are shown in Fig. 5.

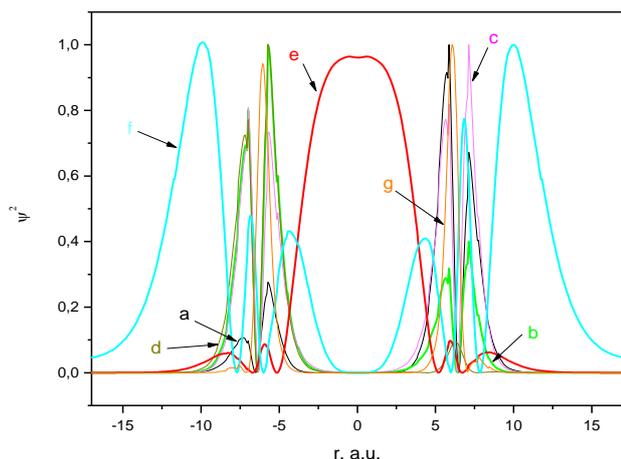


Fig. 4. Cross sections of the square wave functions of a single-walled carbon nanotube of type (5,5) with a charge of +5 (color online)

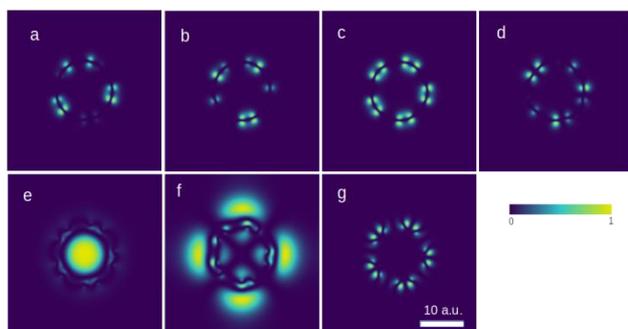


Fig. 5. Two-dimensional cross-sections of the squares of the wave functions of a single-walled carbon nanotube with a charge of +5 (color online)

The Fermi level for this nanotube is -0.2789 a.u. (-7.5883 eV). The potential at the center of the nanotube is -0.2784 a.u. (-7.5755 eV). Thus, state a with energy $E = -0.2977$ a.u. (-8.1001 eV) and state b with energy $E = -0.2977$ a.u. (-8.0997 eV) are located below the Fermi level. State c with energy $E = -0.2775$ a.u. (-7.5519 eV) is located above the Fermi level. State d with energy $E = -0.1947$ a.u. (-5.297 eV), state e with energy $E = -0.0363$ a.u. (-0.9891 eV), state f with energy $E = -0.0230$ a.u. (-0.6259 eV) and state g with energy $E = -0.0078$ a.u. (-0.2116 eV) are located above the potential in the center of the nanotube.

Thus, states a and b must be localized on the surface of the nanotube. Among states c, d, e, f, and g, we can expect states localized in the volume of a nanotube. Indeed, as can be seen in Figs. 4e and 5e, one can see the state with a maximum on the axis of the nanotube and has an electron density distribution similar to s orbital. The state shown in Figs. 4f and 5f shows an electron density distribution similar to the p orbital. The state in Figs. 4g and 5g shows a well-studied shape with localization on the surface of the nanotube. This allows us to assume that our initial assumption about the existence of single-wall carbon nanotubes in charged single-walled carbon nanotubes, along with well-studied electronic states

localized on the nanotube surface, states localized in the nanotube volume is correct. It can also be noted that the overlap of the wave functions of the states localized in the volume of the nanotube and on the surface of the nanotube is small, which should lead to the fact that the dipole moment of the transition between such states should be small and, therefore, the probability of the transition between such states is also small.

4. Conclusions

In this paper, using the method based on the electron density functional theory, the effect of a positive charge on the electronic structure of a single-walled carbon nanotube is numerically calculated. It is shown that the potential in the center of the nanotube decreases with increasing charge. In the energy range above the potential in the center of the nanotube, it is possible that along with well-studied electronic states localized on the surface of the nanotube, exist states localized in the nanotube volume. The dipole moment of the transition between such electronic states should be significantly less than the dipole moment of the transition between states localized on the surface of nanotubes. This is supposed to lead to a small probability of a transition between such states.

Acknowledgements

The reported study was funded by RFBR, project number 20-52-54003.

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