

# SINGLE-WALLED CARBON NANOTUBE AS A NANOSCALE QUANTUM SYSTEM

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**Abstract.** It is shown that a single-walled carbon nanotube based on a carbon monolayer (graphene) rolled up into a cylinder is a nanoscale quantum system characterized by the presence of electron crystals, like graphene. In contrast to the extremely unstable graphene quantum system, the nanotube quantum system is stable at a certain curvature of the carbon skeleton. The curvature causes the redistribution of  $\pi$  electrons between internal and external electron crystals accompanied by the formation of additional one-dimensional or quasi-one-dimensional crystals of pairs of  $\pi^*$  electrons excited into a higher  $3s2p_z$  energy state and located on the nanotube external side. The stability of the nanotube quantum system and its unusual physical properties are due to these crystals of  $\pi^*$  electron pairs.

**Keywords:** carbon nanotubes, electron crystals, nanoscale quantum systems, ballistic conductivity

## 1. Introduction

The interest to single-walled carbon nanotubes is caused by a number of properties that promise their widespread use in electronics based on quantum systems, including the systems based on carbon and its compounds. Of practical interest are the following properties of carbon nanotubes: the tendency to form bundles from individual tubes [1,2], an almost complete absence of defects [2], high emission currents at a relatively low voltage accompanied by light emission in the red and near infrared regions [3,4], ballistic conductivity at room temperature and achievement of intrinsic contact resistance close to a half of the quantum limit ( $h/4e^2$ ) at low temperature [5,6,7], high Josephson supercurrents [8], and also induced and intrinsic superconductivity [9]. The natures of all these phenomena are still unknown. It is not clear even why electrical properties of tubes, such as armchair and zigzag ones, differ from each other, though the only difference between them is in the hexagon orientation relative to the tube axis [7]. The nature of high Schottky barriers at contacts with metals [10] and the nature of the inhomogeneities of electron and light emissions from the tube surface [3,4] also remain unclear.

Since attempts to explain the above phenomena in the approximation of weakly interacting particles were unsuccessful, an attempt will be made to explain them in the approximation of strongly interacting electrons, i.e., in the approximation used earlier for graphene [11]. It was shown in [11] that a strong exchange interaction (resonant  $\pi$  binding) and strong Coulomb interaction between  $\pi$  electrons at neighboring atoms in graphene led to the localization of  $\pi$  electrons on carbon atoms and their strongly correlated state which manifested itself in the formation of two spin-polarized  $\pi$  electron crystals located on opposite sides of the carbon skeleton.

Since the nanotube is a carbon monolayer rolled up into a cylinder and resonant  $\pi$  binding and Coulomb interaction between  $\pi$  electrons are preserved, the formation of electron crystals should be also expected in it. The only difference is that both electron crystals (external and internal with respect to the carbon skeleton) must also have a cylindrical shape. However, it was also noted in [11] that a slightest disturbance in the carbon monolayer flatness (for example, a displacement of a  $\pi$  electron at polarization) causes significant changes in the monolayer quantum system. It is evident that monolayer rolling up must also lead to changes in the nanotube quantum system.

The goals of our study were, first, to consider the features of quantum systems of the armchair and zigzag nanotubes and, second, to show how the unusual properties of these nanotubes can be understood in the approximation of strongly interacting electrons.

It is known that carbon nanotubes are divided into single-walled and multi-walled ones. We consider only single-walled ones, since  $\pi$  electron interactions between neighboring tubes should be taken into account in multi-walled tubes along with interactions between  $\pi$ -electrons in each tube (like in graphite). Therefore, the properties of multi-walled and single-walled tubes can differ considerably.

It is also known that single-walled nanotubes differ in the orientation of carbon hexagons relative to the tube axis (chirality). For the sake of brevity, we consider only two cases of hexagon orientation, which corresponds to two types of tubes, i.e., zigzag and armchair ones.

## 2. On preferred diameter of single-walled nanotubes

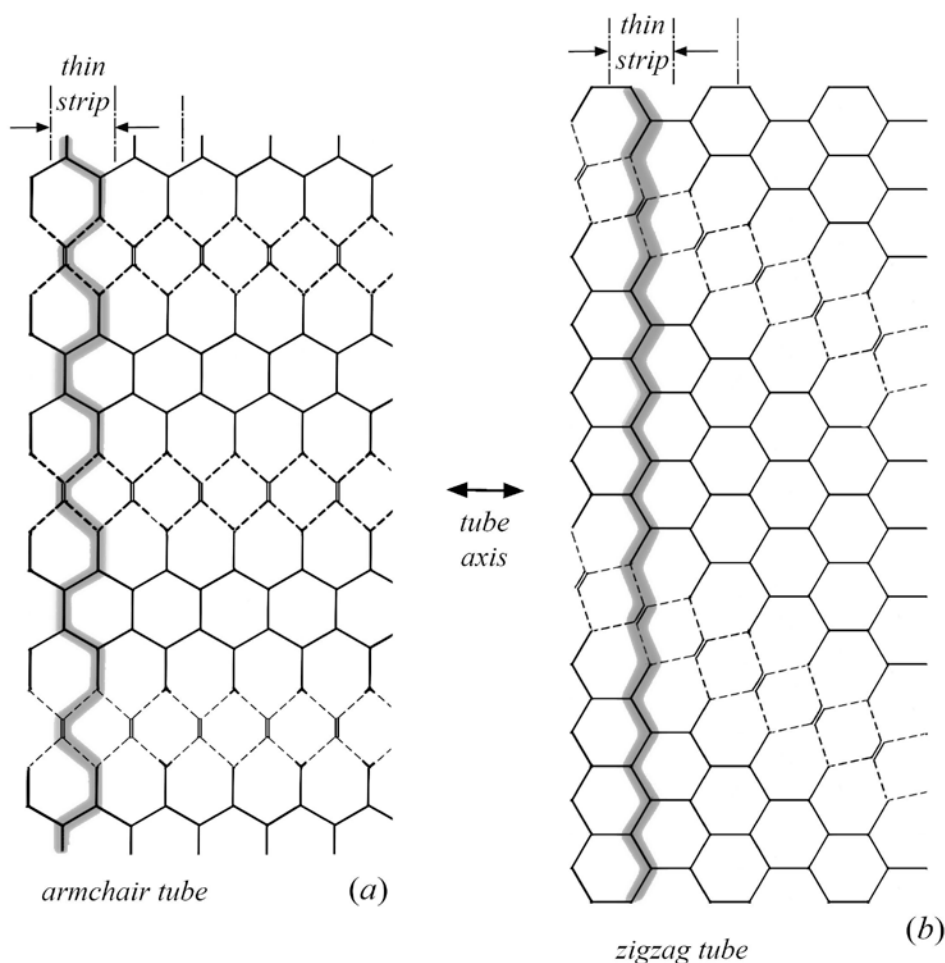
In order to carry out a comparative analysis of two types of nanotubes (armchair and zigzag), we consider the tubes with the same number of hexagon rows parallel to the nanotube axis and determine their diameters. Then we cut out rings five hexagons wide each and draw a projection of these rings on a plane. Fig. 1 (a, b) shows the projections of such tube rings containing 12 rows of hexagons each.

The choice of tubes with 12 hexagon rows is not random. As will be shown below, it is dictated by the conditions of stability of this carbon modification. The diameter of the selected nanotubes is easily calculated if we know the C – C bond length. As the first approximation, we can assume that all bonds in the hexagon are similar and their lengths are equal to the bond length in graphene (1.41 Å). Under these assumptions, the tube diameter with 12 hexagon rows is in the range 8-9 Å (or, more precisely, 8.08 Å and 9.33 Å for the armchair and zigzag tubes, respectively). Note that these diameters are close to those obtained experimentally in [12], where the highest peak in the distribution of single-walled nanotubes in diameter was observed for a diameter of 10.5 Å and a lower peak was observed for a diameter of 8.5 Å.

It is clearly seen from the projection of the armchair tube that the number of rows in these tubes can be only even, since every next row of hexagons is shifted with respect to the preceding row. Further consideration will show that the even number of hexagon rows is also important for zigzag tubes. There is another limitation on the number of rows common to both types of tubes. It is a consequence of the multiplicity of bonds in graphene equal to 1.33 ( $1\sigma + 0.33\pi$ ) corresponding to the maximum binding energy in it. To achieve such a multiplicity of coupling, it must be possible drawing of 9 resonance structures of the Kekule type.

Let us explain this statement. Since only two double bonds out of six are possible in each hexagon of any resonant structure of a carbon monolayer, a multiplicity of  $\pi$  bond equal to 0.33 can be achieved when each bond is a double one in three resonant structures. Hence, the number of structures must be 9. This pattern of 9 resonant structures for both types of tubes is possible if the number of hexagon rows is a multiple of three. If we take into account

the even number of rows noted above, the number of rows in the tubes must be a multiple of 6. The tubes with 12 hexagon rows satisfy this condition.



**Fig. 1.** Projections of nanotube rings containing 5 hexagons in width and 12 hexagon rows in perimeter of a circle for the armchair (a) and zigzag type tubes (b). Resonant  $\pi$  bonds are shown by the thin lines, stationary  $\pi^*$  bonds are shown by the double lines and the single bonds are shown by the dash lines. The dot-and-dash lines with two arrows show the thin strips containing one carbon atom chain highlighted by shading. Three 1D crystals of  $\pi^*$  electron pairs are shown in (a) and two quasi-1D crystals are shown in (b). The line with two arrows on the ends shows the tube axis direction

The tube diameter calculated above is the carbon skeleton diameter. However, to characterize the tube, the diameters of the external and internal  $\pi$  electron crystals, which are at a distance equal to the carbon atomic radius ( $0.91 \text{ \AA}$ ) from the carbon skeleton, are also important. The diameters of the electron crystals calculated with due account for the atomic radius turned out to be  $9.90 \text{ \AA}$  and  $11.15 \text{ \AA}$  (external) and  $6.26 \text{ \AA}$  and  $7.51 \text{ \AA}$  (internal) for the armchair and zigzag tubes, respectively. Note that electron diffraction studies of the nanotube diameter (for example, by transmission electron microscopy) give the diameter of the external electron crystal with which the electron beam interacts rather than the carbon skeleton diameter. Therefore, the experimental data should be compared with the diameter of the external electron crystal. Note that the calculated average (for both types of nanotubes) diameter of the external electron crystal ( $10.5 \text{ \AA}$ ) is in good agreement with the experimental data [12].

A comparison of two types of tubes with the same number of hexagon rows shows that the diameter of the carbon skeleton of the armchair tube is noticeably smaller than the zigzag tube diameter (8.08 versus 9.33 Å). This means that the curvatures of the carbon tube skeleton estimated as  $1/r$ , where  $r$  is the skeleton radius, are different. The curvature of the armchair tube is greater than that of the zigzag tube (0.24 versus 0.21).

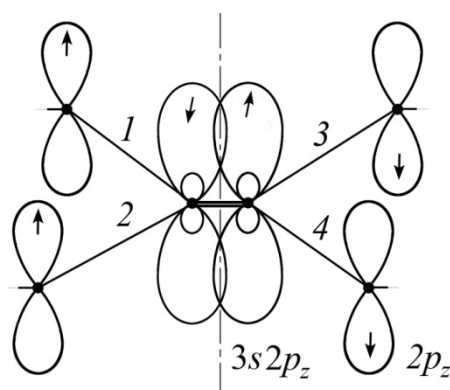
### 3. Curvature of carbon skeleton and number of excited $\pi$ electrons

Let us consider the effect of curvature of the nanotube carbon skeleton on the  $\pi$  electron state in them. The rolling up of a carbon monolayer into a tube leads to an expansion of the external electron crystal and a compression of the internal one. Such changes should be accompanied by changes in the exchange interaction between  $\pi$  electrons, an increase in the Coulomb interaction in the internal electron crystal and its weakening in the external one.

However, to provide stability of a quantum nanotube system, it is important to maintain the equality of electron densities of the external and internal electron crystals, since only when these densities are equal all Coulomb interactions between  $\pi$  electrons are balanced inside and between electron crystals.

Apparently, the condition in the quantum nanotube system can be satisfied due to the transition of a part of  $\pi$  electrons from the internal electron crystal to the external side of the nanotube, i.e., transition of a  $\pi$  electron from the lower lobe of its  $2p_z$  state to the upper one. However, such a transition will encounter a strong Coulomb repulsion from the external electron crystal. The result of such repulsion, as shown in [11] for graphene polarization, can be a change in the hybrid state of the carbon atom to which this  $\pi$  electron belongs from  $sp^2 + 2p_z$  to  $sp^2 + 3s2p_z$  state and excitation of the  $\pi$  electron from the  $2p_z$  state into one of two  $3s2p_z$  hybrid states located on the external side of the nanotube. To distinguish such a excited electron from a  $\pi$  electron in the  $2p_z$  state, we denote it as  $\pi^*$  electron.

A change in the hybrid state of carbon atom will be accompanied by a loss of its resonant  $\pi$  binding with three nearest neighboring atoms. Three resonant  $\pi$  bonds will be replaced by two single bonds with two neighboring atoms and one stationary (non-resonant)  $\pi^*$  bond with the third neighboring atom which is closer to the excited atom than the other two (Fig. 2).



**Fig. 2.** Formation of four single bonds (1-4) and a stationary  $\pi^*$  bond by a pair of  $\pi^*$  electrons excited into the  $3s2p_z$  state. The dot-and-dash line shows the tube axis direction

This point requires some explanation. A monolayer rolling up can be accompanied by a decrease in the distance and the bond length between carbon atoms. This decrease will depend on the bond orientation relative to the tube axis. So, if the length of the bond parallel to the tube axis remains unchanged at a monolayer rolling up, the length of the bond located at an angle to the axis decreases, and the length of the bond perpendicular to the axis also

decreases, but in a greater degree. Therefore, the hexagons are deformed, and the distances between atoms in the hexagon become different (Fig. 1).

The bonds perpendicular to the tube axis are present only in the armchair tubes, and the bonds parallel to the axis are present only in the zigzag ones. Therefore, the  $\pi^*$  electron excited into the  $3s2p_z$  state in the armchair nanotube does not have an alternative when choosing an atom with a  $\pi$  electron of which it can be paired. It will be the  $\pi$  electron of the carbon atom closest to the excited atom because its  $\pi$  electron is redundant in the system of two  $\pi$  electron crystals (it does not have a pair in the internal electron crystal after the excited electron leaves it). Since the number of electrons in the quantum system in the internal and external electron crystals should be the same, the extra electron will also be pushed out of the external electron crystal and excited into the  $3s2p_z$  state, but of its own atom. As a result, two adjacent closely spaced carbon atoms will be in the same hybrid  $3s2p_z$  state, and their  $\pi^*$  electrons can be paired, thus forming a stationary  $\pi^*$  bond (Fig. 2). Such pairing is energetically favorable for a quantum nanotube system, since it partially compensates for the energy loss of two resonant  $\pi$  bonds of three ones.

To evaluate the number of  $\pi$  electrons migrating to the external side of the tube and the type of their ordering, we separate the projections of both tube rings into separate very narrow strips with a width equal to one carbon chain (Fig. 1 a, b). Each such strip in a nanotube corresponds to a thin ring containing only one carbon atom chain. Obviously, such a chain will be a sequence of atoms located in an armchair array for an armchair-type nanotube, and it will be a zigzag array for a zigzag-type nanotube.

The number of  $\pi$  electrons migrating to the external side of such a thin ring can be calculated from the condition of electron density equality on the external and internal sides of the nanotube. This equality suggests that the ratio between the numbers of electrons on two sides of a thin ring is inversely proportional to the ratio between curvatures of the  $\pi$  electron crystals.

The calculations showed that only three  $\pi$  electrons (from 24  $\pi$  electrons) migrate to the external side of the ring in each thin ring of the armchair tube, while only two  $\pi$  electrons migrate to the external side in the thin ring of the zigzag tube. This is because the curvature of the zigzag carbon skeleton is less than the curvature of the armchair carbon skeleton. Thus, the difference between the number of  $\pi$  electrons on the external and internal sides of the thin ring containing one carbon chain will be six electrons for the armchair tube and four for the zigzag tube, or three and two  $\pi^*$  electron pairs, respectively (Fig. 1).

As a result, when a monolayer rolls up into an armchair tube, one fourth of  $\pi$  electrons change their state from the  $2p_z$  to the  $3s2p_z$  one, while only one sixth of  $\pi$  electrons change their state in the zigzag tube. Then the concentration of  $\pi$  electrons in the  $2p_z$  state in the armchair tube decreases from  $4 \times 10^{15}$  to  $3 \times 10^{15}$  electrons per  $\text{cm}^2$ , and it decreases to  $3.3 \times 10^{15}$  electrons per  $\text{cm}^2$  in zigzag tubes. The average concentration of  $\pi^*$  electron pairs in the armchair tubes is estimated to be  $5 \times 10^{14}$ , and it is  $3.5 \times 10^{14}$  electron per  $\text{cm}^2$  in zigzag tubes.

However, the concentration of the electron pairs is not so important for the conductivity of nanotubes, as the type of their ordering on the nanotube surface.

First, we consider the ordering of electron pairs of  $\pi^*$  bonds in one thin ring. Owing to the Coulomb repulsion between pairs, they are apparently distributed in the ring at equal distances from each other, i.e., the thin ring perimeter is divided into three equal parts for the armchair tube and two parts for the zigzag tube.

Let us consider ordering of  $\pi^*$  electron pairs between neighboring thin rings.  $\pi^*$  electron pairs in a quantum system with  $\pi$  electron crystals can be regarded as defects. Since defects in any crystalline structure tend to ordering, which reduces the system free energy, we can assume that they are ordered in nanotubes as well. As the  $\pi^*$  electron concentration is low, ordering is possible only in the form of 1D or quasi-1D crystals.

Since only three  $\pi^*$  electron pairs are formed in each thin ring of the armchair tube, there must also be three 1D crystals of  $\pi^*$  electron pairs. They will be located at equal distances from each other equal to three hexagon rows. The crystals will be oriented along the tube axis, since the shortest bonds in the armchair tubes perpendicular to the tube axis are located along it (Fig. 1a).

Only two quasi-1D crystals of pairs can be formed in a zigzag tube. They will also be located parallel to each other, but already at the distance determined by five hexagon rows. (It becomes clear why the zigzag tube should have an even number of rows). Since the shortest bonds in these tubes are oriented at an angle to the tube axis, the quasi-1D crystals will be located at the same angle to the tube axis and will embrace the tube in a spiral. Since the shortest bonds in each hexagon in the zigzag tubes are neighbors with an angle of about  $120^\circ$  between them, the spiral direction can be either clockwise or counterclockwise (Fig. 1b).

It can be seen from the above that, when a quantum system of graphene is rolled up into a nanotube, two spin-polarized electron crystals of  $2p_z$  electrons are preserved, but with a loss of some of  $\pi$  electrons. In this case, 1D or quasi-1D crystals of pairs of  $\pi^*$  electrons excited into the  $3s2p_z$  state arise in the nanotube quantum system. The number of 1D crystals in the armchair and zigzag tubes is different due to different curvatures of their carbon skeletons. The orientations of these crystals relative to the tube axis are also different, but due to different orientations of stationary  $\pi^*$  bonds.

#### 4. Effect of 1D electron pair crystals on nanotube properties

The presence of 1D crystals of excited  $\pi^*$  electron pairs on the tube external side must lower the ionization potential of the nanotube and decrease the electric field threshold at which electron emission begins. In addition, the electron emission may be accompanied by the emission of electron pairs, pair breaking, and the release of  $\pi^*$  binding energy. The  $\pi^*$  binding energy is unknown. Only the energy of a  $\pi$  bond in carbon compounds is known. It is about 1.5 eV. The  $\pi^*$  bond energy should be slightly higher, since the  $3s2p_z$  state is characterized by a volume larger than the  $2p_z$  state, and the lateral overlapping of electron states can be a little larger. An energy of 1.5 eV and slightly higher correspond to radiation in the red and near infrared. The radiation emission accompanying the electron emission precisely in this range was obtained experimentally [3,4], where a very narrow emission band (0.022 eV) with a maximum of about 1.85 eV was observed. Perhaps, this energy corresponds to the  $\pi^*$  binding energy.

Since emission from nanotubes is associated with 1D crystals, it can be expected that it will be strongly inhomogeneous over the nanotube surface, which was also observed experimentally.

As for the conductivity of armchair nanotubes, it can be assumed that it occurs through tunneling of 1D crystals of pairs as a whole through gaps between adjacent  $\pi^*$  bonds. The geometric gap between the pairs is about  $2.5 \text{ \AA}$ , but if we take into account the volume of two  $3s2p_z$  states, it proves to be less than  $1 \text{ \AA}$ . (Note that direct overlapping of these states is impossible because of their occupation by electron pairs). Since such tunneling occurs without resistance, it can be regarded as a mechanism of ballistic conductivity accomplished by electron pairs.

Tunneling of quasi-1D crystals of pairs is impossible in zigzag tubes, since the field applied along the tube axis cannot provide a spiral motion.

Note also that in the case of conductivity by pairs, the problem of contacts with metals, where there are no pairs, arises. An ideal contact for this case would be a superconductor. Perhaps, the absence of electron pairs in metals is responsible for the high Schottky barrier observed experimentally [10].

The 1D crystals of pairs create a strong inhomogeneity of the electric field on the nanotube surface in the form of negative charge strips protruding from the nanotube surface. Therefore, when the tubes approach each other, the Coulomb interaction can arise between them. As a result, they will be ordered relative to each other. Perhaps, the tendency to form bundles is explained by this Coulomb interaction.

## 5. Conclusions

It is shown that when a carbon monolayer (graphene) rolls up into a single-walled nanotube, the graphene-based system retains its quantum character, but with significant changes in it. In addition to the conservation of the system of  $\pi$  electrons in the  $2p_z$  state forming two spin-polarized electron crystals strongly coupled to the carbon skeleton and providing resonant  $\pi$  binding between atoms, a second system of  $\pi^*$  electrons arises. It is a set of 1D or quasi-1D crystals of pairs of  $\pi^*$  electrons excited into the  $3s2p_z$  state and forming stationary  $\pi^*$  bonds between excited carbon atoms. It has been shown that it is these 1D or quasi-1D crystals of  $\pi^*$  electron pairs that ensure the cylindrical nanotube shape stability and are responsible for the nanotube unusual physical properties.

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