Symmetry and structural properties of carbon nanotube quantum dots and superlattices

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Abstract. The electronic structure and quantum conductance of metallic carbon nanotube quantum dots and superlattices are investigated. We study two kinds of quantum dots and superlattices: rotationally symmetric and rotationally asymmetric ones. It is shown that rotational invariance significantly influences the conductance of quantum dots. In contrast, quantum conductance of superlattices (multiple quantum dots) does not critically depend on their rotational symmetry. All the calculations are performed within the tight-binding model and \(\pi\)-electron nearest-neighbors approximation.

Carbon nanotubes (CN) are quasi-one-dimensional systems made by rolling-up a graphite sheet into a cylinder of nanosize diameter. They were discovered by S. Iijima in 1991\(^1\), and since then, the interest in their fundamental properties and potential applications has been rapidly growing. One of the focus of current interest of nanotubes is their electronic behavior: depending on the rolling direction and on the tube diameter they may have metallic or semiconducting character. Carbon nanotubes are identified by two integers, \((n, m)\), which are the coordinates of the circumference vector \(C_h\) in the graphene primitive basis \(\{a_1, a_2\}\), chosen to form an angle\(^3\) of 60\(^\circ\). If \(C_h\) goes along two neighboring carbon atoms, then \(C_h = na_1 + na_2\), so the tube is labeled \((n, n)\). This kind of nanotube is called armchair; it has \(2n\) atoms around the circumference, and it is invariant under \(C_n\) rotations around the nanotube axis. If \(C_h\) goes along a lattice vector, e.g. \(a_1\), the resulting tube, \((n, 0)\) has \(n\) atoms at the circumference and it is invariant under \(C_n\) rotations. Because of the arrangement of atoms around its circumference, it is called zig-zag. All the other tubes, labeled \((n, m)\), with \(n \neq m\) and \(n, m \neq 0\), are chiral: their atoms are arranged in a helical way around the circumference. Any smallest section of the CN cylinder, periodically repeatable along the tube axis, defines the carbon nanotube unit cell. In general, when \(n\) and \(m\) have a common divisor \(p\), the \((n, m)\) nanotube is invariant under \(C_p\) rotations\(\(^3\)\). The geometrical information in \((n, m)\) is directly related to the electronic properties: if \((n - m)/3\) is integer the tube is metallic, otherwise it is semiconducting.

Introducing topological defects in the hexagonal carbon network allows to connect different tubes, which can have different electronic character, e.g., metallic and semiconductor. The junctions between different nanotubes are most usually realized by the introduction of pentagon/heptagon defects at the interface between them.\(^4\) In the same fashion, one can design

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\(^3\) Initially, the basis with vectors at 120\(^\circ\) was also used \(^2\). With this choice of basis, the labeling of nanotubes changes.

\(^4\) Pentagons and heptagons are the weakest perturbations of the ideal hexagonal lattice. They naturally appear
a double junction, \((n, m)/N(n', m')/(n, m)\), formed by sandwiching a short section of \(N\) unit cells of one nanotube in between of two other (semi-infinite or long enough) tubes. Due to finite size of the central section, the bands of \((n', m')\) quantize into discrete energy levels, so it can be considered as a carbon nanotube quantum dot (QD). And finally, a periodic sequence of junctions, \(M(n, m)/N(n', m')\), is a carbon nanotube superlattice (SL). Such junctions, as well as other types of T-like or Y-like connections, have already been achieved experimentally[4, 5, 6, 7]. Together with the already demonstrated applications as e.g., field-effect and single-electron transistors or rectifying diodes, it opens up a route to an all-carbon based nanoelectronics.

Motivated by such experimental findings and possible future applications, different kinds of carbon nanotube junctions have been theoretically studied showing their unusual electronic and transport properties. Chico et al. [9] first found that when joining two different metallic tubes, a wide conductance gap can open up at the Fermi energy, when the entire system preserves some rotational symmetries and the bands of the joined tubes have different values of the discrete angular momentum[8] in a common energy interval. We use the term ‘discrete angular momentum’ in the meaning explained in Ref. [9]. Because of these apparently unusual behavior of all-metallic junctions, we explored the properties of CN double junctions, and we showed[10] that in quantum dots fulfilling the above-mentioned conditions, the conductance gap is covered by a series of non-conductive localized quantum dots states. In contrast, when the quantum dot does not preserve any rotational symmetry, the gap is covered by a series of conducting resonances, the widths of which depend on the wavevector mismatch[10, 11] between the (band) states of the metallic tubes forming the quantum dot. Finally, we demonstrated that in superlattices, built as periodic sequences of rotationally invariant quantum dots, some localized states transform into conducting minibands[12].

In this work we perform a comparative study of the electronic structure and quantum conductance of rotationally symmetric and rotationally non-symmetric quantum dots and superlattices. Knowing how the rotational invariance affects the conductance of quantum dots (carbon nanotube double junctions), we investigate effect of the rotational invariance on the conductance of superlattices (carbon nanotube multiple junctions). In particular we study: (A) rotationally symmetric \((12, 0)/4(6, 6)/(12, 0)\) quantum dot and \(4(12, 0)/4(6, 6)\) superlattice, (B) rotationally non-symmetric \((8, 2)/4(5, 5)/(8, 2)\) quantum dot and \(4(8, 2)/4(5, 5)\) superlattice, (C) rotationally symmetric \((9, 3)/4(6, 6)/(9, 3)\) quantum dot and \(4(9, 3)/4(6, 6)\) superlattice, (D) rotationally non-symmetric \((9, 3)/4(6, 6)/(9, 3)\) quantum dot and \(4(9, 3)/4(6, 6)\) superlattice. (A) and (B) are structurally different systems, while (C) and (D) differs only by the symmetry of the junction between \((9, 3)\) and \((6, 6)\) nanotubes. In case (C) the junction has a common rotation axis with both tubes, while in case (D) the junction is not rotationally invariant.

We work within the tight-binding model with one \(\pi\)-orbital per atom. The hopping parameter for nearest neighbors is fixed to \(V_{\pi\pi} = t = -2.66\) eV and second-neighbor interactions are neglected. The local density of states (LDOS) of quantum dots is calculated using the Green function matching approach[13]. The band structure and density of states (DOS) of superlattices is calculated by direct diagonalization of the tight-binding Hamiltonian matrix. The conductance of quantum dots is calculated employing the multichannel Landauer formula[14], while for superlattices it is calculated by counting the number of available channels (minibands) at each energy.

Let us consider first the systems built of \((12, 0)\) and \((6, 6)\) tubes. Although the considered tubes have slightly different diameters, they can be easily connected by means of 6 pairs of 5,7 rings. Such a connection is invariant under \(C_6\) rotations around the common axis. Since \((12, 0)\) and \((6, 6)\) undergo the same rotational symmetry \(C_6\), thus any system built of such nanotubes connected along the tube axes is invariant under \(C_6\) rotations. However, the value of the discrete in fullerenes and have also been experimentally detected in carbon nanotubes.
Figure 1. Density of states (local density of states in case of quantum dot) and conductance of rotationally symmetric \((12, 0)/4(6, 6)/(12, 0)\) quantum dot and \((12, 0)/4(6, 6)/(12, 0)\) superlattice. LDOS is taken at the \(4(6, 6)\) side of the interface.

Angular momentum of the bands[15] close the Fermi level \(E_F\) in the \((12, 0)\) tube is equal \(L = 4\), while the corresponding value for the \((6, 6)\) tube is \(L' = 6\). Therefore, the conductance gap, as wide as \(\approx 2.5\) eV, opens up at \(E_F\) in the system built by connecting two such tubes[9]. The conductance gap persists in the \((12, 0)/N(6, 6)/(12, 0)\) quantum dots[10] if \(N > 2\). For \(N = 4\) the gap is visualised in Fig. 1. The figure shows also LDOS at the \(4(6, 6)\) side of the interface. The \(\delta\)-like peaks of LDOS correspond to a series of non-conducting states. Some of these states originate from the quantized bands of \((6, 6)\) and from dispersionless bands of \((12, 0)\) tube[12]. They are localized in the \(4(6, 6)\) quantum dot. The peaks at \(\approx 0.15\) and \(\approx 0.43\) eV correspond to the interface states. The corresponding wavefunctions are not invariant under any rotation.

In Fig. 1 the DOS and conductance of \(4(12, 0)/4(6, 6)\) superlattice is also presented. In this case the localized QD states transform into narrow minibands. Some additional minibands appear also at \(-1.25, 0.3, 1.1, 1.2\) and \(1.4\) eV; they originate from the quantized bands of the short sections of \((12, 0)\) nanotube. All these minibands, except the dispersionless states (e. g., at 1.0 eV), are conductive, as confirmed in the bottom panel of Fig. 1.
Figure 2. Density of states (local density of states in case of quantum dot) and conductance of rotationally asymmetric (8,2)/(5,5)/(8,2) quantum dot and (8,2)/(4(5,5))/(8,2) superlattice.

Now, let us consider systems that do not preserve any rotational symmetry, namely QD and SL built of metallic (8,2) and (5,5) tubes. The pure rotation groups of (8,2) and (5,5) are $C_2$ and $C_5$, respectively, so they have no common rotational symmetry. Furthermore, one can connect these tubes by a sequence of 6,6,5,7,5,7,6,6,5,7 rings, which is not invariant under any rotation. Therefore, no conductance gap opens up when two such tubes are connected to form a single junction. In the case of $(8,2)/N(5,5)/(8,2)$ quantum dot (double junction) the quantized bands of (5,5) as well as interface states yield a series of resonance states, quasi-localized in the $N(5,5)$ dot, but coupled to the bands of (12,0) leads. For $N = 4$ these states are visualized in Fig. 2 as wide LDOS peaks. Fig. 2 shows also that these resonances lead to non-zero conductance. The detailed explanation of different widths of these states is given in Refs.[10, 11]. Similarly to the previous case, when a superlattice is formed as an infinite sequence of multiple 4(8,2)/4(5,5) quantum dots, the resonance states transform into minibands. Again, some additional minibands appear; they originate from quantized bands of the (8,2) tube. As shown in Fig. 2, all the minibands are obviously conducting.

The presented results show that, although the rotational symmetry does critically influence

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The interface state are quasilocalized at the interfaces.
the transport properties of quantum dots, leading even to wide conducting gaps in QDs built of all-metallic nanotubes, it does not significantly influence the conductance of short-period superlattices. In both kinds of superlattices, rotationally symmetric and asymmetric ones, the conductance gap around $E_F$ is always supplemented by a series of narrow conducting minibands.

In the preceding examples we have explored the role of symmetry by comparing systems built of different pairs of nanotubes, so that the non-symmetric case consisted of tubes that had no common rotational symmetries themselves. But the importance of symmetry can be more strikingly shown by choosing one particular pair of tubes with a common rotational symmetry and joining them in different ways, with rotationally symmetric junctions or asymmetric junctions. As an example, let us consider now quantum dots and superlattices built of (9,3) and (6,6) nanotubes. As in the (12,0)/(6,6) case, close to $E_F$ the bands of the joined tubes have different values of the discrete angular momentum. The (9,3) tube is invariant under rotations of $C_3$ around its axis while the rotational symmetry of (6,6) is $C_6$. Both tubes can be connected by a the sequence of 6,6,7,5,6,6,7,5,6,6,7,5 rings. Such a junction assures that the entire system is invariant under $C_3$ rotations. However, one can also connect these tubes by
Figure 4. Density of states (local density of states in case of quantum dot) and conductance of $(9,3)/4(6,6)/(9,3)$ quantum dot and $(9,3)/4(6,6)/(9,3)$ superlattice with asymmetric junction.

rotationally asymmetric junction of $5,7,5,7,6,6,5,7,6,6,6,6$ rings. Such an asymmetric connection makes the entire system rotationally non-invariant. The asymmetric junction can be considered as the perturbation of the symmetric one by a simple transposition of one 5,7 pair with the 6,6 pair. It is interesting to check the influence of such a perturbation on the transport properties of quantum dots and superlattices built of $(9,3)$ and $(6,6)$ nanotubes.

In Fig. 3 the DOS/LDOS and conductance of rotationally symmetric $(9,3)/4(6,6)/(9,3)$ QD and $4(9,3)/4(6,6)$ SL are presented. The results for rotationally asymmetric dot and superlattice are shown in Fig. 4. By comparison to Figs. 1 and 2 one can draw the same conclusions as before: the rotational symmetry of quantum dots built of metallic nanotubes can lead to a wide conductance gap opening at the Fermi energy. If the rotational symmetry is broken, the gap is substituted by a series of conducting minibands. The conductance of the superlattice does not change significantly. In both, symmetric and asymmetric cases the conductance gap is covered by a series of conducting minibands. The main effect of the symmetry breaking on the non-totally-zero conductance of $(9,3)/4(6,6)/(9,3)$ QD is due to the residual tunneling conductance between the $(9,3)$ leads through the finite $4(6,6)$ section.
4(9, 3)/4(6, 6) superlattice minibands is lifting of their degeneracy.

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