ЖЭТФ, 2015, том 148, вып. 2 (8), стр. 333–338

ELECTRON SPECTRUM OF A SINGLE-WALL CARBON NANOTUBE IN THE FRAMEWORK OF THE NONLINEAR SCHRÖDINGER EQUATION

H. A. Ishkhanyan [a,b], ***V. P. Krainov*** [a*]

[a] *Moscow Institute of Physics and Technology*
141700, Dolgoprudny, Moscow Region, Russia

[b] *Institute for Physical Research, National Academy of Sciences of Armenia*
0203, Ashtarak-2, Armenia

Received January 23, 2015

The electron spectrum of a single-wall carbon metal nanotube is analyzed numerically. The interaction of a free electron with atomic ions and bound electrons is approximated by an attractive delta-function potential in the single-particle Schrödinger equation. The interaction of an electron with other free electrons is presented by the Hartree nonlinear repulsive short-range potential.

DOI: 10.7868/S0044451015080179

1. INTRODUCTION

Carbon nanotubes attract significant scientific interest due to their extraordinary properties [1]. They have been considered for a wide range of applications from mechanics to nanoelectronics [2, 3]. The study of their electronic properties was stimulated in 1991, soon giving the first outcome as a series of articles by several groups [4, 5]. Theoretical studies have shown that shell depends on the symmetry of the tube (the chiral angle and radius) and that the tube can exhibit metal or semiconductor behavior. The problems of conductivity of a single-wall nanotube (SWNT) have also been addressed (see, e. g., [6]). Density functional theory (DFT) studies of SWNT electronic properties are described in [7]. However, the first experimental separation of metallic and semiconductor nanotubes [8] was not performed until some time after the publication of first theoretical estimates of carbon nanotube electronic properties. The first experiments were carried out on samples containing bundles of metallic SWNTs, and hence the measured spectra were significantly broadened. Production of separated nanotubes (Fig. 1) allowed investigating their properties much better [9]. In an ideal carbon nanotube, every carbon atom has four valence electrons, three of which form localized σ bonds and the fourth takes part in the formation of a delocalized π system (Fig. 2). The picture is quite similar to the one in benzol. The π electrons are weakly bound to their atoms and may participate in the conductivity of the system. The current of free electrons along the SWNT depends on the positions of separated levels of angular quantization. We consider interacting electrons in a long single-wall carbon metallic armchair nanotube without defects (Fig. 3). Most SWNTs have a diameter close to 1–10 nanometers, with a tube length that can be many millions of times longer. The structure of an SWNT can be conceptualized by wrapping a one-atom-thick layer of graphite called graphene into a seamless cylinder.

An effective linear model that allows studying the electric current consists of a continuous conducting cylinder with an attractive delta-function potential [10]. This potential describes the mean field of atomic ions and bound electrons in the nanotube. Such an approach is applicable to relatively large nanotubes when the tube radius a is large compared with the effective width of the graphite layer $r_0 \approx 0.1$ nm, which is on the atomic scale. Typically, $a \approx 5$ nm. The simple linear single-electron Hamiltonian of an SWNT is of the form (atomic units are used here and hereafter, $\hbar = m = 1$)

*E-mail: vpkrainov@gmail.com

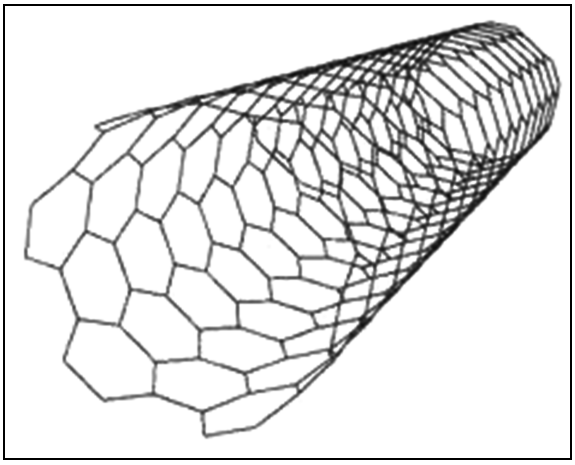

Fig. 1. Ideal metallic carbon nanotube

Fig. 2. Electron orbitals of a carbon atom in a nanotube (trigonal planar carbon with a p orbital)

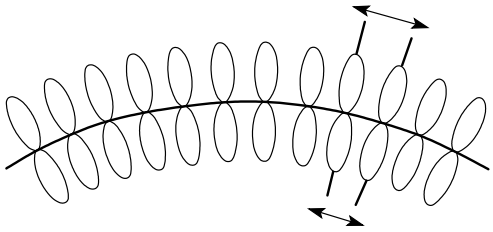

Fig. 3. Arrangement of the electron orbitals of carbon atoms

$$H = -\frac{1}{2}\Delta - Ua\delta\left(r-a\right). \tag{1}$$

Here, r is the radial coordinate in a cylindrical coordinate system with the z axis pointing along the tube; U is the amplitude of the attractive potential, a quantity of the order of the Rydberg energy. Of course, a realistic attraction interaction is described by a screened Coulomb potential. We approximate it by the delta-function because $a > r_0$. This potential is strong such that $U \gg \hbar^2/ma^2$. The quantity U is of the order of 30 eV (pseudopotential of carbon).

The stationary single-particle Schrödinger equation for an electron is written as

$$H\Psi = E\Psi. \tag{2}$$

We take the electron wave function in the form

$$\Psi\left(z,r,\phi\right) = \sum_{n=0}^{\infty} \psi_n\left(r\right)\exp\left(ip_z z + in\phi\right). \tag{3}$$

The electron moves freely with the momentum p_z along the tube. The electron angular motion is determined by the magnetic quantum number n. Separating the variables, we obtain a differential equation for the radial part of the wave function,

$$-\frac{d^2\psi_n}{dr^2} - \frac{1}{r}\frac{d\psi_n}{dr} + \frac{n^2}{r^2}\psi_n - 2Ua\delta\left(r-a\right)\psi_n = 2\left(E - \frac{p_z^2}{2}\right)\psi_n. \tag{4}$$

We assume that the mean potential U is strong such that $U \gg 1/a^2$. This inequality is realized for large nanotubes. We introduce the quantities

$$k = \sqrt{p_z^2 - 2E}, \quad x = kr. \tag{5}$$

Then Eq. (4) can be rewritten in the form

$$x^2\frac{d^2\psi_n}{dx^2} + x\frac{d\psi_n}{dx} - \left(x^2 + n^2\right)\psi_n = -2Uka^3\delta\left(x - x_0\right)\psi_n, \tag{6}$$

where $x_0 = ka$. We now impose boundary conditions and require the wave function to be regular at $x = 0$ and to be zero at $x \to \infty$. The solution of Eq. (6) at $x < x_0$ and at $x > x_0$ is

$$\begin{aligned} \psi_n\left(x\right) &= A_n I_n\left(x\right), \quad x < x_0, \\ \psi_n\left(x\right) &= B_n K_n\left(x\right), \quad x > x_0. \end{aligned} \tag{7}$$

Here, $I_n\left(r\right)$ and $K_n\left(r\right)$ are the respective modified Bessel functions of the first and second kind. Integrating Eq. (6) over an infinitesimal interval in the vicinity

of x_0, we obtain the relation for derivatives of the wave function

$$\frac{d\psi_n(x_0+0)}{dx}-\frac{d\psi_n(x_0-0)}{dx}=-\frac{2Ua}{k}\psi_n(x_0). \qquad (8)$$

Using the matching condition of the wave function at $x = x_0$,

$$A_nI_n(x_0)=B_nK_n(x_0), \qquad (9)$$

and the well-known value for the Wronskian determinant of the modified Bessel functions

$$W(x)=K_n(x)\frac{dI_n(x)}{dx}-I_n(x)\frac{dK_n(x)}{dx}=\frac{1}{x}, \qquad (10)$$

we find the spectral equation

$$2Ua^2K_n(ka)\,I_n(ka)=1. \qquad (11)$$

Under the condition $Ua^2 \gg 1$, this equation has a simple solution for the electron energy [10] (we restore the electron mass m and the Planck constant $\hbar$)

$$E_n=\frac{p_z^2}{2m}-\frac{U^2ma^2}{2\hbar^2}+\frac{\hbar^2\left(n^2-1/4\right)}{2ma^2}. \qquad (12)$$

When $Ua^2 < 1$, Eq. (11) always has the solution with $n = 0$, while if $n = 1, 2, \ldots$, the electron levels disappear when $Ua^2 < n$.

2. NONLINEAR SCHRÖDINGER EQUATION

The main goal of this paper is to take into account the repulsive interaction of a given free electron with other free electrons in the nanotube. The Coulomb long-range repulsion between electrons strongly decreases at large distances because of the screening by atomic ions. Therefore, this interaction can be qualitatively approximated by a short-range delta-function for interacting electrons with opposite spins in accordance with the Pauli principle. Hence, in the Hartree self-consistent approach, we can approximate this interaction by a simple nonlinear potential $g|\psi_n|^2$ with the nonlinearity parameter $g > 0$, analogously to the Hubbard approach [11]. This approximation occurs in different physical situations (e. g., nonlinear optics, spin waves in magnetic films) and in particular has proved to correctly describe the dynamics of Bose–Einstein condensates of dilute alkaline atoms [12]. Analogously to the linear case, the variables in the stationary nonlinear Schrödinger equation separate. Thus, we obtain a generalization of Eq. (4) for radial motion of the electron

$$-\frac{d^2\psi_n}{dr^2}-\frac{1}{r}\frac{d\psi_n}{dr}+\frac{n^2}{r^2}\psi_n-2Ua\delta(r-a)\,\psi_n+ \\ +g|\psi_n|^2\psi_n=2\left(E-\frac{p_z^2}{2}\right)\psi_n. \qquad (13)$$

The generalization of Eq. (6) is of the form

$$x^2\frac{d^2\psi_n}{dx^2}+x\frac{d\psi_n}{dx}-\left(x^2+n^2\right)\psi_n- \\ -gk^2x^2|\psi_n|^2\psi_n=-2Uka^3\delta(x-x_0)\,\psi_n. \qquad (14)$$

In the numerical solution of Eq. (14), the delta-function is substituted by the Lorentz curve

$$\delta(x)\to\frac{1}{\pi}\,\frac{0.01}{0.0001+x^2}. \qquad (15)$$

The typical radius of the tube was chosen as $a = 0.5$ nm $= 10$ a. u., the potential of the order of $U = 13.6$ eV $= 0.5$ a. u. and $g < U$. The boundary condition at infinity is analogous to the one in the linear case, $\psi_n(x \to \infty) = 0$. The second boundary condition at the origin is also analogous to that in the linear case (the solution of the equation for $r < r_0$ should become the solution of the corresponding linear problem when the nonlinearity vanishes, i. e., the modified Bessel function $I_n(r)$ of the first kind). We add an additional (nonobvious) condition of normalization of the wave function for the nonlinear single-particle Schrödinger equation:

$$\int_0^\infty|\psi_n(x)|^2\,dx=1. \qquad (16)$$

2.1. Magnetic quantum number $n = 0$

The Cauchy problem is defined by Eq. (14) with the delta-function substituted by a Lorentzian curve and with three boundary conditions. The first boundary condition states that the wave function vanishes in the limit $x \to \infty$. For the second boundary condition, we consider the region $x \ll 1$. The term with the delta-function is negligible there and Eq. (14) can be written in the equivalent form

$$\frac{d^2\psi_0}{dx^2}+\frac{1}{x}\,\frac{d\psi_0}{dx}-\psi_0-gk^2|\psi_0|^2\psi_0=0, \qquad (17)$$

with the well-known solution $\psi_{0Lin} = c_0I_0(r)$, $c_0 = \text{const}$. Since the initial derivative of ψ_0 must be zero, $\psi_0 = c_0 + O(r^2)$ and Eq. (17) can be approximated by the linear equation (ψ_0 is assumed to be real)

$$\frac{d^2\psi_0}{dx^2}+\frac{1}{x}\,\frac{d\psi_0}{dx}-(1+gk^2c_0^2)\psi_0=0, \qquad (18)$$

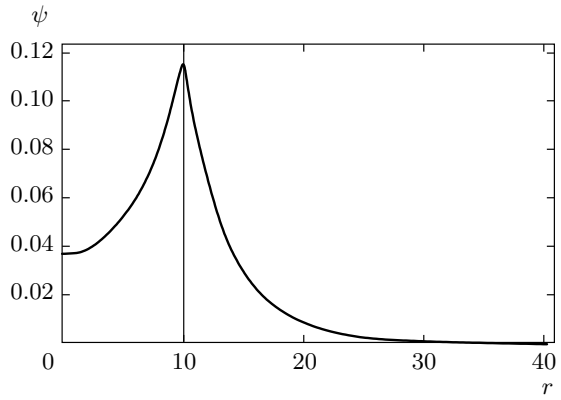

Fig. 4. An example of a physically meaningful solution (the magnetic quantum number $n = 0$ and the nonlinearity parameter $g = 1$). The thin line denotes the delta-potential

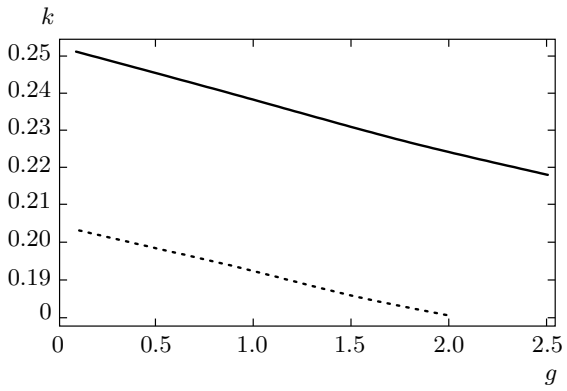

Fig. 5. Electron spectra of an SWNT for the magnetic quantum number $n = 0$ and different values of the delta-potential amplitude ($U = 2.5,\ 2.0$ from top down). Because $k = \sqrt{p_z^2 - 2E}$, the energy levels shift up with an increase in the interaction strength

which has the solution

$$\psi_0 = c_1 I_0(\sqrt{1 + gk^2 c_0^2}\, r), \quad r \ll 1. \tag{19}$$

Thus, the second condition along with Eqs. (14) and (15) for physically meaningful solutions is that $d\psi_0/dx(x \to 0) = 0$. In the linear case, the wave function should be regular at $x = 0$. In the nonlinear case, this requirement is insufficient because the eingenvalue depends on the value $\psi_0(x \to 0)$. The last condition is given by (16).

Figure 4 shows a physically meaningful solution of the problem: a normalized wave function ($\int_0^\infty |\psi_0(x)|^2\, dx = 1$) corresponding to $U = 2.5$, $g = 1$, and $\psi_0(x = 0) = 0.037$. Our goal is to investigate the action of π-electron self-interaction induced nonlinearity on the electron energy.

Figure 5 shows the dependence of the electron energy on the nonlinearity parameter. As is clearly seen, the nonlinearity shifts the values of k down, which means it shifts the energy levels up.

In Sec. 2.2, we see that for $n > 0$ and small values of U, this shift may result in the disappearance of levels.

2.2. $n = 1$

In this case, the linear solution in the region of small x is proportional to the modified Bessel function of first kind, $I_1(r)$. This imposes the condition $\psi_1(x \to 0) = 0$ for the nonlinear solution.

A meaningful solution is shown in Fig. 6 (the thin vertical line denotes the delta-function potential).

Figure 7 illustrates the disappearance of electron energy levels for $Ua_2 < n$. The shift of the levels by

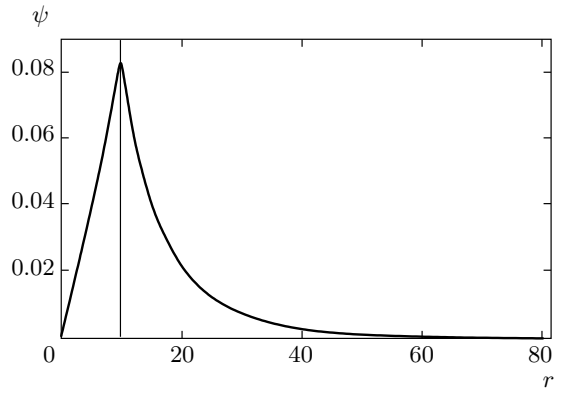

Fig. 6. A physically meaningful solution (the magnetic quantum number $n = 1$ and the nonlinearity parameter $g = 1$). The thin line denotes the delta-potential

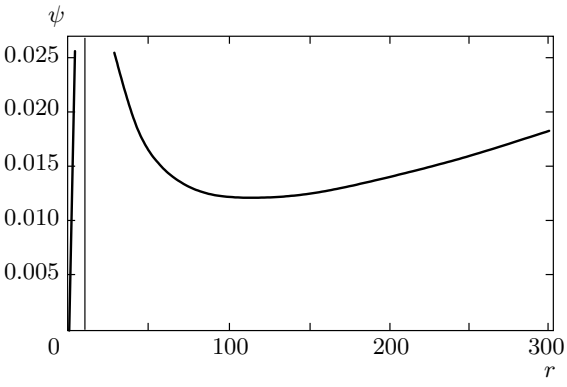

Fig. 7. Disappearance of the energy levels at $Ua^2 < n$ ($k = 0,\ n = 1$)

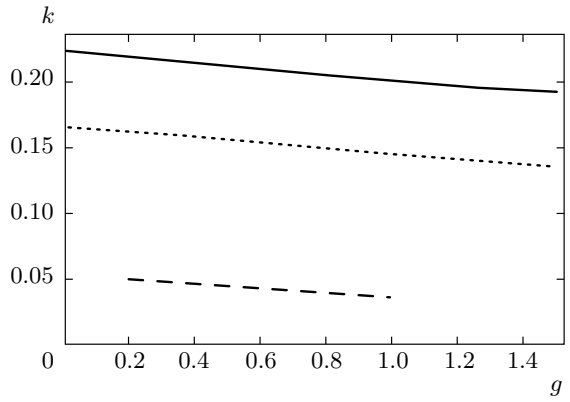

Fig. 8. Electron spectra for the magnetic quantum number $n = 1$ and different values of the delta-potential amplitude ($U = 2.5$, 2, 1.2 from top down). It is seen that the energy levels shift up with an increase in the interaction strength

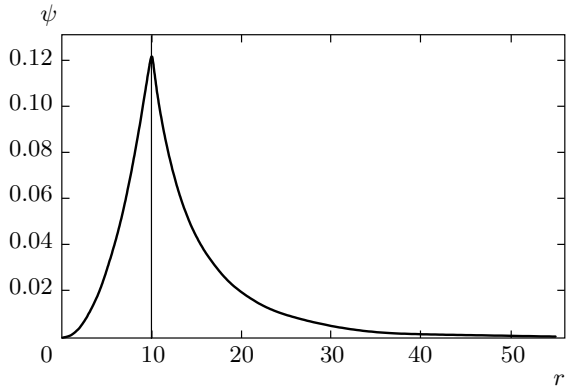

Fig. 9. A realistic solution (magnetic quantum number $n = 2$, $g = 1.5$)

the nonlinearity is shown in Fig. 8 for different values of the delta-potential height U.

2.3. $n = 2$

Because the solution of the linear equation for $x < a$ is equal to $cI_2(r)$ with a constant c, the boundary condition for the wave function in the nonlinear case should be written as $\psi_2(x \to 0) = 0$. The boundary condition for $d\psi_2/dx(x \to 0)$ is given by the normalization of the wave function to unity. A realistic solution and the disappearance of levels are shown in Figs. 9 and 10. Figure 11 illustrates the shift of the electron energy levels due to the nonlinearity for different values of the potential height U.

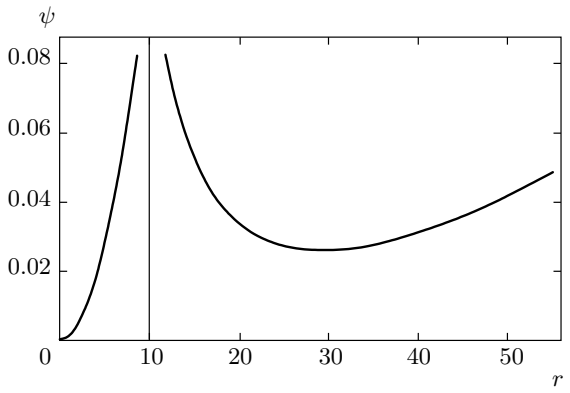

Fig. 10. The energy levels disappear when $Ua^2 < n$ ($k = 0$, $n = 2$)

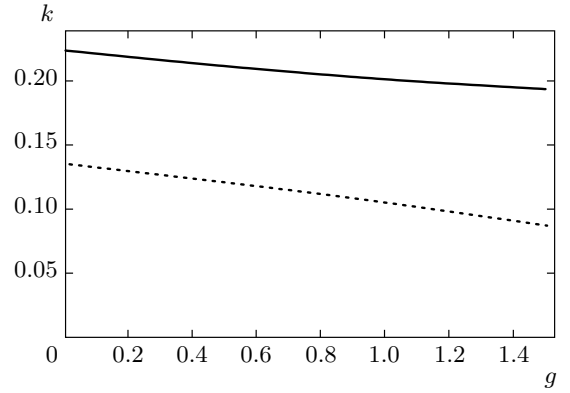

Fig. 11. Action of the strong nonlinearity shifts the energy levels up, $n = 2$, and $U = 2.52$ and 2.3, for the respective upper and lower lines

3. CONCLUSION

Taking the interaction of delocalized π electrons in an ideal metallic single-wall carbon nanotube into account in the Hartree mean-field approximation, we calculated the spectrum of a long metal armchair ideal nanotube. An upward shift of electron energy levels is shown to occur due to this interaction. Moreover, it is shown that levels disappear when $Ua^2 < n$ with an attractive delta-potential amplitude U, the magnetic quantum number n, and the tube radius a.

The work was supported by the State Committee of Science of Armenia (13YR-1C0055), the Dynasty Foundation (Moscow), and the Ministry of Education and Science of Russia (State assignment No. 3.679.2014/K), RFBR (grant № 13-02-00072).

REFERENCES

1. P. J. F. Harris, *Carbon Nanotubes and Related Structures: New Materials for the Twenty-first Century*, Cambridge Univ. Press, Cambridge (2004).
2. P. L. McEuen et al., IEEE Trans. Nanotechnol., **1**(1), 78 (2002).
3. E. T. Thostenson et al., Composites Sci. Technol. **61**, 1899 (2001).
4. J. W. Mintmire et al., Phys. Rev. Lett. **68**, 631 (1992).
5. R. Saito et al., Phys. Rev. B **46**, 1804 (1992); N. Hamada et al., Phys. Rev. Lett. 68, 1579 (1992).
6. A. Kasumov et al., Phys. Rev. B **68**, 214521 (2003); D. R. Barbero et al., Adv. Mater. **26**, 2046 (2014).
7. D. Shah et al., J. Comp. Electron **6**, 395 (2007); R. Demichelis et al., J. Phys. Chem. C **115**, 8876 (2011); J. Luo et al., Phys. Rev. B **66**, 115415 (2002).
8. J. W. G. Wildoer et al., Nature **391**, 59 (1998); Ph. Collins et al., Science **292**, 706 (2007).
9. M. J. O'Connell et al., Science **297**, 593 (2002); J. Lefebvre, Y. Homma, and P. Finnie, Phys. Rev. Lett. **90**, 217401 (2003).
10. A. A. Abrikosov, Jr., D. V. Livanov, and A. A. Varlamov, Phys. Rev. B **71**, 165423 (2005).
11. E. H. Lieb and F. Y. Wu, Physica A **321**, 1 (2003); M. Bockrath et al., Nature (London) **397**, 598 (1999).
12. V. I. Yukalov et al., Phys. Rev. A **56**, 4845 (1997); V. I. Yukalov, Laser Phys. **19**, 1 (2009).