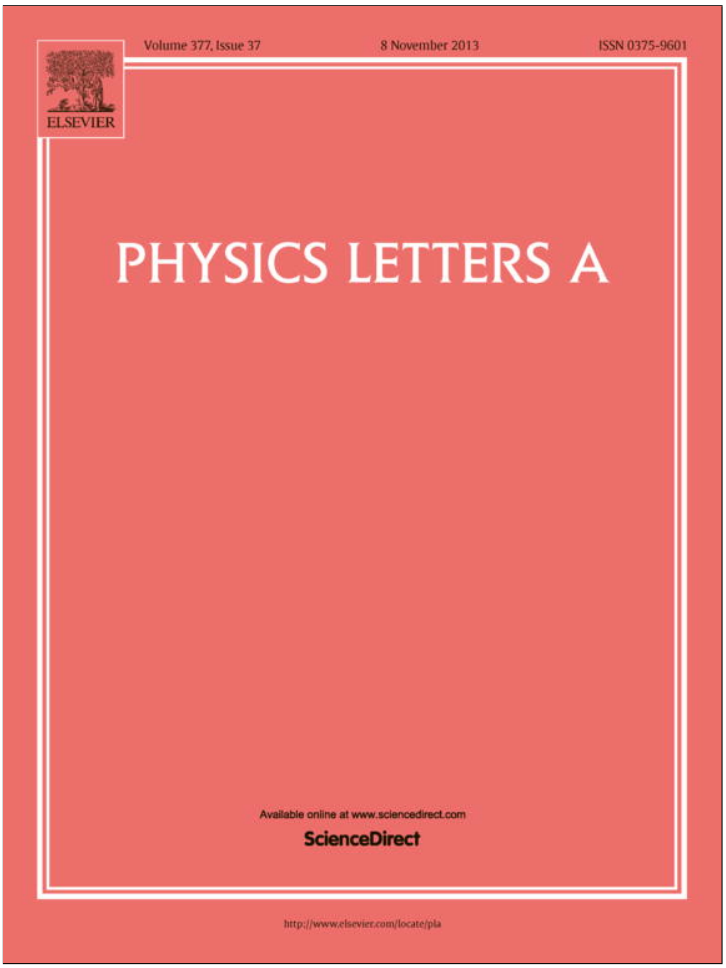

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Effect of the magnetic field on the edge states of zig-zag single wall carbon nanotubes

M. Pudlak [a], R. Pincak [a,b,*]

[a] Institute of Experimental Physics, Slovak Academy of Sciences, Watsonova 47, 043 53 Kosice, Slovak Republic
[b] Bogoliubov Laboratory of Theoretical Physics, Joint Institute for Nuclear Research, 141980 Dubna, Moscow region, Russia

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ABSTRACT

The influence of the static magnetic field on the edge states of finite zig-zag nanotubes has been explored theoretically by the tight-binding approximation. It was found that the magnetic field removes the degeneracy of the energy levels of the edge states. Investigation of the formation of new edge states by the magnetic field indicated the dependence of the number of these states on the length of a nanotube.

1. Introduction

Carbon nanotubes are extensively studied experimentally and theoretically because of their unusual electronic properties. A carbon nanotube can be viewed as a graphene sheet rolled into a cylindrical shape so that the structure is one-dimensional with axial symmetry and in general exhibits a spiral conformation called chirality. Nanotubes show unique mechanical and electronic properties [1]. Properties of the finite-length nanotubes are strongly influenced by the types of edges. From the category of edges the most intensively studied are the zig-zag and armchair types. For the nanographite ribbons with the zig-zag edge the presence of localized states near the Fermi level was already shown. However, similar states were absent in ribbons with armchair edges [2].

The graphite sheet is considered as a zero-gap semiconductor with the density of states (DOS) vanishing at the Fermi level. In contrast, the edge states of the zig-zag ribbons produce a peak in the DOS at the Fermi level. The finite nanotubes with the edges bring about the change of the dimensionality of the system from one to zero dimensional system, as it is in the case of fullerenes [3]. The existence of edge states for arbitrarily oriented graphene ribbons with a large class of edge shapes was already investigated [4]. From these studies new geometrical understanding of the edge state has emerged. The relation of the edge states to the topological nature of nanotubes was also found [5]. In addition, the presence of the edge state results in the relatively important contribution to the density of states (DOS) near the Fermi energy [6]. Apparently, the length of single-wall carbon nanotubes [7] affects the edge states. In short nanotubes the edge states could play an important role by contribution to conductivity. Specifically, it was found [8] that the HOMO–LUMO (highest occupied molecular orbital and lowest unoccupied molecular orbital,respectively) gap is inversely proportional to the length of the zig-zag carbon nanotube segment. Another factor showing the potentiality of controlling the electronic properties of a carbon nanotube is an external magnetic field [9]. To explore this possibility, we have also conducted in this Letter a theoretically study of the electronic properties of finite-length carbon nanotubes under the influence of the magnetic field.

2. Theory

We investigate the zigzag nanotubes in the static magnetic field $\vec{B}$ parallel to the nanotube axis. We assume Hamiltonian for an electron in a potential $V(r)$ and in the magnetic field in the form

$$H = \frac{1}{2m}(\vec{p} - e\vec{A})^2 + V. \tag{1}$$

The potential $V(r)$ reflects the structure of the crystal lattice such as the symmetry and periodicity properties. Here this potential describes the structure of the zig-zag single wall carbon nanotube. The vector potential $\vec{A}$ in the Landau gauge can be expressed in the form [1]

$$\vec{A} = \left(\frac{\Phi}{L}, 0\right), \tag{2}$$

where $\Phi = B\pi r^2$ is the magnetic flux penetrating the cross section of the carbon nanotube, and $L = 2\pi r$ is a circumference of the nanotube (r-nanotube radius). Here the coordinate x is in the circumferential direction, and the coordinate y denotes the direction parallel to the nanotube axis. To describe the parameters which characterize the zig-zag tubules, we start from the graphene

* Corresponding author at: Institute of Experimental Physics, Slovak Academy of Sciences, Watsonova 47, 043 53 Kosice, Slovak Republic. Tel.: +421 907 936 147; fax: +421 55 633 62 92.
E-mail addresses: pudlak@saske.sk (M. Pudlak), pincak@saske.sk (R. Pincak).

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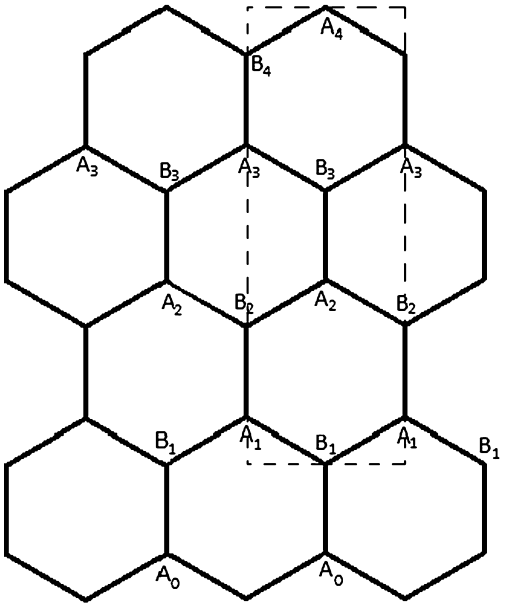

Fig. 1. Structure of the finite-length open ended single wall carbon nanotube with the zig-zag edges. A unit cell for the width $M = 4$ which creates a nanotube is depicted.

layer [10] where we can define the vectors connecting the nearest neighbor carbon atoms for the zig-zag nanotubes in the form:

$$\vec{\tau_1} = a\left(0; \frac{1}{\sqrt{3}}\right),$$
$$\vec{\tau_2} = a\left(\frac{1}{2}; -\frac{1}{2\sqrt{3}}\right),$$
$$\vec{\tau_3} = a\left(-\frac{1}{2}; -\frac{1}{2\sqrt{3}}\right), \tag{3}$$

where $a = 0.246$ nm is the lattice constant. The finite length open ended zig-zag carbon nanotubes can be assumed to be rolled from the finite length zig-zag graphene nanoribbons [2]. In confining the structure along the length, the edge states are induced by terminating the length dimension with the zig-zag shaped edges. We will study the edge and size effects using the tight-binding model for the carbon nanotube shown in Fig. 1. We want to find the solution to the above problem in the form of the Bloch function

$$\psi(\vec{r}) = \sum_{i=0}^{M} (C_{A_i}\psi_{A_i} + C_{B_{i+1}}\psi_{B_{i+1}}) \tag{4}$$

where

$$\psi_\alpha(\vec{k}, \vec{r}) = \frac{1}{\sqrt{M}} \sum_n \exp\left(i\vec{k}(\vec{r_n} + \vec{d}_\alpha) + i\frac{e}{\hbar} G(\vec{r_n} + \vec{d}_\alpha)\right) \times \left|\varphi(\vec{r} - \vec{r}_n - \vec{d}_\alpha)\right\rangle, \tag{5}$$

where α denotes A or B atoms. Here $\vec{d}_\alpha$ are the coordinates of the α atom in the unit cell and $\vec{r_n}$ is a position of a unit cell, M is the number of the unit cell; $|\varphi(\vec{r})\rangle$ is a π orbital which is generally different for the outer and inner shell; $G(\vec{R})$ is the phase factor associated with the magnetic field and is expressed by [11]

$$G(\vec{R}) = \int_{\vec{R}}^{\vec{r}} \vec{A}(\vec{x}).d\vec{x} = \int_0^1 (\vec{r} - \vec{R}).\vec{A}\left(\vec{R} + \lambda(\vec{r} - \vec{R})\right) d\lambda. \tag{6}$$

Employing Eq. (2) we get

$$G(\vec{R}) = \int_0^1 (\vec{r} - \vec{R}).\left(\frac{\Phi}{L}, 0\right) d\lambda = (x - X)\frac{\Phi}{L}. \tag{7}$$

We denote

$$\epsilon = \left\langle\varphi(\vec{r} - \vec{A}_i)\middle|H\middle|\varphi(\vec{r} - \vec{A}_i)\right\rangle = \left\langle\varphi(\vec{r} - \vec{B}_i)\middle|H\middle|\varphi(\vec{r} - \vec{B}_i)\right\rangle. \tag{8}$$

Now we define the hopping integrals

$$\left\langle\varphi(\vec{r} - \vec{A}_i)\middle|H\middle|\varphi(\vec{r} - \vec{B}_i)\right\rangle = \gamma_0\beta,$$
$$\left\langle\varphi(\vec{r} - \vec{A}_i)\middle|H\middle|\varphi(\vec{r} - \vec{B}_{i+1})\right\rangle = \gamma_0. \tag{9}$$

The electronic spectrum of finite zig-zag single wall carbon nanotubes can be described by the following system of equations:

$$\epsilon C_{A_m} + H_{A_m B_{m+1}} C_{B_{m+1}} + H_{A_m B_m} C_{B_m} = E C_{A_m}, \tag{10}$$
$$\epsilon C_{B_m} + H_{B_m A_{m-1}} C_{A_{m-1}} + H_{B_m A_m} C_{A_m} = E C_{B_m}, \tag{11}$$

where

$$H_{A_m B_{m+1}} = \gamma_0, \tag{12}$$
$$H_{A_m B_m} = 2\gamma_0\beta\cos\left(\frac{n\pi}{N} + \frac{\Phi}{2N\Phi_0}\right) \tag{13}$$

here $\Phi_0 = \hbar/e$, $n = 0, \ldots, N-1$, $\beta = 1 - \frac{1}{2}(\frac{\pi}{N})^2$ for the $(N, 0)$ zig-zag nanotube [12] and γ_0 (≈ 3 eV) is the nearest neighbor hopping integral in the flat graphene. The site index $m = 1, \ldots, M$, where M describes the length of the nanotube. So we have

$$\tilde{E} C_{A_m} + \gamma_0 C_{B_{m+1}} + \gamma_0 g_n C_{B_m} = 0, \tag{14}$$
$$\tilde{E} C_{B_m} + \gamma_0 C_{A_{m-1}} + \gamma_0 g_n C_{A_m} = 0, \tag{15}$$

where $\tilde{E} = \epsilon - E$ and

$$g_n = 2\beta\cos\left(\frac{n\pi}{N} + \frac{\Phi}{2N\Phi_0}\right) = 2\beta\cos\left(\frac{n\pi}{N} + \frac{NB}{B_1}\right) \tag{16}$$

where $B_1 = 4h/ea^2$. We assume that the A_0 and B_{M+1} sites are missing. So we have the boundary condition $C_{A_0} = C_{B_{M+1}} = 0$ [13]. The solutions of Eqs. (14) and (15) in two cases (cases I and II) are found. The solution is assumed to be (case I)

$$C_{A_m} = Ae^{ipm} + Be^{-ipm}, \tag{17}$$
$$C_{B_m} = Ce^{ipm} + De^{-ipm}. \tag{18}$$

Here A, B, C and D are the coefficients which have to be determined and p is the wave number in the direction of the nanotube axis. From the boundary condition we have

$$C_{A_0} = A + B = 0, \tag{19}$$
$$C_{B_{M+1}} = Ce^{ip(M+1)} + De^{-ip(M+1)} = 0. \tag{20}$$

And so

$$C_{A_m} = A\left(e^{ipm} - e^{-ipm}\right), \tag{21}$$
$$C_{B_m} = C\left(e^{ipm} - z^2 e^{-ipm}\right) \tag{22}$$

where $z = e^{ip(M+1)}$. Substituting Eqs. (21) and (22) into Eqs. (14) and (15) we obtain

$$\tilde{E}\left(e^{ipm} - z^2 e^{-ipm}\right)C + \gamma_0\left[\left(e^{ip(m-1)} - e^{-ip(m-1)}\right) + g_n\left(e^{ipm} - e^{-ipm}\right)\right]A = 0, \tag{23}$$
$$\gamma_0\left[\left(e^{ip(m+1)} - z^2 e^{-ip(m+1)}\right) + g_n\left(e^{ipm} - z^2 e^{-ipm}\right)\right]C + \tilde{E}\left(e^{ipm} - e^{-ipm}\right)A = 0. \tag{24}$$

This homogenous system of equations has a solution only if the following condition is fulfilled:

$$\begin{aligned}&\left[\tilde{E}^2-\gamma_0^2\left(e^{-ip}+g_n\right)\left(e^{ip}+g_n\right)\right]e^{2ipm}\\&\quad+z^2\left[\tilde{E}^2-\gamma_0^2\left(e^{-ip}+g_n\right)\left(e^{ip}+g_n\right)\right]e^{-2ipm}\\&\quad-\tilde{E}^2\left(z^2+1\right)+\gamma_0^2\left(g_n+e^{ip}\right)^2+z^2\gamma_0^2\left(g_n+e^{-ip}\right)^2=0.\end{aligned}\tag{25}$$

And so the coefficient of the $e^{\pm 2ipm}$ terms and the constant term have to be equal to zero. Thus, we obtain the energy spectrum

$$E=\epsilon+s\gamma_0\sqrt{1+2g_n\cos(p)+g_n^2}.\tag{26}$$

Here, $s=\pm 1$, $s=+1$ ($s=-1$) corresponds to the conductance (valence) energy band. The condition for the longitudinal wave number p is

$$\tilde{E}^2\left(z^2+1\right)=\gamma_0^2\left(g_n+e^{ip}\right)^2+z^2\gamma_0^2\left(g_n+e^{-ip}\right)^2.\tag{27}$$

Substituting Eq. (26) into Eq. (27) we obtain the equation which gives the longitudinal wave number p.

$$\sin[pM]+g_n\sin\left[p(M+1)\right]=0.\tag{28}$$

The longitudinal wave number depends on the transverse wave number n, the length M of the nanotube, the static magnetic field B and also on the parameter β which depends on the nanotube curvature. For $N\gg 1$ Eq. (28) can be written as

$$\sin[pM]=0.\tag{29}$$

The real solution for p is given by

$$p=\frac{2\pi}{M}l.\tag{30}$$

Substituting this solution into Eq. (26) we get the energy spectrum of delocalized electrons (bulk states). The spectrum is similar to that of the infinite zig-zag nanotube with the periodic boundary condition along the y-axis. There is another possibility to solve Eqs. (14), (15). We assume the solution in the form (case II)

$$C_{A_m}=(-1)^m\left(Ae^{ipm}+Be^{-ipm}\right),\tag{31}$$

$$C_{B_m}=(-1)^m\left(Ce^{ipm}+De^{-ipm}\right).\tag{32}$$

This possibility gives

$$E=\epsilon+s\gamma_0\sqrt{1-2g_n\cos(p)+g_n^2}\tag{33}$$

and the equation for the longitudinal wave number

$$\sin[pM]-g_n\sin\left[p(M+1)\right]=0.\tag{34}$$

Now we are interested in the edge state of the zig-zag nanotube. This solution can be obtained in the form $p=\pi+i\eta$ [14]. We get the following equation for η:

$$\sinh[\eta M]\mp g_n\sinh\left[\eta(M+1)\right]=0.\tag{35}$$

The $-$ ($+$) sign is for the case I (II), respectively. The edge state can exist when the condition

$$|g_n|<\frac{1}{1+1/M}\tag{36}$$

is fulfilled. The energy spectrum of a state like this is given as

$$E_{n,s}(\Phi)=\epsilon+s\gamma_0\sqrt{1\mp g_n\cosh(\eta)+g_n^2}.\tag{37}$$

For big enough M the solution of Eq. (35) can be expressed in the form [14]

$$\eta=\ln\left[c_n+\frac{1-c_n^2}{c_n^{2M+1}}\right]\tag{38}$$

where $1/c_n=|g_n|$. From Eq. (38) we have

$$\cosh\eta\approx\frac{1+c_n^2}{2c_n}-\frac{(c_n^2-1)^2}{2c_n^{2M+3}}\tag{39}$$

and so

$$E_{n,s}(\Phi)\approx\epsilon+s\gamma_0\frac{c_n^2-1}{c_n^{M+2}}\tag{40}$$

for the solutions near the Fermi energy ϵ. We can see that for the long enough zig-zag nanotube the band gap becomes small. It means that we get an energy level which is located in the forbidden energy zone of the infinite zig-zag nanotube with periodic boundary conditions and is localized near the edges of the finite nanotube.

So we have the HOMO (highest occupied molecular orbital)–LUMO (lowest unoccupied molecular orbital) gap for finite zig-zag nanotube in the form

$$E_g=2\gamma_0\frac{c_{max}^2-1}{c_{max}^{M+2}}\tag{41}$$

where c_{max} is the maximal entity from c_n. As $c_n>1$, the bigger M the smaller the HOMO–LUMO gap. The parameter M defines the length of the nanotubes and so the HOMO–LUMO gap is inversely proportional to the length of the zig-zag carbon nanotube. A similar result was found numerically in [8].

We would like to start with an analysis of the finite $(12,0)$ zig-zag nanotubes. In the case I with the value $n=5$, the calculated energy levels of the edge states are equal to those derived in the case II for $n=7$. If we assume $\epsilon=0$ (Fermi energy) we obtain $E_{5,7,\pm}(0)=\pm 2.19$ meV for the of $M=10$. Application of the static magnetic field splits the energy levels. Under the influence of the field we have $E_{5,\pm}(1.5\Phi_0)=\pm 0.17$ meV and $E_{7,\pm}(1.5\Phi_0)=\pm 14.3$ meV. However, this $B=1.4\times 10^3$ T magnetic field is beyond the experimentally attainable values. Obviously less strong and accessible fields will cause smaller splitting. Other aspects of the presence of the static magnetic field is a change of the number of edge states [15–17]. The formation of new edge states by the magnetic field shows the dependence on the length of a nanotube. This phenomenon was investigated for the $(12,0)$ zig-zag nanotube (Fig. 2). Particularly, the minimal length of L ($L=\sqrt{3}Ma/2$) for the $(12,0)$ zig-zag nanotube when the new edge state at $n=4$ appears with the magnetic field $B=0$ is 6.3 nm. In contrast, under the same external conditions having the 5.7 nm long zig-zag nanotube ($M=27$) there is no generation of a new edge state. Yet, imposing the magnetic field 20 T will produce the edge state which is not accessible by the fields 15 T and smaller at this length of the nanotube. Interesting, the magnetic field can also reduce the number of the edge states. In the case of the 6.2 nm long $(12,0)$ zig-zag nanotube at $n=8$ the edge-state is present. Yet, the application of the magnetic field of 20 T causes the disappearance of this state. In contrary to the bulk state, where the magnetic field can close the band gap [9], the HOMO–LUMO gap of the edge states can only be reduced by the application of the field. The dependence of energy levels on the magnetic field for the edge states is described by the following expression:

$$\begin{aligned}E_{ns}(B)&\approx E_{ns}(0)\\&\times\left(1+2\beta MN\left(\cos^2(n\pi/N)-1\right)\frac{c_n(c_n^2-2)}{(c_n^2-1)}\frac{B}{B_1}\right)\end{aligned}\tag{42}$$

here $B_1\approx 2.73\times 10^5$ T and the parameter c_n is taken with $B=0$. In derivation of this relation the effect of B, experimentally accessible magnetic field, was treated as perturbation. The magnetic

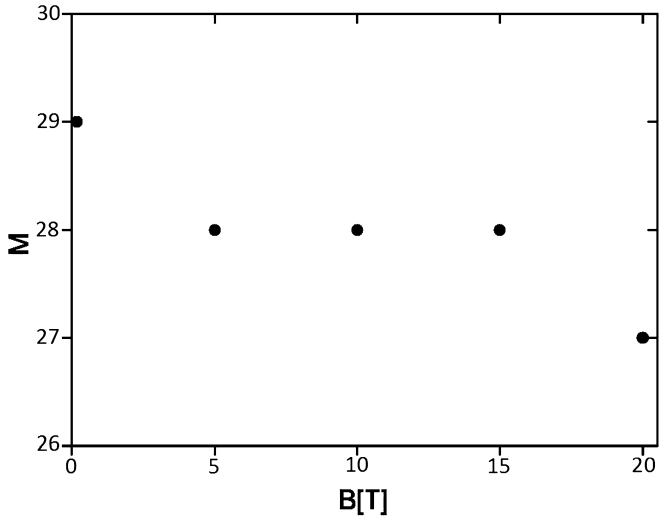

Fig. 2. The minimal length of the $(12, 0)$ zig-zag nanotube as a function of magnetic fields. The length $L = \sqrt{3}Ma/2$.

field influence is determined by both the diameter of the nanotube (parameter N) and the length of the nanotube (parameter M).

3. Conclusion

The present work investigates both the influence of the static magnetic field and the presence of boundaries on the electronic properties of carbon nanotubes. In theoretical analysis the influence of a curvature of the surface of the nanotube on the HOMO–LUMO gap was taken into account. In the case of the finite length zig-zag nanotube, the presence of the edge state results in the gap which is inversely proportional to the length of the zig-zag nanotube. The value of this gap can be smaller in comparison to the gap that is observed after the inclusion of the curvature of the metallic nanotube into the calculation. The results clearly indicate that the presence of the edge states varies the electronic properties of the zig-zag nanotubes. Moreover, the number of these edge states is affected by the static magnetic field. Our work shows that these transitions of the edge states, predicted only for the nanotubes with a larger diameter and length in the previous works, also occur in smaller nanotubes. Additionally, we have observed for the long enough finite nanotubes that the energy spectrum of bulk states is very similar to the spectrum of the nanotube with the periodic boundary condition. However generally, the application of the magnetic field removes the degeneracy of the energy levels of the nanotube.

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