Low-energy electronic properties of carbon nanotubes

T.S. Li\textsuperscript{a}, M.F. Lin\textsuperscript{b,}\textsuperscript{,*}

\textsuperscript{a}Department of Electrical Engineering, Kun Shan University of Technology, Tainan, Taiwan, ROC
\textsuperscript{b}Department of Physics, National Cheng Kung University, Tainan, Taiwan, ROC

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Abstract

Low-energy electronic properties of carbon nanotubes are studied by the tight-binding model. When the bond symmetry of neighboring carbon atoms is broken, the transfer integrals will vary along the different directions. We attempt to develop a general formulation to include the effects of curvature, strain, and magnetic field. Analytic expressions for energy gap and electron effective mass are derived for achiral zigzag and armchair nanotubes. The ratio of electron effective mass to energy gap can be expressed simply as a constant. There are significant differences among (3I + 1, 0), (3I – 1, 0), and (3I, 0) zigzag nanotubes regarding the effects of strain on the semiconductor–metal transition. The critical magnetic flux of the narrow-gap zigzag nanotubes is inversely proportional to the nanotube radius. The dependence of the electronic properties on the chiral angle is strong.

\textsuperscript{*}Corresponding author. Tel.: +886 627 575 7565272; fax: +886 627 47995.
\textsuperscript{E-mail address: mflin@mail.ncku.edu.tw (M.F. Lin).}

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1. Introduction

Carbon nanotubes (CNs) are nanometer-radius tubules consisting of rolled-up graphite sheets in the cylindrical form \cite{1}. They have been extensively studied because of their potential applications in electronics. They can be either metallic or semiconducting depending on their radii and chiral angles. The coexistence of conducting and semiconducting structures within the same class of material opens up many possibilities in developing brand new electronic devices.

CNs can be classified according to their energy gaps into three categories: moderate-gap semiconductors, narrow-gap semiconductors, and metals \cite{2–5}. With the periodic boundary condition along the azimuthal direction, the nanotube Brillouin zone consists of distinct quantization lines of allowed $\mathbf{k}$ states. When the graphitic Fermi points do not lie on the quantization lines, CNs will be moderate-gap semiconductors. The energy gaps ($E_g$’s) are of the order of 1–0.1 eV and were predicted to scale as the inverse of radius ($1/r$). This prediction was verified by scanning tunneling microscopy (STM) \cite{6,7}. For CNs with $2m + n = 3\times I$ ($I$ an integer), their quantization lines will cross the graphitic Fermi points, where $(m,n)$ represents the chiral vector of a CN (Fig. 1). This intersection leads to the “metallic” behavior of CNs. However, when the curvature effect due to the misorientation of $2p_z$ orbitals is taken into consideration, the nearest-neighbor bond symmetry is broken. This causes a $\sim$0.01 eV energy gap, which is inversely proportional to the square of the radius \cite{5}. Therefore, these “metallic” CNs are in fact narrow-gap semiconductors. The predicted energy gaps are consistent with the experimental measurements by STM \cite{8}. Except for the $(m,m)$ armchair nanotubes (ACNs), the high symmetry of the nanotube lattice compensates the symmetry breaking effect of the curvature, and preserves the metallic property.

One of the fundamental parameters in semiconductor physics is the effective mass ($M^*$). Precise information of the effective mass is essential in the understanding of
The nanotube axis is in the direction of the vector \( \mathbf{T} = p\mathbf{a}_1 + q\mathbf{a}_2 \), where \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) are the primitive lattice vectors of the graphite sheet. The rectangle formed by \( \mathbf{C}_h \) and \( \mathbf{T} \) is the primitive unit cell of the CN.

Fig. 1. A CN is a graphite sheet rolled from the origin to the vector \( \mathbf{C}_h = ma_1 + na_2 \), where \( a_1 \) and \( a_2 \) are the primitive lattice vectors of the graphite sheet.

transport properties and optical excitonic excitations. Experimental values for the effective mass in common semiconductors can be obtained from a wide variety of experiments \([9–12]\). These included cyclotron resonance measurements of Dresselhaus et al. \([9]\), optically detected cyclotron resonance results by Son et al. \([10]\), resonant magnetotunneling spectroscopy measurements of Vdovin et al. \([11]\), and magnetotransport results by Leadley et al. \([12]\).

Despite the importance of the effective-mass, there are surprisingly few studies concerning the effective-mass problem in CNs, presumably due to the experimental difficulties in handling a single CN, which is too small for many conventional measurements. Recently, Korovyanko et al. \([13]\) reported the observation of excitonic excitations in semiconducting CNs. Knowledge about the electron effective mass of different subbands will be helpful in understanding the excitonic behavior. Li and Lin \([14]\) investigated the impurity levels in semiconducting CNs by the tight-binding method. They found that the electron effective mass oscillates with the nanotube radius, and the amplitude of the oscillation decreases with increasing radius.

There are experimental evidences that the band structure of a CN can be dramatically altered by strain (\( \varepsilon \)) \([15,16]\). Employing atomic force microscopy, Minot et al. \([15]\) reported that \( |dE_g/d\varepsilon| = 53 \text{ meV/%} \) for moderate-gap CNs and 35 meV/% for narrow-gap CNs. Therefore, it is of interest to investigate the electromechanical properties of CNs.

Curvature, strain, and magnetic field will modify the energy gap of a CN, which have been investigated separately in the previous theoretical works by Kane and Mele \([5]\) on the effect of curvature, Yang and Han \([17]\) on strain, and Ajiki and Ando \([18]\) on magnetic field. In this study, we develop a unified formulation to include effects of curvature, strain, and magnetic field on the energy gap. Furthermore, we also examine their influences on the electron effective mass, which have not been reported in any previous work according to our knowledge.

In this work, the tight-binding model is used to calculate the electronic structure of a CN. Once the bond symmetry of neighboring carbon atoms is broken, the transfer integrals \( \gamma_i \)'s will no longer be constant. Then we arrive at a general formulation to include effects of curvature, strain, and magnetic field. Analytic expressions for energy gap and electron effective mass are derived. These expressions provide a quick and easy way to determine the energy gap and effective mass.

This paper is organized as follows. The tight-binding formulation with effects of curvature, strain, and magnetic field is given in Section 2. Derivations of the analytic expressions for band gap and electron effective mass, and discussions of the results are presented in Section 3. Some concluding remarks are made in Section 4.

2. Theory

A CN can be regarded as a rolled-up graphene sheet, as shown in Fig. 1. It is formed by rolling a graphite sheet from the origin to the vector \( \mathbf{C}_h = ma_1 + na_2 \), where \( a_1 \) and \( a_2 \) are the primitive lattice vectors of a graphite sheet. A CN is specifically characterized by the parameters \((m,n)\). A \((m,n)\) CN has the radius \( r = |\mathbf{C}_h|/2\pi = b\sqrt{3(m^2 + mn + n^2)}/2\pi \) and the chiral angle \( \theta = \tan^{-1}[\sqrt{3}n/(2m + n)] \). \( b = 1.42 \text{ Å} \) is the C–C bond length.

The tight-binding method is employed to calculate the \( \pi \)-electronic states of a CN. \( H_{12} = \sum_{j=1}^{3} \gamma_j \mathbf{d}_j \) is the nearest-neighbor Hamiltonian matrix element. Here \( \mathbf{d}_j \)'s are the...
three nearest-neighbor vectors. When the curvature effect is taken into account, the nearest-neighboring transfer integrals may differ along different directions. On a curved surface, the π-electron orbitals of the two neighboring atoms are no longer in perfect alignment, and this misorientation will modify the transfer integrals. Following the Kane and Mele’s [5] approach, the transfer integrals are given by $\gamma_1 = \gamma_0(1 - b^2 \sin^2 \theta/8r^2)$, $\gamma_2 = \gamma_0[1 - b^2(\sin \theta + \sqrt{3} \cos \theta)^2/32r^2]$, and $\gamma_3 = \gamma_0[1 - b^2(\sin \theta - \sqrt{3} \cos \theta)^2/32r^2]$. $\gamma_0$ is the transfer integral without curvature effect. Their model had been applied successfully in explaining the measured energy gaps by STM [8].

After diagonalizing the Hamiltonian $H = \left( \begin{array}{cc} \epsilon & H_{12} \\ H_{12} & 0 \end{array} \right)$, energy dispersions of the $(m, n)$ CN are given by

$$E^{ck}(J, k_y) = \pm \left[ x_1^2 + 4x_1x_2 \cos \phi \sin \theta \cos \beta + 4x_2^2 \cos^2 \phi \right. \\
+ 4x_1x_2 \sin \phi \sin \theta \cos \beta + 4x_2^2 \sin^2 \phi \right]^{1/2},$$

where

$$x_1 = \gamma_1 = \gamma_0 \left[ 1 - \frac{b^2 \sin^2 \theta}{8r^2} \right],$$

$$x_2 = \frac{\gamma_3 + \gamma_2}{2} = \gamma_0 \left[ 1 - \frac{b^2(2 \cos^2 \theta + 1)}{32r^2} \right],$$

$$x_3 = \frac{\gamma_3 - \gamma_2}{2} = \gamma_0 \left[ 1 - \frac{3b^2 \sin 2\theta}{32r^2} \right],$$

$$\phi = \frac{b}{2} \left[ J \sin \theta / r + k_y \cos \theta \right].$$

The superscripts $c$ and $v$ represent the conduction and the valence bands, respectively. $k_y$ is the wavevector along the nanotube axis; $J$ is the angular momentum in the azimuthal direction. The azimuthal wavevector $k_x$ is determined by the periodic boundary condition. To be specific, $k_x = J/r$ where $J = 1, 2, \ldots, N_a/2$. $J$ could serve as the subband index. The number of carbon atoms in a primitive unit cell is $N_a = 4\sqrt{(p^2 + pq + q^2)(m^2 + mn + n^2)/3}$.

We now examine the effects of a uniaxial, homogenous, stress applying along the axial direction. Based on the elasticity theory,

$$\mathbf{R}' = \begin{pmatrix} 1 + \varepsilon_2 & 0 \\ 0 & 1 + \varepsilon_1 \end{pmatrix} \mathbf{R}.$$

When both curvature effect and uniaxial stress are taken into account, the transfer integrals can be reexpressed as

$$\gamma_1 = \frac{\gamma_0(1 - b^2 \sin^2 \theta/8r^2)}{(1 + \varepsilon_1)^2 \cos^2 \theta + (1 + \varepsilon_2)^2 \sin^2 \theta},$$

$$\gamma_2 = \frac{4\gamma_0[1 - b^2(\sin \theta + \sqrt{3} \cos \theta)^2/32r^2]}{(1 + \varepsilon_1)^2(\cos \theta - \sqrt{3} \sin \theta)^2 + (1 + \varepsilon_2)^2(\sqrt{3} \cos \theta + \sin \theta)^2},$$

$$\gamma_3 = \frac{4\gamma_0[1 - b^2(\sin \theta - \sqrt{3} \cos \theta)^2/32r^2]}{(1 + \varepsilon_1)^2(\cos \theta + \sqrt{3} \sin \theta)^2 + (1 + \varepsilon_2)^2(\sqrt{3} \cos \theta + \sin \theta)^2}.\quad (4)$$

CNs are assumed to exist in a uniform magnetic field along the nanotube axis. Its main effect is to change the angular momentum from $J$ to $J + (\phi_B/\phi_B)\cos \theta$, where $\phi_B$ is the magnetic flux and $\phi_B = hc/e$. The above formulations can be easily generalized to incorporate the effects of magnetic flux with $J$ replaced by $J + (\phi_B/\phi_B)$.

3. Energy gap and electron effective mass

We first examine zigzag nanotubes with $n = 0, \theta = 0^\circ; r = \sqrt{3}bn/2\pi$. With these substitutions, $\gamma_1 = \gamma_0$ and $\gamma_2 = \gamma_3 = \gamma_0(1 - 3b^2/32r^2)$ are obtained. The energy dispersions of the $J_1$ subbands nearest to the Fermi level ($E_F = 0$) are

$$E^{ck}(J_1, k_y) = \pm \gamma_0 \left[ 1 + 4 \left( 1 - \frac{3b^2}{32r^2} \right) \cos \phi \cos \beta \right. \right.$$

$$\left. + 4 \left( 1 - \frac{3b^2}{32r^2} \right)^2 \cos^2 \phi \right]^{1/2},$$

where $\phi = \pi J_1/m$ and $\beta = bk_y/2$. It is obvious that the band edge locates at $k_y = 0$, and the energy gap is

$$E_g = 2E_c(J_1, k_y = 0) = 2\gamma_0 \left[ 1 + 4 \left( 1 - \frac{3b^2}{32r^2} \right) \cos \frac{\pi J_1}{m} \right. \right.$$

$$\left. + 4 \left( 1 - \frac{3b^2}{32r^2} \right)^2 \cos^2 \frac{\pi J_1}{m} \right]^{1/2}. \quad (5)$$

Making use of the energy dispersion in Eq. (5), we perform the Taylor series expansion around the band edge state, and keep terms up to second order in $k_y$. The $k_y$-dependent energy dispersion is approximately given by

$$E^{ck}(J_1, k_y) \approx \frac{E_g}{2} \left[ 1 - \frac{9\gamma_0 b^2}{E_c} \left( 1 - \frac{3b^2}{32r^2} \right) \cos \frac{\pi J_1}{m} \right]^{1/2}. \quad (6)$$

It is straightforward to calculate the electron effective mass

$$M^* = \left. \frac{\hbar^2}{\partial_i^2 E_c / \partial k_y^2} \right|_{k_y = 0} = \left. \frac{\hbar^2 E_g}{9\gamma_0 b^2 (1 - 3b^2/32r^2) \cos(\pi J_1/m)} \right|.$$
The electron effective mass, which corresponds to the inverse of the curvature of energy band, is just proportional to the energy gap. It was also noted that the linear relationship could be generalized to all CNs with or without the external perturbations.

For a moderate-gap zigzag CN (MGZCN), \( m = 3I \pm 1 \) and \( J_1 = (2m + 1)/3 \). By assuming \( b/r \) to be small, a simple expression for energy gap can be obtained:

\[
E_g(m = 3I \pm 1) = \frac{\gamma_0 b}{r} \left( 1 + \frac{3b}{16r^2} \right).
\]

The electron effective mass is also simplified to

\[
M^e(m = 3I \pm 1) = \frac{2b^2}{9br_0} \left( 1 + \frac{11b}{16r^2} \right).
\]

As to a narrow-gap zigzag CN (NGZCN), \( m = 3I \) and \( J_1 = 2m/3 \). \( E_g \) and \( M^e \) are given by

\[
E_g(m = 3I) = \frac{3\gamma_0 b^2}{16r^3},
\]

\[
M^e(m = 3I) = \frac{h^2}{24\gamma_0 r^2}.
\]

In the case of an armchair CN, \( m = n, \ \theta = 30^\circ, \ r = 3bn/(2\pi); \ J_1 = m \). The transfer integrals become \( \gamma_1 = \gamma_3 = \gamma_0(1 - b^2/32r^2) \) and \( \gamma_2 = \gamma_0(1 - b^2/8r^2) \). With these substitutions, Eq. (1) yields

\[
E_{\nu}^\ell(J_1, k_y) = \pm \left[ \gamma_2^2 - 4\gamma_1 \gamma_2 \cos\left(\frac{\sqrt{3}}{2} k_y b\right) \right. \\
\left. + 4\gamma_1^2 \cos^2\left(\frac{\sqrt{3}}{2} k_y b\right) \right]^{1/2}.
\]

If curvature effect is neglected, the band edge state of the linear \( J_1 = m \) subbands resides at \( k_y = G/3 \) (\( G \) the reciprocal lattice vector). With Eq. (13), one can deduce that the curvature effect only shifts the band edge state slightly away from \( G/3 \), while the energy gap remains zero, or the linear subbands with vanishing electron effective mass remains unchanged. Hence, even with curvature effect, the new Fermi points still lie on the allowed quantization lines, so ACNs are truly metallic. Exploiting the fact that the new band edge state \( k_y^{*} \) is close to \( G/3 \), and after a few manipulations, we find that \( k_y^{*} \) has the simple form

\[
k_y^{*} = \frac{G}{3} + \frac{b/16r^2}{1 - 3b^2/16r^2}.
\]

### 3.1. Effects of uniaxial stress

With the inclusion of uniaxial stress, the transfer integrals for zigzag CNs are

\[
\gamma_1 = \frac{\gamma_0}{(1 + \epsilon)^2},
\]

\[
\gamma_2 = \gamma_3 = \frac{4(1 - 3b^2/32r^2)\gamma_0}{(1 + \epsilon)^2 + 3(1 - \epsilon/6)r^2}.
\]

A positive or negative value of the strain represents a tension or compression, respectively. The energy dispersions of the \( J_1 \) subbands become

\[
E_{\nu}^\ell(J_1, k_y) = \pm \left[ \gamma_2^2 + 4\gamma_1 \gamma_2 \cos \epsilon \cos 3\beta + 4\gamma_1^2 \cos^2 \epsilon \right]^{1/2}.
\]

With Eq. (16), and the assumption that \( \epsilon \) and \( b/r \) are small, energy gap and effective mass can be expressed in a simple analytic form. For moderate-gap zigzag nanotubes,

\[
E_g(m = 3I \pm 1) = \gamma_0 \left| \frac{b}{r} \right| \pm \left( \frac{7\epsilon}{2} - \frac{3b^2}{16r^2} \right).
\]

Concerning narrow-gap zigzag nanotubes,

\[
E_g(m = 3I) = \gamma_0 \left| \frac{7\epsilon}{2} - \frac{3b^2}{16r^2} \right|.
\]

\[
M^e(m = 3I) = \frac{2b^2}{9br_0} \left| \frac{7\epsilon}{2} - \frac{3b^2}{16r^2} \right|.
\]

Making use of Eqs. (1) and (4), one can compute \( E_g \) and \( M^e \) numerically without assuming \( b/r \) or \( \epsilon \) to be small. They are referred to as the numerical results. Fig. 2(a) shows the radius-dependence of energy gaps for various zigzag CNs at \( \epsilon = 0.005 \). The analytic models from Eqs. (17)–(20) agree remarkably well with the numerical results. Energy gaps of MGZCNs are inversely proportional to the nanotube radius [Eq. (17)], similar to the case without stress [2–5]. The effects of curvature and stress are weak, and the radius-dependence of \( E_g \) is dominated by the periodic boundary condition. Those of NGZCNs exhibit nonmonotonous radius-dependence, i.e., \( E_g \)'s decrease and then grow with increasing radius, this behavior is a direct consequence of Eq. (19). For a fixed \( \epsilon \), band gap can be \( \gamma_0(3b^2/16r^2 - 7\epsilon/2), 0 \) or \( \gamma_0(7\epsilon/2 - 3b^2/16r^2) \) as the radius increases. The \( E_g \)'s are small, and the curvature effect would compete with the uniaxial stress. The electron effective mass, as shown in Fig. 3(a), displays similar radius-dependence. The special linear relationship \( M^e \propto E_g \), as discussed later in Eq. (38), is the main reason.

Eqs. (17)–(20) predict that the variation of energy gap and electron effective mass with strain will be sawtooth patterns, as shown in Figs. 2(b) and 3(b). It is interesting to notice that for any zigzag nanotube, there is a critical strain \( \epsilon^c \) causing the energy gap to be zero, and provoking semiconductor–metal transition. The critical strain \( \epsilon^c \) is determined as

\[
\epsilon^c(m = 3I \pm 1) = \frac{b}{7r} \left( \frac{3b}{8r} \mp \frac{2}{3} \right).
\]

\[
\epsilon^c(m = 3I) = \frac{3b^2}{56r^2}.
\]
When a CN has zero energy gap at $\varepsilon = \varepsilon_c$, the $J_1$ subbands have linear energy dispersions, or own vanishing effective mass.

The radius-dependence of the critical strain varies widely relying on whether $m = 3I + 1$, $3I - 1$, or $3I$, as shown in Fig. 4(a). There are important differences among $m = 3I + 1$, $3I - 1$, and $3I$ zigzag nanotubes. The critical strain for $m = 3I + 1$ is always negative while those of $m = 3I - 1$ and $3I$ are positive. The magnitude of the critical strain signifies that a tension (compression) of the nanotube would bring about the semiconductor–metal transition. The different behavior among $m = 3I + 1$, $3I - 1$, and $3I$ zigzag nanotubes is due to the different effects of strain on the allowed $\sim k$ quantization lines. In the case of $m = 3I + 1$, the quantization lines move away from the graphene Fermi point and enhance the energy gap. Hence, a negative critical strain is required to bring the gap to zero. For the case of $m = 3I - 1$ and $3I$, the quantization lines move towards the graphene Fermi point and reduce the energy gap. Therefore, their critical strains are positive.

The magnitudes of the slopes of the energy gap versus strain for MGZCNs and NGZCNs are the same and are

![Graph showing energy gap versus radius and strain for MGZCNs and NGZCNs](image-url)
Yang and Han [17] have derived $dE_g/C15 = d/C15$ for MGZCNs and NGZCNs by a simple tight-binding model without curvature effects:

$$\frac{dE_g}{dC15} = 3(1 + v)\gamma_0 = 3.6\gamma_0, \quad (24)$$

where $v = 0.2$ is the Poisson’s ratio for nanotubes.

Experimental measurements with the use of atomic force microscopy [15] revealed that $|dE_g/dC15| = 53$ meV/% for MGZCNs and 35 meV/% for NGZCNs. Both Yang and Han [17] and our models predict that $|dE_g/dC15|$ is about 100 meV/%, which roughly describes the experimental value.

With the inclusion of the deformation potential energy term, Charlier et al. [19] obtained analytic expressions for the energy gaps of MGZCNs and NGZCNs under uniaxial stress with curvature effects:

$$E_g(m = 3I \pm 1) = \gamma_0 \left( \pm 2.07e + \frac{0.998b}{r} \right), \quad (25)$$

$$E_g(m = 3I) = \gamma_0 \left( 3.19e + \frac{0.16b^2}{r^2} \right), \quad (26)$$
However, for NGZCNs, there is a fundamental difference which is roughly consistent with the Charlier’s result. Making use of Eq. (17), neglecting the \( b^2/r^2 \) term, our model yields

\[
E_g(m = 3I \pm 1) = \frac{\gamma_0 b}{r} \left( \pm 3.5e + \frac{1.001b^3}{r} \right),
\]

which is roughly consistent with the Charlier’s result. However, for NGZCNs, there is a fundamental difference between Charlier’s result and our work [Eq. (19)]. Charlier’s model predicts a negative critical strain \( \nu = -0.05b^2/r^2 \), whereas ours is positive [Eq. (22)].

Finally, for ACNs, the application of uniaxial stress does not cause an energy gap due to the high symmetry of the nanotube lattice.

### 3.2. Effects of magnetic field

For zigzag nanotubes, Eq. (5) gives us the energy dispersions, in which \( \cos \beta \) needs to be modified as \( \cos[(\pi/m)(J_1 + \phi_B/\phi_{B0})] \). With the assumption that both \( \phi_B/\phi_{B0} \) and \( b/r \) are small, the magnetic-flux-dependence of energy gap and effective mass is obtained:

\[
E_g(m = 3I \pm 1) = \frac{\gamma_0 b}{r} \left( 1 - \frac{3\phi_B}{\phi_{B0}} \right) \left( 1 \pm \frac{3b}{16r} \right),
\]

\[
M^*(m = 3I \pm 1) = \frac{2h^2}{9b\tau_0} \left( 1 \mp \frac{11b}{16r} \right) \left[ 1 - \left( 1 \pm \frac{b}{2r} \right) \frac{3\phi_B}{\phi_{B0}} \right],
\]

\[
E_g(m = 3I) = \frac{3\gamma_0 b}{r} \left[ \frac{\phi_B}{\phi_{B0}} - \frac{b}{16r} \right],
\]

\[
M^*(m = 3I) = \frac{2h^2}{3b\tau_0} \left( 1 - \frac{3b}{2r} \frac{\phi_B}{\phi_{B0}} \right) \left[ \frac{\phi_B}{\phi_{B0}} - \frac{b}{16r} \right].
\]

Ajiki and Ando [18] have derived expressions for the energy gaps of MGZCNs and NGZCNs by the effective-mass model without considering curvature effects:

\[
E_g(m = 3I \pm 1) = \frac{\gamma_0 b}{r} \left( 1 - \frac{3\phi_B}{\phi_{B0}} \right),
\]

\[
E_g(m = 3I) = \frac{3\gamma_0 b}{r} \frac{\phi_B}{\phi_{B0}}.
\]

Their results are the special cases of Eqs. (28) and (30) with very large assigned radius.

Analytic \( E_g \) and \( M^* \) obtained from Eqs. (28)–(31) describe the numerical results nicely in Figs. 2(c), (d), 3(c), and (d). \( E_g \)’s (\( M^* \)’s) are, respectively, inversely proportional to \( r \) and \( r^2 \) for MGZCNs and NGZCNs (Figs. 2(c) and 3(c)). \( E_g \)’s (\( M^* \)’s) of MGZCNs and NGZCNs decrease in the same slope as the magnetic flux increases from zero (Figs. 2(d) and 3(d)). Notice that the decreasing part of the NGZCN data only constitutes a very small proportion of the graph. The slope of energy gap versus magnetic flux is

\[
\frac{dE_g}{d(\phi_B/\phi_{B0})} = -\frac{3\gamma_0 b}{r}.
\]

The latter will first exhibit the semiconductor–metal transition at the small critical magnetic flux \( (\phi_B/\phi_{B0})^\star \) \((m = 3I) = b/16r\), and then \( E_g \)’s (\( M^* \)’s) begin to increase in the opposite slope. The critical magnetic flux of NGZCNs is proportional to the inverse of radius (Fig. 4(b)), whereas that of MGZCNs equals to \( \frac{1}{2} \), which is identical to the previous prediction in the absence of curvature effects [Eq. (32)].

For ACNs, the band edge state is unaffected by the magnetic field [Eq. (13)], and it is still given by Eq. (14). However, the \( J_1 = m \) linear subbands are changed into the parabolic subbands, and there exists an energy gap between the parabolic subbands. At weak magnetic flux, the energy gap is

\[
E_g = 2E^\star(J_1, k_z = k^\star_z) = \frac{3\sqrt{2} b}{r} \frac{\phi_B}{\phi_{B0}} \sqrt{\gamma_1/2} \cos \left( \sqrt{\frac{3}{2}} k^\star_z b \right).
\]
We proceed further by taking the Taylor series expansion on the energy dispersion given in Eq. (13) around \( k_y^* \), then the effective mass is obtained. With the approximation that \( b/r \) is small, \( E_g \) and \( M^* \) can be explicitly expressed as

\[
E_g = \frac{3\gamma_0 b \phi_B}{r} \left( 1 - \frac{b^2}{8r^2} \right),
\]

(36)

\[
M^* = \frac{2\hbar^2}{3b\gamma_0 \phi_B} \left( 1 - \frac{b^2}{8r^2} \right) \left[ 1 + \frac{1}{6} \left( \frac{3b \phi_B}{2\phi_B} \right)^2 \right].
\]

(37)

The semiconductor–metal transition occurs at the vanishing magnetic flux \((\phi_B/\phi_B^0)_i = 0\). \( E_g \)'s of ACNs grow with the positive slope \( dE_g/d(\phi_B/\phi_B^0) = 3\gamma_0 b/r \), which is opposite to those of MGZCNs and NGZCNs. However, the magnitudes of the slopes are identical for all achiral CNs. Explanations of the above energy gap behavior are as follows. In the presence of magnetic field, the allowed \( k \) quantization lines of a nanotube will be shifted by a distance of \( \phi_B/\phi_B^0 \) in \( k \)-space, and the change in energy gap is approximately given by \( 3b\gamma_0 \phi_B/(\phi_B^0) \). For ACNs, even with the inclusion of curvature effect, the allowed \( k \) lines still cross the graphene Fermi points, leading to zero band gap, and magnetic field will open up an energy gap with the value \( 3b\gamma_0 \phi_B/(\phi_B^0) \). Therefore band gap of an ACN grows monotonously with \( \phi_B/\phi_B^0 \) (and the slope is \( 3b\gamma_0/\phi_B^0 \)). For a NGZCN, the band gap without magnetic field is small and is given as \( 3b^2\gamma_0/(16r^2) \) [Eq. (11)]. Under the influence of magnetic field, the new energy gap can be \((3b\gamma_0/b)/(16r - \phi_B/\phi_B^0)\), \( 0 \) or \((3b\gamma_0/b)(\phi_B/\phi_B^0 - b/16r)\) as the magnetic field increases from zero. Therefore energy gain of a NGZCN diminishes initially and then raises with the increment of flux. For a MGZCN, the band gap without magnetic field is large, the effect of magnetic field will just reduce the energy gap by \( 3b\gamma_0 \phi_B/(\phi_B^0) \). It is straight forward to deduce that the magnitudes of the slopes are identical for all achiral CNs, and the value is \( 3b\gamma_0/\phi_B^0 \).

The radius, magnetic flux, and strain dependence of the electron effective mass are surprisingly similar to those of the energy gap, as shown in Figs. 2(a)–(d) and 3(a)–(d). It can be explained as follows. For all cases (MGZCNs, NGZCNs, ACNs, with or without magnetic flux, and with or without uniaxial stress), making use of the above derived analytic expressions, assuming \( b/r, \phi_B/\phi_B^0, \) and \( \epsilon \) to be small, we can obtain a simple expression for \( M^*/E_g \) after a few derivations:

\[
\frac{M^*}{E_g} \approx \frac{2\hbar^2}{9b^2\gamma_0},
\]

(38)

which is just a constant.

The formulation developed in Section 2 can also be applied to chiral CNs. We have examined the (21,10) moderate-gap nanotube \((r = 10.7 \text{ Å}, \theta = 18.4^\circ)\) and the (23,8) narrow-gap nanotube \((r = 10.9 \text{ Å}, \theta = 14.4^\circ)\). The former is chosen to compare with the (28,0) MGZCN \((r = 11.0 \text{ Å}, \theta = 0^\circ)\), while the latter nanotube compared with the (27,0) NGZCN \((r = 10.6 \text{ Å}, \theta = 0^\circ)\). These CNs have roughly the same radii but different chiral angles. Concerning energy gaps and electron effective masses, the strain-dependence and magnetic-flux-dependence strongly rely on the chiral angles, as shown in Figs. 2(b), (d), 3(b), and (d). For example, there are important differences in the slopes of \((E_g, M^*)\) versus \((\epsilon, \phi_B/\phi_B^0)\), the critical strain, and the critical magnetic flux. Such differences are mainly caused by the different curvature effects and periodic boundary conditions. This result further illustrates that electronic properties are mainly determined by the nanotube geometries, both radius and chirality. \( r \) and \( \theta \) need to be taken into consideration simultaneously in explaining the measured electronic spectra. It is worth mentioning that the relationship between \( M^* \) and \( E_g \) given in Eq. (38) also holds for these two chiral nanotubes.

4. Concluding remarks

A general tight-binding formulation including effects of curvature, strain, and magnetic field is developed. Analytic expressions for energy gap and electron effective mass are derived for achiral zigzag and armchair CNs. The ratio of electron effective mass to band gap can be expressed simply as a constant \((2\hbar^2/9b^2\gamma_0^2)\). The semiconductor–metal transition could be modulated by the application of stress or magnetic flux. The critical strain is different for \( m = 3I + 1, 3I - 1, \) and \( 3I \) zigzag CNs. The critical magnetic flux of the narrow-gap zigzag CNs is inversely proportional to the nanotube radius, while that of the moderate-gap zigzag CNs keeps at \( \phi_B^0/3 \) even with curvature effects. It is found that the dependence of the electronic properties on the chiral angle is strong, e.g., the critical strain and the critical magnetic flux. We have clearly demonstrated that concerning electromechanical properties, there are fundamental differences among different CNs. Therefore, it is feasible to develop brand new CNs electronic devices or switches modulated by strain or magnetic field, and our derived analytic expressions can provide guidelines in the early stage of device design. The predicted energy gap and electron effective mass could be verified by experimental measurements.

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References