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Electric field effects on the energy spectrum of carbon nanotubes

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Abstract

Electronic properties of straight carbon nanotubes under an external electric field are investigated, following a single- π -orbital tight binding approximation. Metal–insulator transitions in metallic tubes and energy gap modulations in semiconducting ones were found due to the action of the electric field. Reductions in the tube symmetry operations induced by the field are manifested in the energy spectrum as a function of the angle determined by the field direction and equivalent in-plane atomic positions along the circumferential direction. We find that particular energies in the spectra exhibit a periodic oscillation with this dephasing angle. The range and position of those energies, as well the amplitude of the oscillation, can be properly manipulated by changing the strength and direction of the applied electric field.

(Some figures in this article are in colour only in the electronic version)

Intensive research into straight carbon nanotubes (CNs) and complex structures made of tubes, such as heterostructures, toroids and even carbon rings, has been developing in recent years. These interesting nanostructures present a variety of unique features with electronic properties depending upon their intrinsic geometric formation [1]. An ideal CN can be described as a layer of graphite that has been wrapped into a cylindrical form. They exhibit remarkable tensile strength and varying electronic properties which have been experimentally verified [2–4]. A large number of applications of CNs have recently been suggested and even observed, based mainly on the peculiar physical property of behaving both as metallic and semiconducting materials [5–9]. The idea of changing the electronic properties of CNs, resulting in metal to semiconductor transitions, has been realized by allowing structural perturbations such as twisting [10] and squashing [11, 12] the metallic tubes. Moreover, external electric and magnetic fields can modify the energy spectrum of CNs and related structures, modulating their optical and transport responses. Opening and closing of the electronic gap have been found to occur in metallic and semiconducting achiral zigzag nanotubes [13–19], respectively.

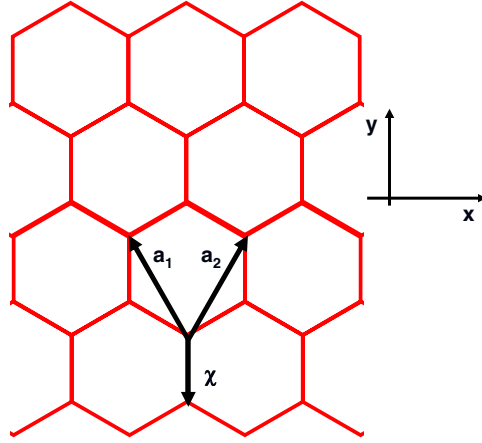


Figure 1. Schematic representation of the graphite lattice and the related unit vectors \mathbf{a}_1 and \mathbf{a}_2 . χ denotes the vector position of site B with respect to atom A.

Also, under high electric field conditions, typical nanojunctions may be formed by fusion of two adjacent tubes [20].

Recently, we have performed a detailed study of the role played by external magnetic and electric fields in the electronic properties of toroidal carbon nanotubes [18, 21]. We have also reported preliminary results on a particular electric field effect in the energy spectrum of carbon nanotori [18]. For an electric field applied parallel to the toroid plane, we find that the spectrum contains some energies that oscillate as a function of a dephasing angle, defined between the field direction and the in-plane position of the carbon atoms along the toroid. Here we analyse this effect in straight achiral CNs under a transverse electric field. We investigate adequate conditions under which this angular dependence of the spectrum on the electric field can be controlled for desired energy gap modulations. Depolarization effects, which lower the applied fields, have not been included in this simpler picture.

The electronic structure of a CN is calculated following a single- π -band tight binding approach starting from a graphite sheet and applying periodic boundary conditions along the transverse direction. The energy spectrum of a graphite sheet in this approximation can be obtained by expanding the wavefunction as a linear combination of atomic orbitals:

$$\psi(\vec{r}) = \sum_{n_1, n_2} \left[C_{n_1, n_2}^A \phi_A^S(\vec{r} - \vec{R}_{n_1, n_2}) + C_{n_1, n_2}^B \phi_B^S(\vec{r} - \vec{R}_{n_1, n_2} - \vec{\chi}_B) \right], \quad (1)$$

where $\vec{R}_{n_1, n_2} = n_1 \vec{a}_1 + n_2 \vec{a}_2$ denotes the position of a carbon atom A and $\vec{\chi} = -(\vec{a}_1 + \vec{a}_2)/3$ is the position of the corresponding atom B in the same unit cell. The hexagonal lattice unit vectors are given by $\vec{a}_1 = a_{cc} \frac{\sqrt{3}}{2} (1, \sqrt{3})$ and $\vec{a}_2 = a_{cc} \frac{\sqrt{3}}{2} (-1, \sqrt{3})$, with $a_{cc} = 1.42 \text{ \AA}$, and are shown in figure 1 together with vector $\vec{\chi}$.

By considering only nearest neighbour interactions and neglecting the overlap integral of the nearest A and B atoms, the following set of coupled equations for the expansion coefficients is obtained:

$$\begin{aligned} \varepsilon C_{n_1, n_2}^A - \gamma [C_{n_1, n_2}^B + C_{n_1+1, n_2}^B + C_{n_1, n_2+1}^B] &= 0 \\ \varepsilon C_{n_1, n_2}^B - \gamma [C_{n_1, n_2}^A + C_{n_1-1, n_2}^A + C_{n_1, n_2-1}^A] &= 0 \end{aligned} \quad (2)$$

with γ being the nearest neighbour transfer integral. The energy of the carbon 2p orbital has been considered equal to zero. In the absence of an electric field, the energy dispersion

relations for the 2D graphite system can be found analytically using the translational symmetry of the unit cells in the direction of the lattice vectors.

The unit cell of straight CNs is specified by a chiral vector $\vec{C}_h = n\vec{a}_1 + m\vec{a}_2$ in the circumferential direction and a translational vector $\vec{T} = p\vec{a}_1 + q\vec{a}_2$ along the longitudinal direction. The integers (n, m) define the diameter and chirality of the CN, whereas p and q are determined by the condition $\vec{C}_h \cdot \vec{T} = 0$. On using periodic boundary conditions, the wavevector associated with the direction of the chiral vector becomes quantized, while the corresponding wavevector associated with the translational vector \vec{T} remains continuous for a CN of infinite length. For the sake of simplicity, we focus on the study of zigzag $(n, 0)$ and armchair (n, n) CNs.

If one assumes an armchair (zigzag) nanotube in the presence of a uniform electric field \vec{F} , applied perpendicular to the tube axis, the translational symmetry along the $\alpha = x(y)$ direction is preserved and we may redefine the coefficients using a k_α wavevector:

$$\begin{aligned} C_i^A &= e^{ik_\alpha R_\alpha} A_i \\ C_i^B &= e^{ik_\alpha R_\alpha} B_i, \end{aligned} \quad (3)$$

where $R_x = \sqrt{3}a_{cc}/2(n_1 - n_2)$ and $R_y = 3a_{cc}/2(n_1 + n_2)$. For an armchair nanotube, one gets

$$\begin{aligned} (\varepsilon - \varepsilon_A(i))A_i - \gamma \left[B_i + 2 \cos(\sqrt{3}k_x a_{cc}/2) B_{i+1} \right] &= 0 \\ (\varepsilon - \varepsilon_B(i))B_i - \gamma \left[A_i + 2 \cos(\sqrt{3}k_x a_{cc}/2) A_{i-1} \right] &= 0, \end{aligned} \quad (4)$$

with $i = 1, \dots, 4n$, whereas for a zigzag nanotube,

$$\begin{aligned} (\varepsilon - \varepsilon_A(i))A_i - \gamma \left[B_i + e^{\frac{i\pi}{2}k_y a_{cc}} (B_{i+1} + B_{i-1}) \right] &= 0 \\ (\varepsilon - \varepsilon_B(i))B_i - \gamma \left[A_i + e^{\frac{i\pi}{2}k_y a_{cc}} (A_{i+1} + A_{i-1}) \right] &= 0, \end{aligned} \quad (5)$$

with $i = 1, \dots, 2n$. Notice that the quantization of the corresponding wavevector component given by the periodic boundary condition in the circumferential direction determines the number of solutions given by the subindex i , which depends upon the CN chiral angle. On the other hand, the wavevectors k_α are defined within the interval $-\frac{\pi}{T_\alpha} < k_\alpha < \frac{\pi}{T_\alpha}$, where the magnitude of the translation vector along the tube is $T_x = \sqrt{3}a_{cc}$ for armchair or $T_y = 3a_{cc}$ for zigzag tubes. By direct diagonalization of the above equations one gets the energy spectra of the tube under consideration.

Within the tight binding approximation adopted, the effect of a transverse electric field is included in the on-site energies of the carbon atoms, following a direct analysis of the potential energy differences along the nanotube diameter. This implies incorporation of the microscopic details of the spatial distribution of the carbon atoms along the annular structure, leading to the following relation:

$$\varepsilon_{A(B)}(i) = -V(n) \cos(\theta_{A(B)}^i), \quad (6)$$

where the electrostatic potential energy along the tube cross-section $V(n)$ and the electric field value are related by $V(n) = eFn\sqrt{3}a_{cc}/\pi$ for a zigzag CN and $V(n) = eFn3a_{cc}/\pi$ for an armchair. The azimuthal angle θ^i is defined by the electric field direction and the position of the carbon atoms along the cylindrical surface of the tube. For a zigzag $\theta_{A(B)}^i = (i-1)\pi/n$ while for an armchair $\theta_A^i = (i-1)\pi/n$ and $\theta_B^i = (i-5/3)\pi/n$. The electric field intensity appearing in the above equation, $V(n)$, may be considered as being a screened field value, following the results obtained by using first-principles density functional calculations [19, 22].

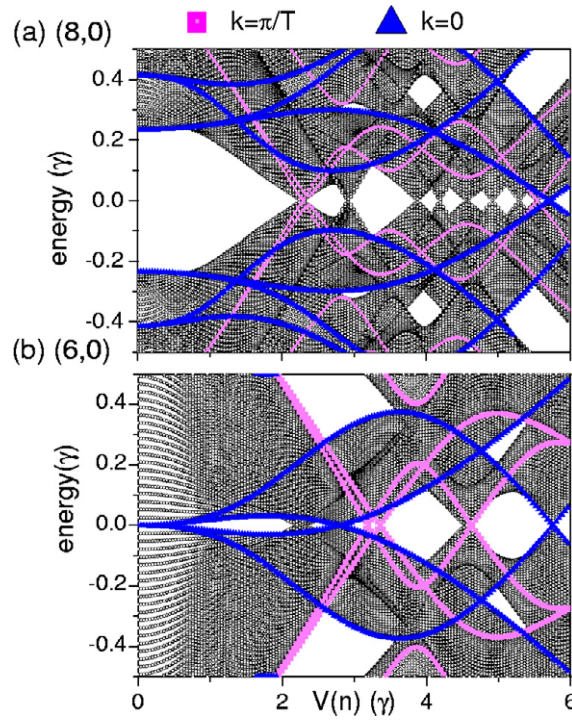


Figure 2. Energy spectra of zigzag (a) semiconducting (8, 0) and (b) semi-metallic (6, 0) CNs as a function of the electric field potential energy and for $N = 120$. Curves of full upward-pointing triangles and squares denote the solutions for the particular wavevectors $k = 0$ and $k = \pi/T$, respectively.

Periodic boundary conditions are used along the axial direction, and hence the tube length is given by $L = NT_\alpha$, N being the number of cells considered along the longitudinal direction. Using this picture the wavevector takes $2N$ discrete values separated by $\Delta k_\alpha = \frac{\pi}{N}$. Large values of N may be considered to describe the infinite tube.

The electronic energy spectrum of CNs as a function of the transverse electric field is illustrated in figure 2. The upper layer shows the energies for a zigzag (8, 0) semiconductor while the lower one corresponds to the spectrum of a metallic (6, 0) tube. We have plotted the spectrum for a limited range of energies next to the Fermi level to emphasize the occurrence of typical gap modulations induced by the electric field in the semiconducting CN, and the gap opening in the case of the metallic one. All the energies are written in units of the hopping parameter ($\gamma \approx 2.8$ eV). One may notice in both cases that for low field values, the energy levels lying closer to the Fermi energy are almost unaffected by the field. The states more distant in energy, mainly those degenerate at zero field, are strongly affected, resulting in splitting and crossing of levels for increasing electric field intensities. In the high field regime, a strong band-gap modulation is induced for both types of zigzag tube. It is worth noticing the occurrence of large energy gaps in different zones of both of the spectra as a function of the electric field energy.

The solutions corresponding to contributions of particular k vector values, which at zero field present high degeneracy, are highlighted in figure 2. The upward-pointing triangle curves (blue in the online version) depict the Γ point ($k = 0$) while the squares (pink in the online version) correspond to the boundary zone at the X point with $k = \pi/T$. The lifting of the

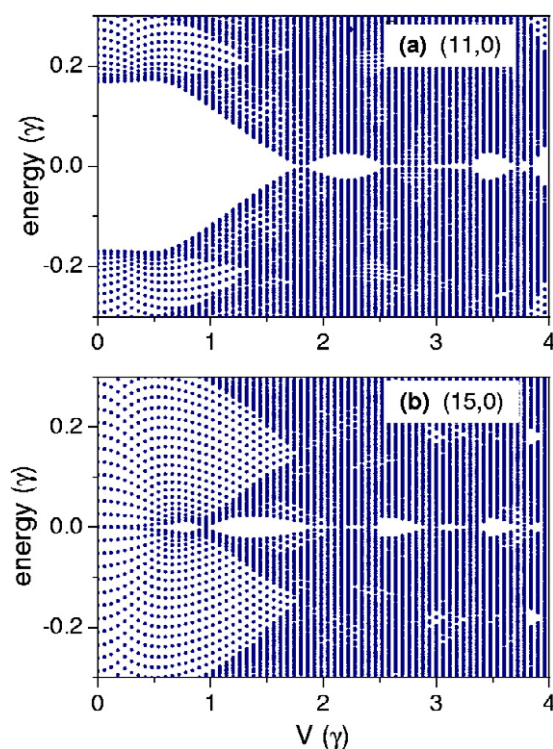


Figure 3. Energy spectra of zigzag (a) semiconducting (11, 0) and (b) semi-metallic (15, 0) tubes as a function of the electric field potential energy. Both tubes are composed of $N = 120$ cells.

double degeneracy of the two band-edge states corresponding to $k = 0$ is only meaningful for large electric field energies. One interesting point is that the closure of the (8, 0) gap involves a transition from the $k = 0$ state to another wavevector contribution at a critical field value. For a metallic (6, 0) CN the fourfold degeneracy of the $k = 0$ state at the Fermi level is completely lifted by the field. A small gap is opened and after a critical field value one notes the mixing of different k wavevectors corresponding to the energy states next to the Fermi level, and also the occurrence of further gaps. To investigate how the main features of the spectrum discussed depend on the nanotube diameters, we consider larger zigzag tubes. The energy spectra of (11, 0) and (15, 0) CNs, with $N = 120$, are displayed in figure 3 as a function of the electric field potential. The same type of semiconductor–metal transitions marked by gap formation and gap evolutions are verified. As expected, the sizes of the gaps become smaller as the zigzag tube radius increases, and the gap closing/opening occurs for lower electric field values as the tube radius increases. We emphasize here that our results are in quite good agreement with those obtained using the local density approximation (LDA) presented by Kim *et al* [14] for zigzag CNs. It is also interesting to note that the present results show that the perturbation theory developed in that work is a good approximation in the low electric field regime. In particular, Li *et al* [15] have previously shown that for pseudo-metallic zigzag tubes, the gap increases quadratically with the electric field. A similar behaviour for the field dependence of the electronic spectrum is also exhibited in figure 3(b) for the (15, 0) CNT.

The possibility of a band gap opening in armchair CNs, under a uniform transverse electric field, is a controversial subject with opposite results reported. By performing band-structure

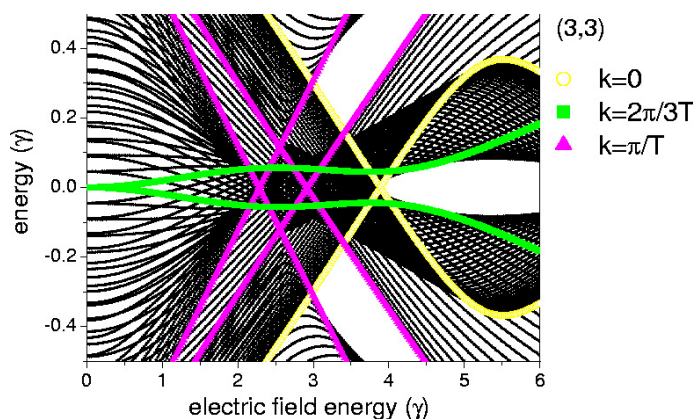


Figure 4. Energy spectrum of an armchair (3, 3) CN as a function of the electric potential energy, with $N = 120$. The full square curve denotes wavevector $k = 2\pi/3T$, and open circles and upward-pointing triangles correspond to $k = 0$ and $k = \pi/T$, respectively.

calculations based on the tight binding model for particular values of the electric field strength, Li *et al* [15, 16] found that the two lowest subbands of armchair CNs always cross, even at very large electric field values. In contrast, Zhou *et al* [13] reported the occurrence of field-induced energy gaps in all (n, n) CNs. Our results for the energy spectrum of a (3, 3) armchair tube, with $N = 120$ cells, as a function of the electric field energy potential are displayed in figure 4. The choice of quite a small tube is just to help in illustrating the evolution of the states with the field. Besides the wavevectors corresponding to the Γ and X points of the graphite Brillouin zone, we have also depicted the vector $k = 2\pi/3T$ which denotes the crossing point of the valence and conduction bands for armchair CNs at zero electric field. One should note that a gap opening was found for all armchair tubes studied, although the fields required are quite strong ($\approx 2.0 \text{ V \AA}^{-1}$). The dependence of the electrical field on the tube diameter, measured by the integer n of the CN number (n, n) , is shown in figure 5 for n up to 15. An analysis of the local density of states of infinite armchair CNs allows one to obtain the critical electric field value for which a gap is opened at the Fermi level (see the inset in figure 5). Sizable gap reductions were previously reported for boron nitride nanotubes of large radii [23] on applying lower intensity electric fields.

The electrostatic potential in the CN cylindrical surface depends on the field direction with respect to equivalent in-plane atomic positions. Here we define an angle ϕ as that between the electric field direction and a rotation symmetry axis perpendicular to the tube axis. In what follows, we discuss the effects of this angle on the energy spectrum of CNs. To allow an electric field rotation between two equivalent in-plane atomic positions lying in one single ring of the tube, we add this ϕ angle to the azimuthal angle in the site energy expression, $\epsilon_i^\alpha = -\cos(\theta_i^\alpha + \phi)V(n)$. As expected, the presence of this phase leads to an extra reduction in the symmetry operations of each carbon ring composing the tube. Figure 6(a) shows the dependence of the energy spectrum on the electric field for a (6, 0) CN, considering 120 cells, and for $\phi = 0$ and $\pi/12$. In the range of energies near the Fermi energy, the changes in the spectrum are more remarkable for higher fields. We have highlighted with a circle a particular zone where the difference between the spectra is clearly seen. The explicit dependence of the energy spectra on the ϕ angle, for a fixed electric field energy value ($V/\gamma = 3.18$), is shown in figure 6(b). Clear oscillations around the Fermi energy are found, with a period of π/n , corresponding to the angular distance between two carbon atoms in one of the rings composing

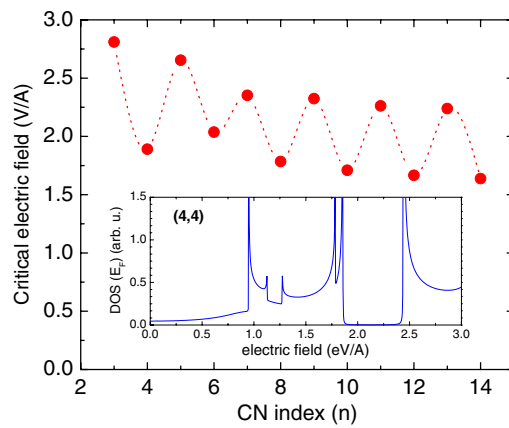


Figure 5. Dependence of the electric field on the index n of the armchair CN (n, n) , for which a gap is opened at the Fermi level. Inset: density of electronic states at the Fermi level as a function of the electric field for a $(4, 4)$ CN.

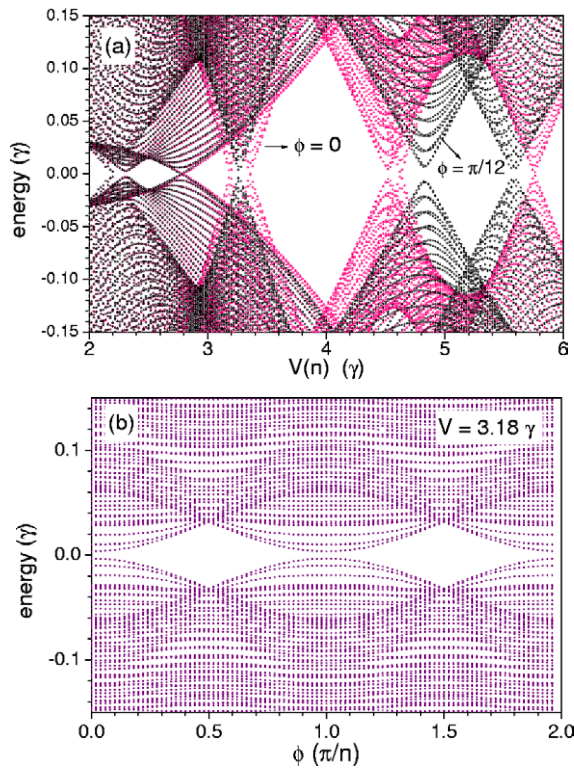


Figure 6. (a) Electric field dependence of the energy spectrum of a $(6, 0)$ nanotube for two values of the dephasing angle ($N = 120$), $\phi = 0$ (squares) and $\phi = \pi/12$ (full dots). (b) Energy spectrum as a function of the dephasing angle for an electric field value of 3.18γ .

the $(n, 0)$ CN. For higher electric field strengths, the band gap can be tuned over a wide range of energies by changing the angle.

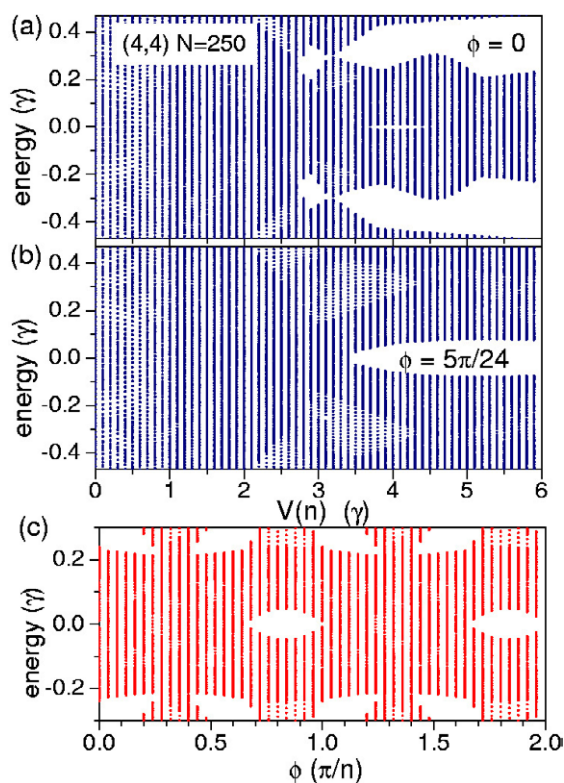


Figure 7. Electric field dependence of the energy spectrum of a (4, 4) CN ($N = 250$) for (a) $\phi = 0$ and (b) $\phi = 5\pi/24$. (c) Energy spectrum as a function of the ϕ angle for an electric field energy equal to 3.8γ .

The effect of the ϕ angle on the energy spectrum of an armchair (4, 4) tube is shown in figure 7 ($N = 250$). In the upper (figure 7(a)) and middle (figure 7(b)) parts of the figure we compare the spectra results for $\phi = 0$ and $5\pi/24$ as functions of the electric field energy. For high electric field strengths the energy spectra are clearly modified. The aperture of an energy gap is also apparent for a wide range of field values. A particular electric field intensity is considered in figure 7(c) to illustrate the periodic oscillation pattern exhibited by the spectrum as a function of the angle. For armchair tubes in general, we found that the most remarkable dependence of the energy spectrum on the ϕ angle occurs for the $k_x = \pi/T_x$ states, corresponding to the X point of the Brillouin zone, which at zero electric field are highly degenerate.

The possibility of not considering perfect alignment of the electric field direction with the microscopic atomic positions opens up then a new source of symmetry breaking that allows new features in the corresponding energy spectra of the carbon nanotubes. Alternatively, the angle effect described may also be understood as imperfection mechanisms that are incorporated in our theoretical approach and that may change the gap modulations predicted before, in the absence of the phase. Also, the optical response may be tuned by properly taking into account the electric field directions.

In summary, we have studied the electronic properties of straight carbon nanotubes under an external electric field applied perpendicular to the tube axis. Our calculations are based on

the single- π -orbital tight binding approximation, and the effect of the electric field is included in the on-site energies of the carbon atoms. Depolarization effects on the CNs, due to changes in the charge distribution induced by the electric field, have not been taken into account. A proper calculation of those effects would require self-consistent calculations. Within the simpler picture, our results show that a strong electric field can always induce metal-insulator transitions in metallic tubes and energy gap modulations in semiconducting nanotubes. In addition, we have analysed the effect of a rotation of the electric field along the circumferential direction between two equivalent in-plane atomic positions. In the high field regime, we found a strong angular dependence of the energy spectrum for the rotation angle. Some particular energies oscillate as a function of this ϕ angle. The range and position of these energies and the amplitude of the oscillation can be modified by changing the strength and direction of the electric field applied. Interesting cases occur when the oscillating energies correspond to the two states closest to the Fermi energy leading to gap modulations for fixed electric field strength.

Acknowledgments

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