Electronic structure of zigzag carbon nanotubes

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The method of zero-range potentials is used to investigate the band structure of the one-electron spectrum of zigzag single-walled carbon nanotubes. It is shown that the formation of a narrow forbidden band in $(3N,0)$ zigzag nanotubes is due to the influence of the curvature of their walls on the one-electron spectrum of the π electrons. Expressions are obtained for the widths of the forbidden bands (band gaps) and effective masses of $(3N,0)$, $(3N-1,0)$, and $(3N+1,0)$ nanotubes as functions of their diameter. © *2006 American Institute of Physics*.
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INTRODUCTION

Studies of the electronic structure of single-walled carbon nanotubes in the tight-binding approximation[1] have shown that $(3N-1,0)$ and $(3N+1,0)$ zigzag tubes are one-dimensional semiconductors with a wide band gap $E_g=2\gamma b/d$, where $\gamma=2.5$ eV is the overlap integral, b is the bond length, and d is the tube diameter, whereas $(3N,0)$ tubes are narrow-gap semiconductors with a band gap $\sim 1/d^2$. In particular, in Ref. 1, in the framework of the approximation adopted, the band gap for a (9,0) tube was found to be 0.14 eV. In Refs. 1 and 2 it was conjectured that in $(3N,0)$ tubes of not very large diameter, the curvature leads to hybridization of the σ and π orbitals of carbon, which give the main contribution to the formation of the narrow ($\sim$0.01 eV) gap between the valence and conduction bands.[3,4] Later such a gap was observed experimentally by the methods of infrared spectroscopy[5] and inferred from conductivity measurements[6] at temperatures of $\sim$1 K.

In this paper it is shown that the appearance of the band gap in $(3N,0)$ tubes is mainly due to the influence of the curvature of the surface of the tube on the one-electron spectrum of collectivized π electrons. The corresponding dispersion relations are derived using the well-known method of zero-range potentials.[7] Although in the framework of that method the interaction of a valence electron with an individual ion in a multi-atomic cluster is described in a rather schematic way, the spatial structure of the cluster is taken into account in full. In this paper we briefly describe the corresponding technique for calculating the Bloch functions and band structure of a zigzag tube. Here instead of the overlap integral γ, we use only a single universal parameter for all the tubes, obtained from the requirement of agreement as to the distance between the two experimental Van Hove points in the density of states of the (15,0) tube.

As an example we present the results of a calculation of the band structure and density of states for the (9,0) and (10,0) tubes and give interpolation formulas for the band gaps in all zigzag tubes and for the effective masses at the band edges. The results are compared with the experimental data obtained for (10,0) nanotubes[8,9] and with the results of band structure calculations[10] by the LCAO method for single-walled nanotubes with the real spatial structure of the tubes taken into account.

ONE-ELECTRON SPECTRUM OF SINGLE-WALLED ZIGZAG AND ARMCHAIR NANOTUBES

It is known that graphite consists of weakly coupled monoatomic carbon layers forming a regular hexagonal structure. Figure 1a shows one such layer, where the atoms are located at the vertices of a regular hexagon. We recall that three of the four valence electrons of carbon form localized σ bonds (illustrated by lines), while the fourth forms a delocalized π bond. It is the π electrons that take part in conduction.

If one cuts a strip of this layer along the dashed lines and rolls it into a tube so as to make the dashed lines coincide, a single-wall (3,0) zigzag carbon nanotube is formed. If the distance between dashed lines is increased, one obtains an $(M,0)$ zigzag tube of larger diameter. If the dashed lines are rotated by 90° and the layer is cut along them and rolled into a tube, one obtains an (M,M) armchair nanotube. In both cases the atoms are found at the vertices of hexagons on a cylindrical surface.

Let us consider the $(M,0)$ zigzag nanotube. To describe the position of the atoms in it, we take as the basis the four atoms labeled by numbers in Fig. 1a. Rotating those atoms by angles that are multiples of $\varphi=2\pi/M$ and translating along the axis of the nanotube by a vector $\mathbf{a}$ ($|\mathbf{a}|=3b$, where $b=0.142$ nm is the bond length), one can obtain the whole nanotube. The radius vector specifying the position of each atom in Cartesian coordinates can be written in the form

$$\mathbf{r}_{ns}^{l}=(R\cos(s\varphi+\delta_l),R\sin(s\varphi+\delta_l),na+b_l),$$
$$n=0,\pm 1,\pm 2,\ldots,\pm\infty,\quad s=0,1,\ldots,M-1,$$
$$l=0,1,2,3, \tag{1}$$

where $\delta_0=0$, $\delta_1=0$, $\delta_2=\varphi/2$, $\delta_3=\varphi/2$, $b_0=0$, $b_1=b$, $b_2=3b/2$, $b_3=5b/2$. Here the radius of the tube $R=(\sqrt{3}b/4)\sin^{-1}(\varphi/4)$.

The one-electron spectrum of this system will be modeled on the basis of the zero-range potential (ZRP) model.[7] The essence of this method is that the interaction of an elec-

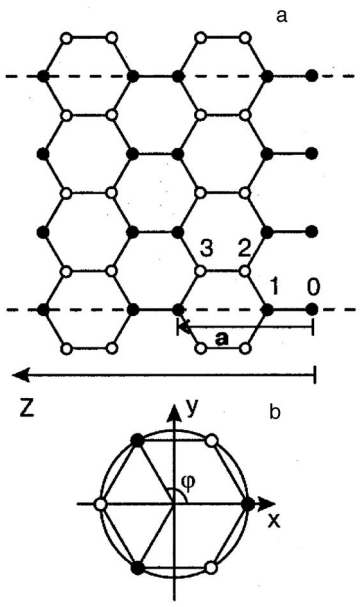

FIG. 1. a—The dashed lines bound a strip of the graphite plane that can be rolled to form a (3,0) zigzag nanotube; b—the transverse cross section of a (3,0) zigzag nanotube: the atoms are located at the vertices of a regular hexagon.

tron with the atoms of the lattice is taken into account by boundary conditions imposed on the wave function at the points where the atoms are located:

$$\lim_{\rho^l_{ns}\to 0}\left[\frac{\partial}{\partial\rho^l_{ns}}(\rho^l_{ns}\Psi)-\lambda\rho^l_{ns}\Psi\right]=0,\quad \rho^l_{ns}=|\mathbf{r}-\mathbf{r}^l_{ns}|, \tag{2}$$

where $\lambda=-\sqrt{(2\mu/\hbar^2)|E_0|}$ is the interaction parameter, which is expressed in terms of the effective mass μ of the carriers and interaction energy E_0 of an electron with an isolated atom. The model contains two parameters, the choice of which will be discussed below. At the other points of space the wave function satisfies the Schrödinger equation for a free particle:

$$-\frac{\hbar^2}{2\mu}\nabla^2\Psi=E\Psi. \tag{3}$$

We seek the wave function in the form

$$\Psi(\mathbf{r})=\sum_{l=0}^{3}\sum_{s=0}^{M-1}\sum_{n=-\infty}^{+\infty}A^l_{ns}\frac{e^{-\gamma|\mathbf{r}-\mathbf{r}^l_{ns}|}}{|\mathbf{r}-\mathbf{r}^l_{ns}|},\quad \gamma=\sqrt{-\frac{2\mu}{\hbar^2}E}. \tag{4}$$

Substituting this expression into the boundary conditions (2), we obtain a homogeneous system of algebraic equations for the coefficients A^l_{ns}:

$$(-\gamma-\lambda)A^j_{mi}+\sum_{\substack{n=-\infty\\ n\neq m}}^{-\infty}A^j_{ni}\frac{e^{-\gamma|\mathbf{r}^j_{mi}-\mathbf{r}^j_{ni}|}}{|\mathbf{r}^j_{mi}-\mathbf{r}^j_{ni}|}+\sum_{\substack{s=0\\ s\neq i}}^{M-1}\sum_{n=-\infty}^{+\infty}A^j_{ns}\frac{e^{-\gamma|\mathbf{r}^j_{mi}-\mathbf{r}^j_{ns}|}}{|\mathbf{r}^j_{mi}-\mathbf{r}^j_{ns}|}$$
$$+\sum_{\substack{l=0\\ l\neq j}}^{3}\sum_{s=0}^{M-1}\sum_{n=-\infty}^{+\infty}A^l_{ns}\frac{e^{-\gamma|\mathbf{r}^j_{mi}-\mathbf{r}^l_{ns}|}}{|\mathbf{r}^j_{mi}-\mathbf{r}^l_{ns}|}=0,$$

$$m=0,\pm1,\pm2,\ldots,\pm\infty,\ i=0,1,\ldots,M-1,$$

$$j=0,1,2,3. \tag{5}$$

In accordance with the symmetry of the system considered, we seek these coefficients in the form $A^l_{ns}=A^l_0e^{-ikna}e^{-i\varphi qs}$. As a result, system (5) reduces to a system of four equations:

$$H(\gamma,k,q)A^j_0+\sum_{\substack{l=0\\ l\neq j}}^{3}A^l_0E_{jl}(\gamma,k,q)=0,\quad j=0,1,2,3, \tag{6}$$

where

$$H(\gamma,k,q)=-\gamma-\lambda+\sum_{\substack{n=-\infty\\ n\neq 0}}^{-\infty}\frac{e^{-\gamma|n|a}}{|n|a}e^{ikna}$$
$$+\sum_{s=1}^{M-1}\sum_{n=-\infty}^{+\infty}\frac{e^{-\gamma\sqrt{(na)^2+2R^2[1-\cos(s\varphi)]}}}{\sqrt{(na)^2+2R^2[1-\cos(s\varphi)]}}e^{ikna}e^{i\varphi qs}, \tag{7}$$

$$E_{jl}(\gamma,k,q)=\sum_{s=0}^{M-1}\sum_{n=-\infty}^{+\infty}\frac{e^{-\gamma\sqrt{(na+b_j-b_l)^2+2R^2[1-\cos(s\varphi+\delta_j-\delta_l)]}}}{\sqrt{(na+b_j-b_l)^2+2R^2[1-\cos(s\varphi+\delta_j-\delta_l)]}}$$
$$\times e^{ikna}e^{i\varphi qs}. \tag{8}$$

We note that $E_{jl}=\bar{E}_{lj}$.

The condition of solvability of this system

$$\det\begin{pmatrix}H & E_{01} & E_{02} & E_{03}\\ \bar{E}_{01} & H & E_{12} & E_{02}\\ \bar{E}_{02} & \bar{E}_{12} & H & E_{01}\\ \bar{E}_{03} & \bar{E}_{02} & \bar{E}_{01} & H\end{pmatrix}=0 \tag{9}$$

at negative energies gives dispersion relations for the band states of the π electrons of the nanotube. Analogously one can obtain a dispersion relation for the (M,M) armchair nanotubes.

Solving Eq. (9) numerically, one can obtain the energies of the band states for various zigzag and armchair nanotubes (Fig. 2).

For choosing the parameters of the model we have used the experimental data from Ref. 11. One of the objects of study in that paper was the (15,0) zigzag tube, the electronic structure of which was studied by means of a scanning tunneling microscope. In that way the electronic density of states was successfully obtained. The small value of the band gap was not observed on account of the features of the method. However, the distance between the two adjacent peaks of the electronic density of states, lying on different sides of the Fermi level, was measured and found to be 1.9 eV. The fitting parameters of the model were chosen so as to make this distance in the model agree with the experimental result. As previously mentioned, the model contains only two parameters: the ionization energy of an isolated atom, E_0, and the bare mass μ of the carriers in the tube. When the bare mass was chosen equal to the mass of a free electron, agreement with the existing experiments could not be achieved by choice of the parameter E_0. Then the value of E_0 was taken equal to the known first ionization potential of

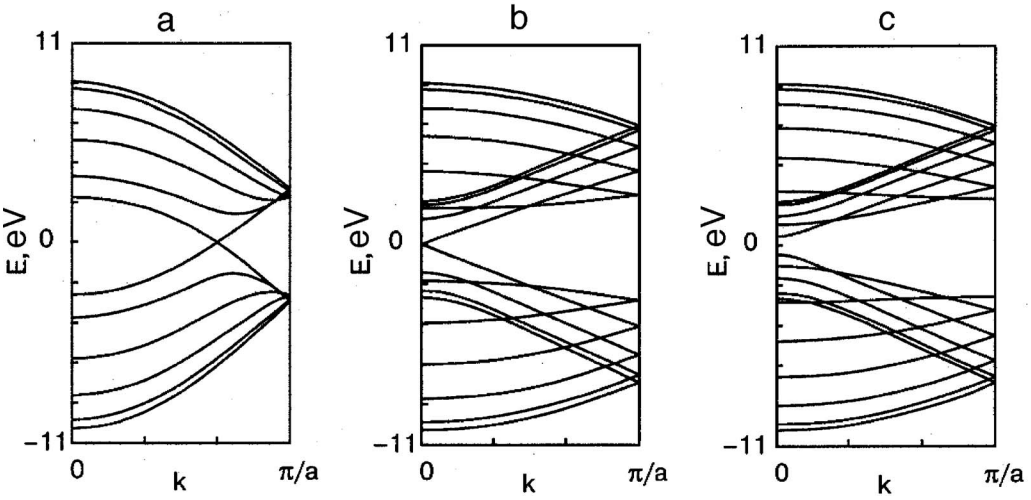

FIG. 2. Band structures of nanotubes: armchair (5,5) (a), zigzag (9,0) (b), zigzag (10,0) (c). The zero value of the energy is placed at the Fermi energy.

the carbon atom, 11.268 eV, in which case the bare mass was found to be $m_e/2.41$. These values of the parameters were used in a calculation of the electronic structure of different tubes. It is as yet not clear why the fitted value of the bare mass of the carriers in the tubes turns out to be less than the free electron mass.

On the basis of the dispersion relation (9) we obtained the electronic density of states for (9,0) and (10,0) zigzag nanotubes (Fig. 3). On the graphs one can clearly see the singularities corresponding to the band edges, thereby confirming the one-dimensional nature of the objects. In Fig. 3a, for the (9,0) zigzag tube, there is a doubled peak at the Fermi level, indicating the presence of a narrow band gap.

INFLUENCE OF THE CURVATURE OF THE TUBES ON THE WIDTH OF THE BAND GAP AND THE EFFECTIVE MASSES

In order to determine how the curvature influences the electronic structure of the nanotubes we used the zero-range potential method to obtain the dispersion relation for an infinite graphite plane. Then, following Ref. 1, periodic boundary conditions were imposed perpendicular to the axis of the nanotube, as a result of which the transverse component of the wave vector took on only a finite set of discrete values. As in Ref. 1, these values of the transverse wave vector were substituted into the dispersion relation for the graphite plane, yielding the dispersion relations for the bands of the nanotube. Obviously, in such an approach the curvature of the tubes cannot be fully taken into account. Because of this, in particular, the $(3N,0)$ tube turns out to be metallic in this approximation.

When the band structure calculation described above is applied directly to cylindrical tubes with their spatial structure taken completely into account, one obtains a certain shift of the energy bands for all the tubes, and, most importantly, a narrow gap appears at the position of the Fermi level in the $(3N,0)$ zigzag nanotube. The cause of its appearance was discussed in Refs. 1–4, where it was stated that the narrow band gap is a consequence of hybridization of the σ and π orbitals. However, in our model only the π electrons are considered, and the possibility of hybridization is not taken into account at all. Experimental studies[6] have shown the existence of a narrow band gap E_g=7.5–8 meV for a

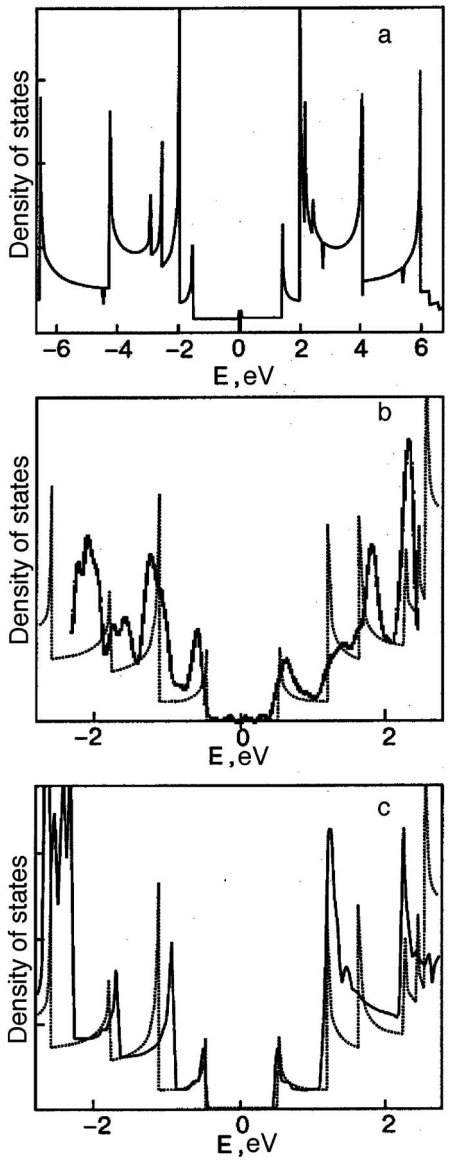

FIG. 3. Electronic density of states for (9,0) zigzag nanotubes, obtained by the ZRP method (a). A comparison of the graphs of the density of states of the (10,0) zigzag tube obtained by the ZRP method (dashed line) with the experimental data[8] (b) and with the data obtained by the LCAO method[10] (solid line) (c).

nanotube of diameter 1.3 nm. This result is in good agreement with the results of our calculations for the (15,0) tube ($d=1.18$ nm, $E_g=0.011$ eV) and the (18,0) tube ($d=1.41$ nm, $E_g=0.0077$ eV). Therefore the main cause of the appearance of a band gap is a purely geometric factor.

With the aid of Eq. (9) we have found the widths of the band gap for zigzag tubes of various diameters. Using the least-squares method, we have obtained the following dependence of the width of the band gap (in eV) on the diameter (in nm) of a $(3N+m,0)$ zigzag nanotube, $m=-1,0,1$:

$$E_g = \frac{C_1}{d}m^2 + \frac{C_2}{d^2}m + \left(\frac{C_3}{d^2} + \frac{C_4}{d^4}\right)(1-m^2), \tag{10}$$

where $C_1=0.823$, $C_2=0.044$, $C_3=0.0155$, $C_4=0.000575$.

Nanotubes with $m\neq 0$ are semiconductors with a relatively wide band gap that narrows in inverse proportion to the diameter d:

$$E_g = \frac{2\gamma b}{d} + O\left(\frac{1}{d^2}\right).$$

Comparing this last expression with the corresponding known expression, in which γ represents the overlap integral in the tight binding approximation, we see that for wide tubes of the type considered, the widths of the band gaps coincide with those obtained in the tight binding approximation if one sets $\gamma=2.79$ eV in that approximation. This value falls within the range of values 2.5–2.9 eV obtained theoretically and experimentally by various authors.[9,11–13]

Thus we have found the values of the effective masses m^* of the carriers at the bottom of the conduction band and top of the valence band, which, like the width of the band gap, decrease with increasing nanotube diameter. We have the following interpolation formulas:

$$\text{zigzag}(3N-1,0)\quad \frac{m^*}{m_e} = \frac{0.0845}{d} + \frac{0.0135}{d^2} + \frac{0.0130}{d^3},$$

$$\text{zigzag}(3N,0)\quad \frac{m^*}{m_e} = \frac{0.00149}{d^2} + \frac{0.0000838}{d^4},$$

$$\text{zigzag}(3N+1,0)\quad \frac{m^*}{m_e} = \frac{0.0815}{d} - \frac{0.0176}{d^2} + \frac{0.0021}{d^3}. \tag{11}$$

CONCLUSION

The simplest version of the zero-range potential method with a single universal fitting constant in application to π electrons of zigzag carbon nanotubes and without taking effects of σ-π hybridization into account turns out to be completely sufficient for a qualitative and satisfactory quantitative description of the observed electronic structure of such tubes, particularly near the gap separating the valence band and conduction band. Here it becomes clear that the appearance of a band gap $\sim$0.01 eV in the spectrum of $(3N,0)$ nanotubes is mainly determined by their geometric structure and not by effects of σ-π hybridization, was stated previously.[1–4,9] Furthermore, the results of this paper are in good agreement with a recent careful *ab initio* description of the electronic properties of single-walled nanotubes in the LCAO formalism.[10] It seems obvious that the results obtained with the aid of the proposed ZRP method should be of lower accuracy as compared to those obtained on the basis of the LCAO formalism with a large number of atomic orbitals taken into account. However, a juxta position with the available experimental data does not yet show this.

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