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Tight-binding model for carbon nanotubes from *ab initio* calculations

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Abstract

Here we present a parametrized tight-binding (TB) model to calculate the band structure of single-wall carbon nanotubes (SWNTs). On the basis of *ab initio* calculations we fit the band structure of nanotubes of different radii with results obtained with an orthogonal TB model to third neighbors, which includes the effects of orbital hybridization by means of a reduced set of parameters. The functional form for the dependence of these parameters on the radius of the tubes can be used to interpolate appropriate TB parameters for different SWNTs and to study the effects of curvature on their electronic properties. Additionally, we have shown that the model gives an appropriate description of the optical spectra of SWNTs, which can be useful for a proper assignation of SWNTs' specific chirality from optical absorption experiments.

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

1. Introduction

Since the discovery of carbon nanotubes by Iijima [1, 2] almost two decades ago, a large amount of theoretical work has been done [3–19] to study their physical properties. A complete review of the electronic and transport properties of carbon nanotubes can be found in the paper of Charlier *et al* [3]. The tight-binding (TB) model of π-bands using the zone-folding approximation has been widely used due to its simplicity, its low computational cost, and its good qualitative agreement with experimental results. To study the electronic structure of single-wall carbon nanotubes (SWNTs) in the TB approximation most authors take into account only the first neighboring interactions for hopping and overlap [4–6]. In general in TB calculations of SWNTs, the hopping and overlap parameters adopted are those corresponding to the graphene since they allow good qualitative results for band structure calculations, in particular for SWNTs of large diameter. The parameters are calculated from optical transition energies, scanning tunneling microscopy (STM), and first principle calculations. The STM measurements [24–26] give the local density of states and the gap energy of SWNTs. Theoretically it was found that the gap energy in the SWNTs depends on the diameter of the tube [7, 26], this dependence is given by $E_{\mathrm{gap}} = \frac{2\gamma_0 a_{\mathrm{cc}}}{d}$ or $E_{\mathrm{gap}} = \frac{3\gamma_0 a_{\mathrm{cc}}^2}{4d^2}$, for semiconductor or narrow gap SWNTs, where a_{cc} is the distance between carbon atoms, d is the nanotube diameter and γ_0 is the first-neighbor hopping. From these relations it is found that the first-neighbor hopping value is close to 2.7 eV; however, the rest of the parameters (next-neighbor hopping, overlaps, and site energy) remain unknown. To give a better quantitative description based on TB models several authors have extended the simple π-band model. Cao *et al* [11] used the TB sp3s* model for first neighboring interactions to calculate the electronic structure in $(n, 0)$ SWNTs with $n = 6, 7, 8, 9$. Valentin *et al* [12, 13] using a non-orthogonal TB 2s, 2p model studied the curvature effects on the electronic structure and optical absorption spectrum of SWNTs; they showed that in this model the absorption peak agrees with first-principle calculations. On the basis of *ab initio* calculations Reich *et al* [14] studied the band structure of isolated and bundled carbon nanotubes and discussed the limits of the graphene π-band TB model in describing the carbon nanotube bands. They [15] also made the TB parametrization for the graphene taking into account the interaction to third neighbors and fitting the graphene band structure to the calculated TB parameters. They used a different SIESTA basis to show the TB parameter dependence of the chosen basis. With such parametrization they showed that the TB model for third-nearest neighbors describes properly the π and π^* graphene bands. The electronic structure for SWNTs of large diameter within this model, is in very good agreement with *ab initio* calculations [16, 17].

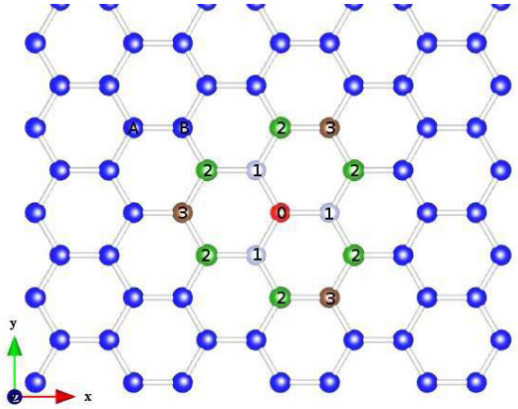

Figure 1. Schematic picture of a graphene sheet indicating the third-nearest neighbors of a carbon atom.

In the last two years it has been shown that curvature effects change the optical response of SWNTs [18, 19]. The SWNTs quirality is usually assigned from experimental data of optical absorption or Raman spectroscopy. However, this is made in an indirect way by using Kataura plots usually calculated in the approximation TB [20]. This makes the assigned chirality depend on the accuracy of the model employed. Motivated by the importance that an adequate knowledge of the TB parameters has in the study of the electronics and optical properties in SWNTs, we have used a modified TB model as proposed by Reich *et al* [15] to make a direct adjustment of the band structure of SWNTs. Our model has been improved using a direct fitting to our SIESTA to find the radius dependence of the different TB parameters. The model considers the hybridization effects caused for the SWNTs curvature by adapting the model of the TB π-band zone-folding, such that all the effects of hybridization are included in the radial dependence of the hopping, overlap, and site energy parameters. The density-functional-theory (DFT) band structure was calculated using the code SIESTA [21].

2. Theory

The electronics properties of SWNTs are studied in the zone-folding approximation of graphene using the third-nearest-neighbor TB model, taking into account only the contribution of the orbital π. Figure 1 displays a schematic picture of a graphene sheet indicating the third-nearest neighbors of a carbon atom. The eigenvalue problem for the TB Hamiltonian is given by

$$\widehat{H}\Psi^n_{\mathbf{k}}(\mathbf{r}) = E^n_{\mathbf{k}}\Psi^n_{\mathbf{k}}(\mathbf{r}) \tag{1}$$

where

$$\Psi^n_{\mathbf{k}}(\mathbf{r}) = \sum_i C^n_{i,\mathbf{k}}\chi_{\mathbf{k},i}(\mathbf{r}), \tag{2}$$

$\mathbf{k}$ is the wavevector and i denotes different atomic species. The function $\chi_{\mathbf{k},i}$ satisfies the Bloch theorem such that

$$\chi_{\mathbf{k},i}(\mathbf{r}) = \frac{1}{\sqrt{N}}\sum_{\mathbf{R}_i} e^{i\mathbf{k}\cdot\mathbf{R}_i}\phi(\mathbf{r}-\mathbf{R}_i). \tag{3}$$

Here $\phi(\mathbf{r}-\mathbf{R}_i)$ are the atomic orbitals for all sites in the lattice and $\mathbf{R}_i$ is the position vector of the different sites. Taking only the π orbital for both carbon atoms in the graphene unit cell we have

$$\begin{pmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{pmatrix}\begin{pmatrix} C^n_{\mathbf{k},A} \\ C^n_{\mathbf{k},B} \end{pmatrix} = E^n_{\mathbf{K}}\begin{pmatrix} S_{AA} & S_{AB} \\ S_{BA} & S_{BB} \end{pmatrix}\begin{pmatrix} C^n_{\mathbf{k},A} \\ C^n_{\mathbf{k},B} \end{pmatrix}. \tag{4}$$

By considering third-nearest-neighbor interaction, each element of the matrix is given by

$$H_{AA} = E_{2p_z} + \gamma_1\sum_{\mathbf{d}_2} e^{-i\mathbf{k}\cdot\mathbf{d}_2} \tag{5}$$

$$H_{AB} = \gamma_0\sum_{\mathbf{d}_1} e^{i\mathbf{k}\cdot\mathbf{d}_1} + \gamma_2\sum_{\mathbf{d}_3} e^{-i\mathbf{k}\cdot\mathbf{d}_3} \tag{6}$$

$$S_{AA} = 1 + S_1\sum_{\mathbf{d}_2} e^{-i\mathbf{k}\cdot\mathbf{d}_2} \tag{7}$$

$$S_{AB} = S_0\sum_{\mathbf{d}_1} e^{i\mathbf{k}\cdot\mathbf{d}_1} + S_2\sum_{\mathbf{d}_3} e^{-i\mathbf{k}\cdot\mathbf{d}_3}. \tag{8}$$

The rest of the elements satisfy $H_{BB} = H_{AA}$, $H_{BA} = H^*_{AB}$, $S_{BB} = S_{AA}$, and $S_{BA} = S^*_{AB}$. Here $\mathbf{d}_1$, $\mathbf{d}_2$, and $\mathbf{d}_3$ correspond to the distances to the first, second, and third neighbor, respectively. The fitted parameters obtained with the DFT band structure calculations are: γ_0, γ_1, γ_2, S_0, S_1, S_2, and E_{2p_z}, where

$$\gamma_i = \langle\phi_0|\hat{H}|\phi_i\rangle \tag{9}$$

$$S_i = \langle\phi_0|\phi_i\rangle. \tag{10}$$

To calculate the optical absorption spectrum we use the dipolar approximation, in which the absorption coefficient is given by

$$\alpha = \frac{\alpha_0}{\hbar\omega}\sum_{i,f}|\langle f \mid H_{Re} \mid i\rangle|^2\delta(E_f - E_i - \hbar\omega) \tag{11}$$

where

$$H_{Re} = -e\mathbf{E}\cdot\mathbf{r}. \tag{12}$$

The dipolar matrix can be written as [22]

$$\langle f \mid H_{Re} \mid i\rangle = \sum_{\mathbf{b}_l,i,i'} C^{c*}_{i'}C^v_i \exp(i\mathbf{k}\cdot\mathbf{b}_l)\mathbf{b}_l \times \langle\phi(\mathbf{r}) \mid H \mid \phi(\mathbf{r}-\mathbf{b}_l)\rangle, \tag{13}$$

where $\mathbf{b}_l$ corresponds to the position vector of the carbon atoms to third neighbors.

3. Results

The *ab initio* calculations of the electronic structure of graphene and SWNTs were performed using the generalized gradient approximation (GGA) for the exchange correlation potential using the Perdew, Burke, and Ernzerhof (PBE) [23] parametrization together with norm-conserving pseudopotentials. We used the SIESTA code with atomic bases DZP, $E_{\text{cut}} =$ 270 Ryd, and we used Monkhorst–Pack k points originating at the Γ point $1\times1\times50$ for all structures. The structures are fully relaxed using the gradient conjugate algorithm with a tolerance of 0.02 eV Å^{-1}, we obtain for zigzag carbon nanotubes a lattice constant of 4.36 Å.

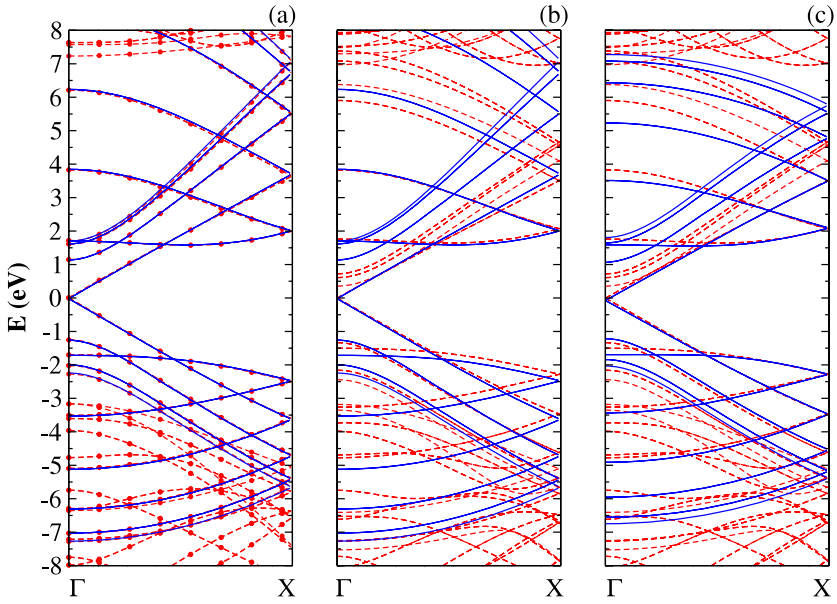

Figure 2. *Ab initio* and third-nearest-neighbor π-band TB dispersions of a (9, 0) SWNT. (a) DFT calculations in the graphene zone-folding approximation (red dashed line with dot symbols) and TB calculations (blue full line). (b) DFT calculations for the nanotube (red dashed line) and TB calculations (blue full line) combined with zone-folding. (c) DFT calculations for the nanotube (red dashed line) and TB calculations (blue full line) using the direct parametrization of the band structure obtained from DFT calculations.

Table 1. Direct fitting of TB parameters from graphene.

	i		
Parameter	0	1	2
γ_i	−2.7354	−0.9149	−0.2722
S_i	0.3749	0.0373	0.0097
E_{2p}	−2.7639	−2.7639	−2.7639

Table 2. Set of coefficients a_i in equation (14) for fitting the radius dependence of the different TB parameters.

Parameter	a_1	a_2	a_3	a_4
γ_0'	−0.52	4.95	−17.46	19.37
γ_1'	−1.62	29.95	−185.02	271.74
S_0'	−1.24	23.22	−149.13	220.26
E_{2p}'	−2.41	37.19	−205.29	290.34

In table 1 we show the TB parameters fitted from the graphene bands. In figure 2 we display the band structure for a (9, 0) SWNT obtained by *ab initio* and third-nearest-neighbor π-band TB dispersions. In all plots the *ab initio* calculations are shown by (red) dashed lines and TB bands are shown by (blue) full lines. Figure 2(a) displays the DFT calculations in the graphene zone-folding approximation (dots symbols) and TB calculations using the graphene parameters from table 1. We observe that under this approximation the *ab initio* calculations for bands π and π^* are very well reproduced by the third-nearest-neighbor TB model. However, beyond the zone-folding approximation taking into account the curvature effects in the DFT calculations, the third-nearest-neighbor TB model, with the graphene parameters of table 1, does not give a good description of the band structure of a (9, 0) SWNT. This case is shown in figure 2(b) where it is possible to observe in the *ab initio* band structure the σ–π hybridization induced by the nanotube curvature. The hybridization caused a shift in the bands structure, this effect is more noticeable in zigzag tubes than armchair tubes, as discussed in [14].

In order to get a better quantitative agreement with *ab initio* results we have tested a direct fitting of the TB parameters with the DFT calculated band structure of the nanotube. Figure 2(c) displays the TB dispersions obtained with this set of parameters and the corresponding DFT calculations (red dashed lines). The agreement for π bands is very good and it improves for tubes of larger radius, as can be observed in figures 3 and 4 which display the comparison between TB and DFT results for several $(n,\ 0)$ SWNTs. In all cases the agreement is excellent for almost the entire Brillouin zone.

We have investigated the dependence of TB parameters on the nanotube radius and we noticed that this dependence occurs mainly for the TB parameters γ_0, γ_1, S_0, and E_{2p}. In figure 5 we have plotted the dependence of these parameters on the radius of different SWNTs. We found that the radius dependence of hopping, site energy, and overlap parameters can be fitted with a fifth-degree polynomial:

$$f_i'(R) = f_i(1 + a_1x + a_2x^2 + a_3x^3 + a_4x^4), \qquad (14)$$

where f_i represents the TB parameter for graphene (table 1) and $x = \frac{a_{cc}}{R}$, with a_{cc} the distance between carbon atoms in the graphene layer. In table 2 we show the set of coefficients a_i.

To check whether this fitting works for other SWNTs we calculate the TB electronic energy dispersion in the third-nearest-neighbor approximation for armchair nanotubes of different radii with TB parameters calculated using equation (14), and compare this with the corresponding

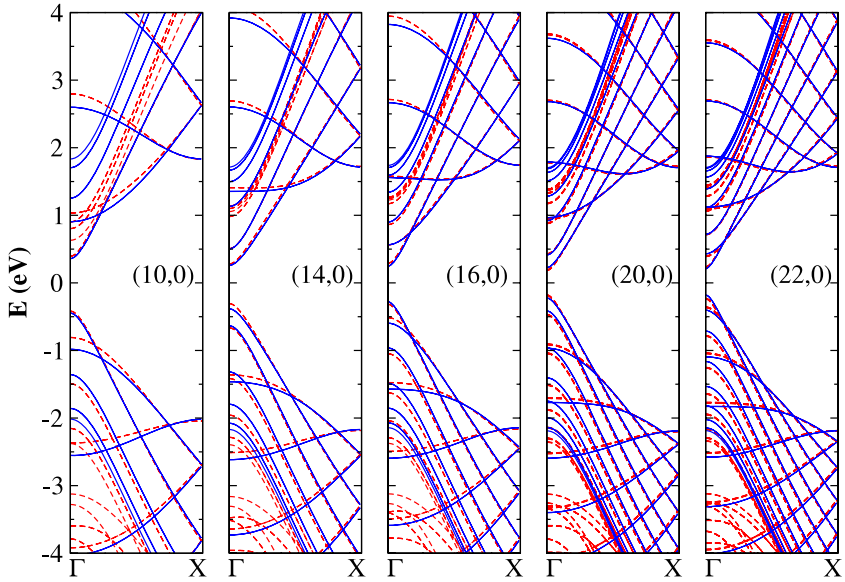

Figure 3. *Ab initio* and third-nearest-neighbor TB band structure of (10, 0), (14, 0), (16, 0), (20, 0), and (22,0) zigzag SWNTs. The solid lines correspond to TB calculations, dashed lines show the DFT calculations.

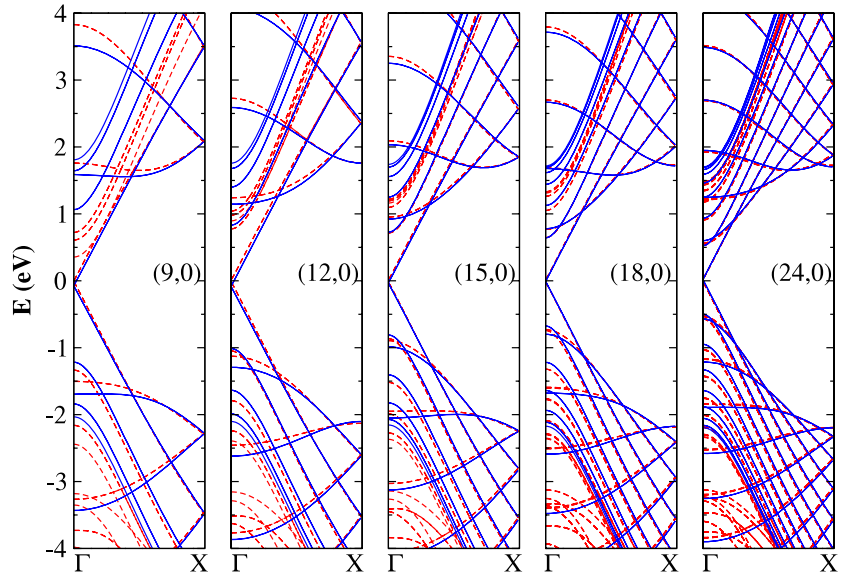

Figure 4. *Ab initio* and third-nearest-neighbor TB band structure of (9, 0), (12, 0), (15, 0), (18, 0), and (24, 0) zigzag SWNTs. The solid lines correspond to TB calculations and dashed lines show the DFT calculations.

ab initio calculations. In figure 6 we have displayed results for the band structure of (5, 5), (7, 7), (9, 9), and (15, 15) SWNTs. We observe excellent agreement in particular for the range of k values around the K point.

In order to apply our model to study optical properties of SWNTs we have calculated the optical absorption coefficient as a function of the photon energy using *ab initio* calculations and we have compared this with the corresponding calculations performed using the first- and third-nearest-neighbor TB approximation. In figure 7 we show results of the absorption coefficient for (a) (9, 0) and (b) (18, 0) SWNTs calculated using the TB parametrization proposed in this work. The inset shows the absorption spectrum obtained by DFT calculations. Red broken lines show the results calculated with a first-neighbor TB model. It is clear that the simple first-neighbor TB model does not display well the main features of the absorption spectrum obtained by first-principles calculations. The agreement obtained with our parametrized third-neighbor TB model is very good both in the position and the shape of the resonances, in particular for the wider (18, 0) SWNTs of figure 7(b). The main differences between the absorption spectra occur in the region between 3 and 5 eV where TB models display three absorption peaks while the DFT spectrum shows only two resonances. This is because we have chosen the K point to make the fitting of the TB parameters and therefore the bands near the Fermi level are represented with less accuracy by the TB model.

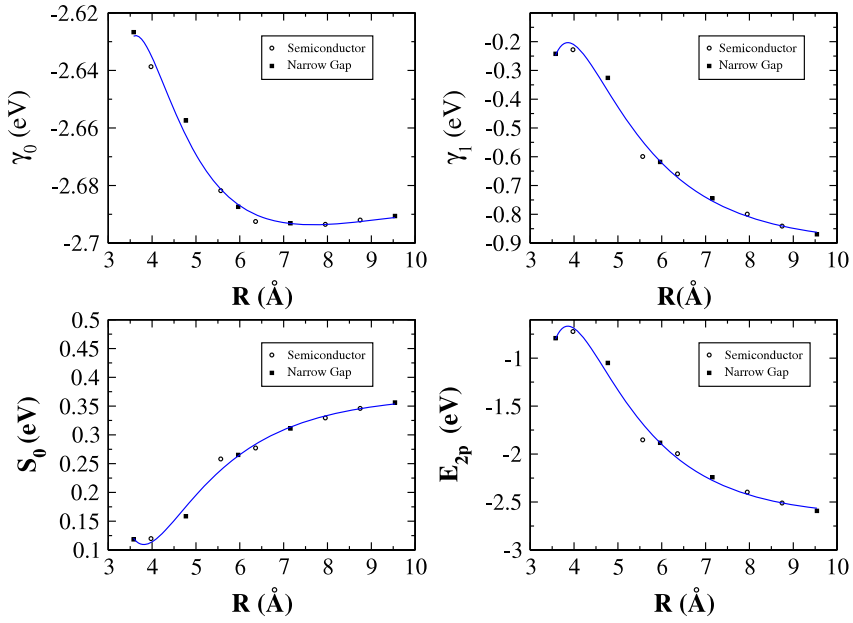

Figure 5. Dependence of γ_0, γ_1, S_0, and E_{2p} TB parameters on the nanotube radius.

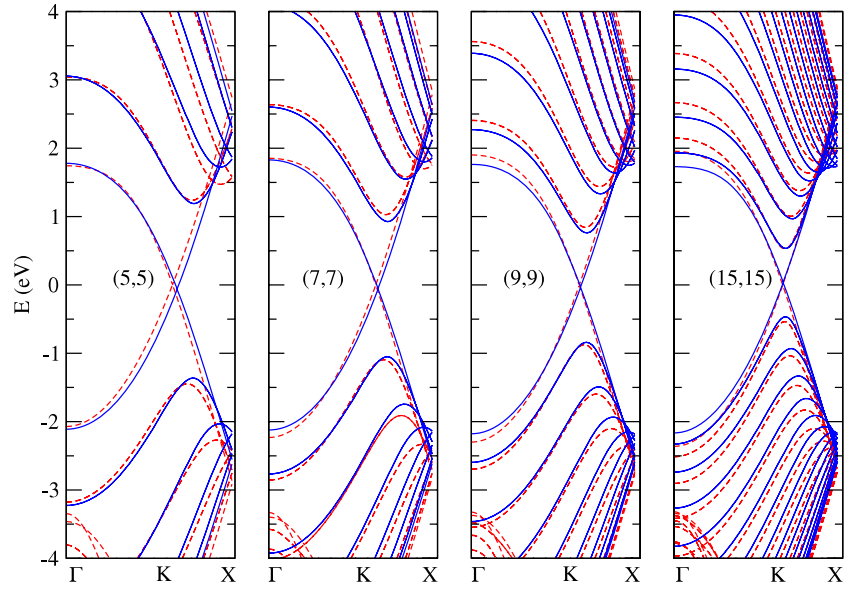

Figure 6. *Ab initio* and third-nearest-neighbor TB band structure of (5, 5), (7, 7), (9, 9), and (15, 15) armchair SWNTs. The solid lines correspond to TB calculations with parameters obtained from equation (14) and dashed lines correspond to DFT calculations.

Finally, in figure 8 we show (a) the band structure, (b) the optical absorption spectrum, and (c) the dipolar matrix elements for SWNT (10, 10), calculated with our third-nearest-neighbor TB model. We have found excellent agreement by comparing the transition energies with previously obtained DFT results. An example is the transition $e1$ whose absorption peak is at 1.49 eV, which is comparable with the value of 1.52 eV reported in [27] and the value of 1.59 eV reported in [28]. Also, figure 8(c) for the dipole matrix shows the same behavior as previous results obtained by first-neighbor TB models and DFT calculations [29, 30].

4. Summary

An adequate knowledge of TB parameters is of great importance for a good description of the electronic structure of nanostructures. However, in the case of carbon nanotubes the inclusion of curvature effects would involve too many TB parameters to give an adequate description in a wide range of energies. Our parametrization using an orthogonal TB model to third neighbors includes the effects of orbital hybridization by means of a reduced set of parameters. The functional form for the dependence of these parameters with the radius of the tubes can be used to interpolate appropriate TB parameters

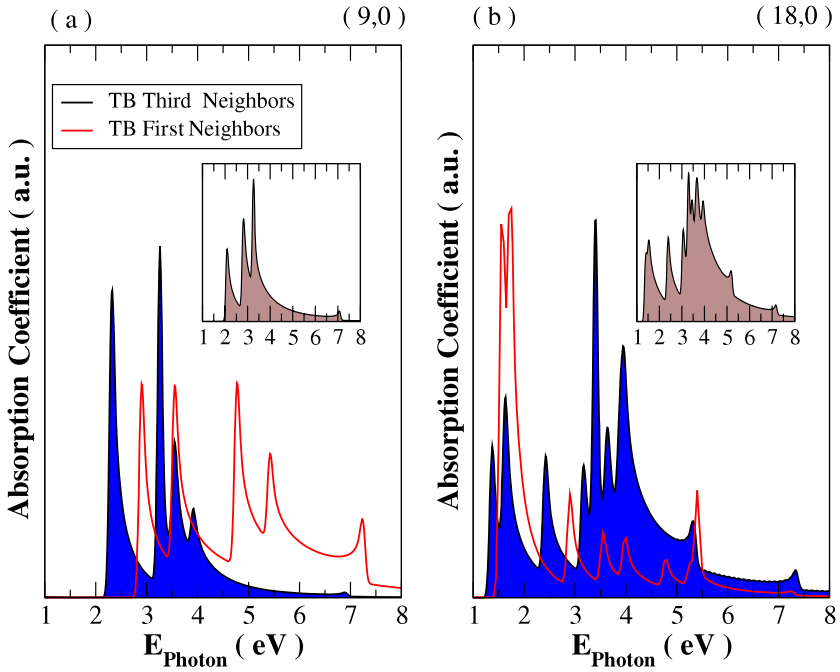

Figure 7. Optical absorption spectrum as a function of photon energy for (a) (9, 0) and (b) (18, 0) SWNTs.

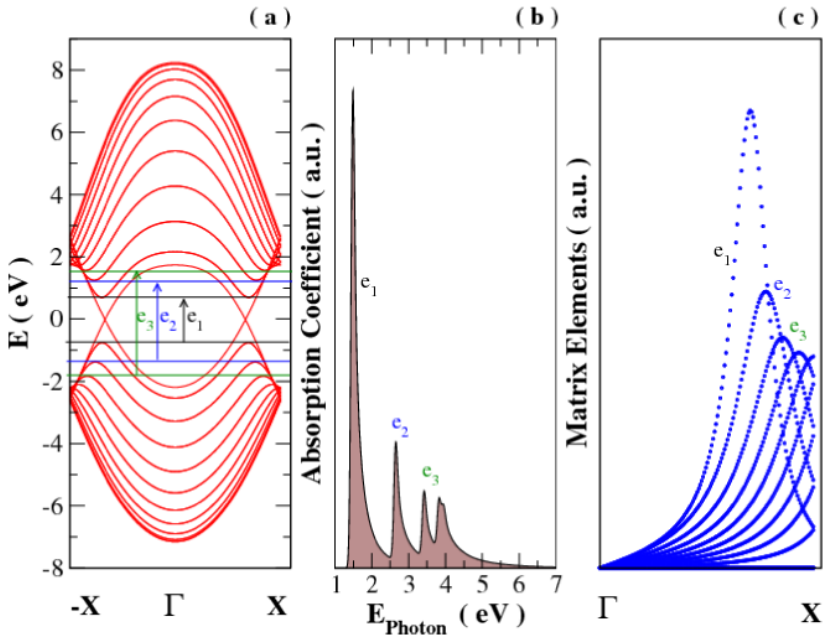

Figure 8. (a) Band structure, (b) optical absorption spectrum, and (c) dipolar matrix elements for a (10, 10) SWNT.

for different SWNTs and to study the effects of curvature on their electronic properties. Additionally it is shown that the model gives an appropriate description of the optical spectra of SWNTs, which can be useful for a proper determination of the SWNTs' chirality in optical absorption experiments.

Acknowledgments

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