Tight-binding and $\vec{k} \cdot \vec{p}$ methods in carbon nanotubes: features, comparison and improvements

Paolo Marconcini · Massimo Macucci

Published online: 9 December 2006
© Springer Science + Business Media, LLC 2007

Abstract We use the tight-binding and the $\vec{k} \cdot \vec{p}$ methods to compute the energy dispersion relations and the density of states of carbon nanotubes, comparing the obtained results and pointing out the advantages and the drawbacks of the two techniques. We discuss a numerical method to easily obtain with the tight-binding technique only the most interesting energy bands, introducing an unusual but convenient choice of graphene unit vectors.

Keywords Carbon nanotubes · Graphene · Energy bands · Tight-binding · $\vec{k} \cdot \vec{p}$ method · Unit vectors

1 Introduction

Carbon nanotubes, discovered in 1991 by Iijima [1], are a very promising material for nanoelectronic applications, due to their very small size, high mechanical strength and thermal conductivity, and unusual electronic properties (indeed they can behave both as a metallic material and as a semiconducting material, depending on their geometrical features).

From the electronic point of view, the first step for the analysis of their transport behavior is the computation of the energy dispersion relations. This can be done both with global methods, like the tight-binding technique, which yield results in the complete reciprocal space, and with local methods, like the $\vec{k} \cdot \vec{p}$ method, which allow to obtain the correct relations only around the maxima and minima of the energy bands, but with less computational effort.

2 Numerical methods

A carbon nanotube can be described as a graphene sheet rolled along one of its translational vectors $\vec{C}_h$ (the chiral vector), into a cylindrical shape. Its energy dispersion relations can therefore be found from the ones of graphene enforcing the periodic closure relation along the chiral vector. This condition determines a discretization of the component along $\vec{C}_h$ of the graphene wave vectors, which has to be equal to integer multiples of $2\pi/L$ (with $L = |\vec{C}_h|$).

The computation of the energy bands of a carbon nanotube is therefore recast into the calculation of the graphene dispersion relations. The numerical results that we show have been obtained under some simplifying hypotheses. In particular, we have neglected the effects of the curvature of the nanotube and we have considered only one atomic orbital for each carbon atom, as well as the effect on each carbon atom only of its nearest-neighbors.

Graphene is a two dimensional lattice, characterized by two unit vectors $\vec{a}_1 = (\sqrt{3}a/2)\hat{x} + (a/2)\hat{y}$ and $\vec{a}_2 = (\sqrt{3}a/2)\hat{x} - (a/2)\hat{y}$; its unit cell contains two inequivalent carbon atoms $A$ and $B$ ($\hat{x}$ is taken along the line joining the two nearest-neighbor atoms $A$ and $B$, and $(\hat{x}, \hat{y})$ is a right-hand orthonormal reference frame).

A tight-binding study of the graphene energy bands has been carried out by Wallace [2] and (more recently) by Saito...
et al. [3]. The graphene electron wave function can be written as linear combination of two Bloch functions \( \Phi_j(\vec{k}, \vec{r}) \) (with \( j = A, B \)) given by a proper weighted sum of the atomic orbitals of all the atoms of the \( j \)-th type in the lattice [3]. The minimization of the energy of the structure leads to the secular equation \( \det[H - ES] = 0 \), where \( H \) and \( S \) are the transfer integral matrix and the overlap integral matrix (both \( 2 \times 2 \) matrices), respectively, with elements \( H_{ij} = \langle \Phi_j | \hat{H} | \Phi_i \rangle \) (\( \hat{H} \) is the Hamiltonian operator) and \( S_{ij} = \langle \Phi_j | \Phi_i \rangle \). In particular, if one considers only the interaction between nearest-neighbor atoms, we obtain, around the values of the envelope functions at distances equal to the overlap integral and assuming \( K \) along the chiral vector and the axis of the nanotube, respectively and an analogous equation around \( K' \), with the only difference that the plus and minus signs in the l.h.s. are interchanged.

The matrices appearing in the equations represent the \( \vec{k} \cdot \vec{p} \) Hamiltonian matrices for the envelope functions, the eigenvalues of which are the dispersion relations \( E(\vec{k}) = \pm \sqrt{\gamma_0 \omega(\vec{k})} \) (with \( \gamma = (\sqrt{3}/2)\gamma_0 a \), where \( a = |\vec{a}_1| = |\vec{a}_2| \)).

The dispersion relations of carbon nanotubes are obtained by sectioning the graphene energy bands along segments parallel to the nanotube axis and distant \( 2\pi/L \) from each other and folding them onto the Brillouin zone of the nanotube, which corresponds to the segment on the nanotube axis going from \(-\pi/2\) to \( \pi/2 \) (\( L \) is the length of the nanotube unit cell, which repeats along the nanotube axis, i.e. in the \( T \) direction). This is done in a region of the reciprocal space containing all and only the inequivalent graphene wave vectors, which is usually taken as the rectangular zone (Fig. 1) with an edge coincident with the nanotube Brillouin zone and extending for \( N(2\pi/L) \) along the direction of the chiral vector \( N \) is the number of graphene unit cells inside a nanotube unit cell), in order to easily obtain the projection on the nanotube Brillouin zone.

Once the nanotube dispersion relations have been found, the density of states per unit length and per unit energy interval can be obtained numerically with the following differentiation:

\[
\rho(E_0) = \frac{1}{\pi} \sum_{\nu} \sum_{i:E_i(k_i)=E_0} \frac{1}{|\partial E_i/\partial k_i|}
\]

where the \( k_i \)'s are the values of the wave vector in correspondence of which the \( \nu \)-th band \( E_i(k) \) of the nanotube assumes the value \( E_0 \). In particular, when we use the \( \vec{k} \cdot \vec{p} \) method the analitical differentiation of the dispersion relations gives the following formula proposed by Mintmire and White [5] (which is indeed based on such an approximation of the energy bands near their extrema):

\[
\rho(E_0) = \frac{4}{\pi \gamma} \sum_{\nu} g(E_0, \varepsilon_\nu)
\]

with \( g(E_0, \varepsilon_\nu) = |E_0|/\sqrt{E_0^2 - \varepsilon_\nu^2} \) if \( |E_0| > |\varepsilon_\nu| \) and \( g(E_0, \varepsilon_\nu) = 0 \) if \( |E_0| < |\varepsilon_\nu| \) (\( \varepsilon_\nu \) is the extremum of the \( \nu \)-th band). Therefore in the case of the \( \vec{k} \cdot \vec{p} \) method we can directly use this expression.

In the inset of Fig. 1 we show, for example, the graphene energy bands obtained assuming \( s = 0 \) and \( \gamma_0 = 3.033 \) eV.

Fig. 1 The rectangular zone and the graphene Brillouin zone where we can take the cross-sections ((10, 0) nanotube). In the inset we show the graphene dispersion relations.
Fig. 2 Energy dispersion relations (upper panels) and density of states (lower panels) of the (6, 0) (left panels), (5, 0) (central panels) and (10, 0) nanotube (right panels): the first one is metallic, while the other two are semiconducting. The solid curves have been obtained with the tight-binding method, while the dashed ones are results from the \( \vec{k} \cdot \vec{p} \) technique. With the latter method we have computed only the bands (three for the metallic nanotube, four for the semiconducting ones) nearest to each graphene degeneration point.

3 Results, comparison and optimization

In Fig. 2 we show the results obtained using the two methods for nanotubes with different electronic properties and values of the circumference \( L \) (notice that for a nanotube \((n, 0)\) we have that \( L/a = n \)). In particular, the energy bands obtained with the \( \vec{k} \cdot \vec{p} \) method (computed as a function of the component along the nanotube axis of the relative graphene wave vector \( \vec{\kappa} \)) can be easily represented in terms of the component along the nanotube axis of the absolute graphene wave vector \( \vec{k} \), noting that for the nanotube \((n, m)\) the projections on the nanotube Brillouin zone of the graphene degeneration points can be only 0 or \( \pm 2\pi/3T \), depending on the value of \( n \) and \( m \) [3].

As one could expect, the tight-binding and the \( \vec{k} \cdot \vec{p} \) methods give similar results for the bands obtained cross-sectioning the graphene dispersion relations near their maximum and minimum points, where the \( \vec{k} \cdot \vec{p} \) approximation of the graphene energy bands is supposed to be valid. The first nanotube shown in Fig. 2 is metallic, since two of the cross-sections pass through the degeneration points of graphene, while the second and the third one are semiconducting, because the sections nearest to the graphene degeneration points pass at distances \( 1/3(2\pi/L) \) and \( 2/3(2\pi/L) \) from these points. Therefore, if we consider only the nanotube energy bands obtained taking the cross-sections nearest to the points \( \vec{K} \) and \( \vec{K}' \) (or equivalent ones) it is evident that the \( \vec{k} \cdot \vec{p} \) approximation gives the best results in the case of metallic nanotubes, and in the case of semiconducting nanotubes the approximation of the nearest cross-sections is better for nanotubes with larger circumferences \( L \) (such as \((10, 0)\)).

Analogously, the density of states obtained with the tight-binding and the \( \vec{k} \cdot \vec{p} \) methods is similar for small values of the energy.

In our simulations, the \( \vec{k} \cdot \vec{p} \) method turns out to be faster than the tight-binding technique. Indeed, the \( \vec{k} \cdot \vec{p} \) expression is simpler than the tight-binding one. Moreover the allowed graphene wave vectors are easily selected using the (discretized) component along the chiral vector and the (non discretized) component along the nanotube axis; such components have to be converted into the components along the \( x \) and \( y \) axis to use the tight-binding expression, while this is not necessary to obtain the \( \vec{k} \cdot \vec{p} \) result.

Another advantage of the \( \vec{k} \cdot \vec{p} \) method is due to the fact that we are generally interested only in the conduction bands containing the lowest energy values and in the valence bands containing the highest energy values because these are the bands populated by the charge carriers of the nanotube. Since the \( \vec{k} \cdot \vec{p} \) graphene dispersion relations are computed as a function of the wave vectors \( \vec{k} \) considered relatively to the graphene degeneration points, the natural choice (which we have followed also in our simulations) is to compute only the \( \vec{k} \cdot \vec{p} \) energy bands corresponding to the smallest absolute values of the discretized component along \( \hat{C}_h \) of \( \vec{k} \), thus obtaining the most interesting (and most exactly reproduced) bands. This suggests a correspondent optimization for the tight-binding method, that however, for its own nature, is not directly suitable for such a selection of the energy bands. In particular, to compute only the most interesting bands it is necessary to find the wave vectors equivalent to \( \vec{K} \) and \( \vec{K}' \) inside the region of the graphene reciprocal space where we take the cross-sections.
If we take the cross-sections inside the rectangular zone having an edge coincident with the nanotube Brillouin zone and extending $N(2\pi/L)$ along the $\hat{C}_h$ direction, to find the wave vectors equivalent to $\vec{K}$ and $\vec{K}'$ inside the zone it is useful to introduce a particular choice of the graphene unit vectors [6]. In detail, we can consider as unit vectors in the direct space (instead of $\vec{a}_1$ and $\vec{a}_2$) the symmetry vector $\vec{R} = p\vec{a}_1 + q\vec{a}_2$ (normally used to define all the graphene lattice points inside the nanotube unit cell) and the translational vector $\vec{T} = t_1\vec{a}_1 + t_2\vec{a}_2$ of the nanotube (the unit vector of the nanotube) [3]. The correspondent unit vectors in the reciprocal space are $\vec{b}_A = N\vec{K}_1$ (an edge of the rectangular zone) and $\vec{b}_B = -M\vec{K}_1 + \vec{K}_2$ (with component along the nanotube axis equal to the other edge of the rectangular zone), where $\vec{K}_1 = (2\pi/L)\hat{C}_h$, $\vec{K}_2 = (2\pi/T)\hat{T}$ and $M = mp - nq$. Since all the wave vectors equivalent to $\vec{K}$ (and $\vec{K}'$) are obtained adding a linear combination with integer coefficients of $\vec{b}_A$ (which has a zero component along $\hat{T}$) and $\vec{b}_B$, it is immediate to find, from the components along $\hat{T}$ and $\hat{C}_h$ of $\vec{K}$ (and $\vec{K}'$), first the number of vectors $\vec{b}_B$ and then the number of vectors $\vec{b}_A$ to be added to $\vec{K}$ (and $\vec{K}'$) to obtain the equivalent wave vector inside the rectangular zone. We have then limited the tight-binding computation to the only cross-sections nearest to the equivalent wave vectors found with this method, significantly reducing the computational time.

Alternatively, we can change the region in which the cross-sections are taken: if we take them (instead of inside the above mentioned rectangular zone) inside the hexagonal Brillouin zone of graphene (Fig. 1), the position of the graphene degeneration points is known, since they are located at the vertices of the hexagon. The computation can therefore be limited to the zones around such vertices. Nevertheless, in this case the computational time is increased by the fact that now each cross-section of the region is not projected onto the nanotube Brillouin zone simply considering the component of each wave vector along the nanotube axis, but has to be folded onto the nanotube Brillouin zone in a more computationally expensive way, subdividing each section in sub-sections to be folded separately. Moreover, being the graphene degeneration points on the border of the hexagonal zone, we have necessarily to consider the cross-sections inside all the six regions near the vertices of the hexagon.

Finally, we notice that the proposed optimization can be applied, with even greater advantage, also in cases in which the tight-binding calculation is performed considering more atomic orbitals for each carbon atom [3] or the effect on each atom of atoms more distant than the nearest-neighbor ones [7].

We acknowledge financial support from the Italian Ministry of Education, University and Research (MIUR) through the FIRB project “Nanotechnologies and Nanodevices for the Information Society”.

References