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Research Article

A Model Based on LCAO Theory to Evaluate the Dispersion Equation of Carbon Nanotubes

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ABSTRACT

In this paper we propose a model to evaluate the dispersion relationship of Carbon Nanotubes. The model is based on the application to band-structure calculation of both of them the tight-binding approximation and the theory of Linear Combination of Atomic Orbitals (LCAO), obtaining a reduction of computational time compared to other methods proposed in literature, without losing in accuracy.

1. INRODUCTION

Due to their low dimensionality, nano-structures such as quantum dots, nanowires and carbon nanotubes (CNTs) possess unique properties that make them promising candidates for future technology applications

[1-11]. However, to truly harness the potential of nanostructures, it is essential to develop a fundamental understanding of the basic physics that governs their behaviour in devices. This is especially true for CNTs, where research has shown that the concepts learned from bulk device physics do not simply carry over to nanotube devices, leading to unusual device operation. For example, the properties of bulk metal/semiconductor contacts are usually dominated by Fermi level pinning; in contrast, the quasi-one-dimensional structure of nanotubes leads to a much weaker effect of Fermi level pinning, allowing for tailoring of contacts by metal selection. Similarly, while strain effects in conventional silicon devices have been associated with mobility enhancements, strain in CNTs takes an entirely new perspective, with strain-induced bandgap and conductivity changes.

CNTs also present a unique opportunity as one of the few systems where atomistic based modelling may reach the experimental device size, thus in principle allowing the experimental testing of computational approaches and computational device design. While similar approaches are under development for nanoscale silicon devices, the much different properties of CNTs require an entirely separate field of research [12-15].

In this paper a procedure to determine the dispersion relationship of the Carbon NanoTubes (CNT) is proposed. The method is based on the application to band-structure calculation of both of them the tight-binding approximation and the theory of Linear Combination of Atomic Orbitals (LCAO), obtaining a reduction of computational time compared to other methods proposed in literature [16-18], without losing in accuracy.

The presentation is organized as follows: in Section 2 we describe briefly the CNTs structure, while Section 3 gives a description of the proposed model. The conclusions are reported in Section 4.

2. STRUCTURE PARAMETERS OF CNT

A CNT is a sheet of hexagonal arranged carbon atoms rolled up in a tube of a few nanometers in diameter, which can be many microns long. Graphene is a single sheet of carbon atoms arranged in the well known honeycomb structure [19-21]. Carbon has four valence electrons, three of which are used for the sp^2 bonds. In sp^2-hybridization an electron is promoted from the 2*s*-orbital to a *p*-orbital, and then two electrons from different 2*p*-orbitals combine with the single electron left in the 2*s*-orbital to generate three equivalent sp^2-orbitals. These orbitals are planar with 120^o between the major lobes, and the remaining *p*-orbital is perpendicular to this plane. The leftover *p*-orbital is perpendicular to the graphene, and electrons in this orbital bond to other carbon atoms through weak π-bonds. The electrons in the *p*-orbitals are thus loosely bound and responsible for the conductance of graphite. Since the CNT is made up of one or more sheets of graphene rolled up in a tubular structure, the binding in the CNT is nearly identical to that of graphite. The differences in binding are due to the larger inter-shell distance in CNT compared to the interlayer distance of graphite, and the curvature of the graphene sheets.

3. MODELLING

The conductance of most periodic solids can be explained in terms of the tight binding approximation [1]. The starting point of this theory lies in the individual atoms with well-known wave-functions. The wave-function of a solid is then derived as a linear combination of several atomic wave-functions (LCAO). For the sake of simplicity henceforth only nearest neighbour interactions will be taken into account.

The tight binding approximation is based on the assumption that if a solid is periodic, then the wave-function of the lattice should be periodic with the same period. This suggests that the wave-function at two identical lattice points are only different by a phase factor. This is called **Bloch's Theorem** and can be cast as:

$$\Psi\left(\bar{r}+\bar{R}\right)=e^{i\bar{k}\cdot\bar{R}}\Psi\left(\bar{r}\right)$$

A wave-function which satisfies Bloch's theorem is the Bloch wave-function that reads as:

$$\Phi_j\left(\bar{k},\bar{r}\right)=\frac{1}{N}\sum_{\bar{R}}^{N}e^{i\bar{k}\cdot\bar{R}}\Psi_j\left(\bar{r}-\bar{R}\right)$$

According to the theory of LCAO the wave-function of a molecule can be written as a linear combination of the wave-functions on the individual atoms. The total wave-function of the molecule can thus be expressed in terms of eigenstates of the individual atoms.

Therefore:

$$\left|\Psi_{mol}\geq\sum_k C_k\left|\Psi_{atomo}\right.>\right.\;\Rightarrow\;\left|\Psi_{mol}\geq\sum_{i,k}C_kC_i\left|\Phi_i\right.\right.$$

where $\left|\Phi_i\right.>$ is the eigenstate *i*.

In order to work out the eigenstates of a molecule, one has to solve the eigen equation:

$$\hat{H}\left|\Psi_\alpha\geq E_\alpha\right|\Psi_\alpha>$$

Moreover $\left|\Psi_{mol}\right.>$ can be formulated in the following way by collecting the terms relevant to the same eigenstate:

$$\left|\Psi_{mol}\geq\sum_j C_j\left|\Phi_j\right.\right.>$$

Multiplying by the complex conjugate $<\Psi_{mol}\left|=\sum_j C_j<\Phi_j\right|$ it can be found:

$$\hat{H}\sum_i C_{i,\alpha}\left|\Phi_i\geq E_\alpha\sum_i C_{i,\alpha}\right|\Phi_i>\;\Rightarrow$$

$$\sum_j C_{j,\alpha}<\Phi_j\left|\hat{H}\sum_i C_{i,\alpha}\right|\Phi_i>$$

$$=\sum_j C_{j,\alpha}<\Phi_j\left|E_\alpha\sum_i C_{i,\alpha}\right|\Phi_i>\;\Rightarrow$$

$$<\Phi_j\left|\hat{H}\right|\Phi_i>\sum_{i,j}C_{j,\alpha}C_{i,\alpha}\geq$$

$$E_\alpha<\Phi_j\left|\Phi_i\right.>\sum_{i,j}C_{j,\alpha}C_{i,\alpha}\;\Rightarrow$$

$$\bar{H}\bar{C}_\alpha=E_\alpha\bar{S}\bar{C}_\alpha$$

where *H* is the Hamilton matrix and S is the overlap matrix.

The eigen values are found by solving the secular equation:

$$\left(\bar{H}-E\bar{S}\right)=0$$

As only the electrons in the π bonds contribute to the conductance of graphite, the dispersion relation can be found by only taking into account these electrons using the tight binding approximation.

The basis-cell of graphite contains two atoms making the Hamiltonian and the overlap matrix 2x2-matrices. The diagonal elements of the Hamiltonian are given by the Fermi energy of the carbon atoms and the off-diagonal elements are functions of the interaction between neighbouring atoms and an empirical constant $\gamma_0=t$ included between 2.5 and 3 eV. The same holds for the overlap matrix, where the diagonal elements are unity, and the off-diagonal elements are a

function of the interaction between neighbouring atoms and another empirical constant s taken in the interval $0 \div 0.129$. Hence:

$$\bar{H} = \begin{bmatrix} e_f & t \cdot f(k) \\ t \cdot f(k)^* & e_f \end{bmatrix} \qquad \bar{S} = \begin{bmatrix} 1 & t \cdot s \cdot f(k) \\ s \cdot f(k)^* & 1 \end{bmatrix}$$

where

$$f(k) = e^{ik_x \frac{a}{\sqrt{3}}} + 2e^{-ik_x \frac{a}{2\sqrt{3}}} \cos\left(\frac{k_y a}{2}\right)$$

The eigenvalues of the secular equation are:

$$E_g(\bar{k}) = \frac{e_f \pm \gamma_0 w(\bar{k})}{1 \pm s w(\bar{k})} \qquad w(\bar{k}) = \sqrt{|f(\bar{k})|^2}$$

$$= \sqrt{1 + 4\cos\left(\frac{k_x a\sqrt{3}}{2}\right)\cos\left(\frac{k_y a}{2}\right) + 4\cos^2\left(\frac{k_y a}{2}\right)}$$

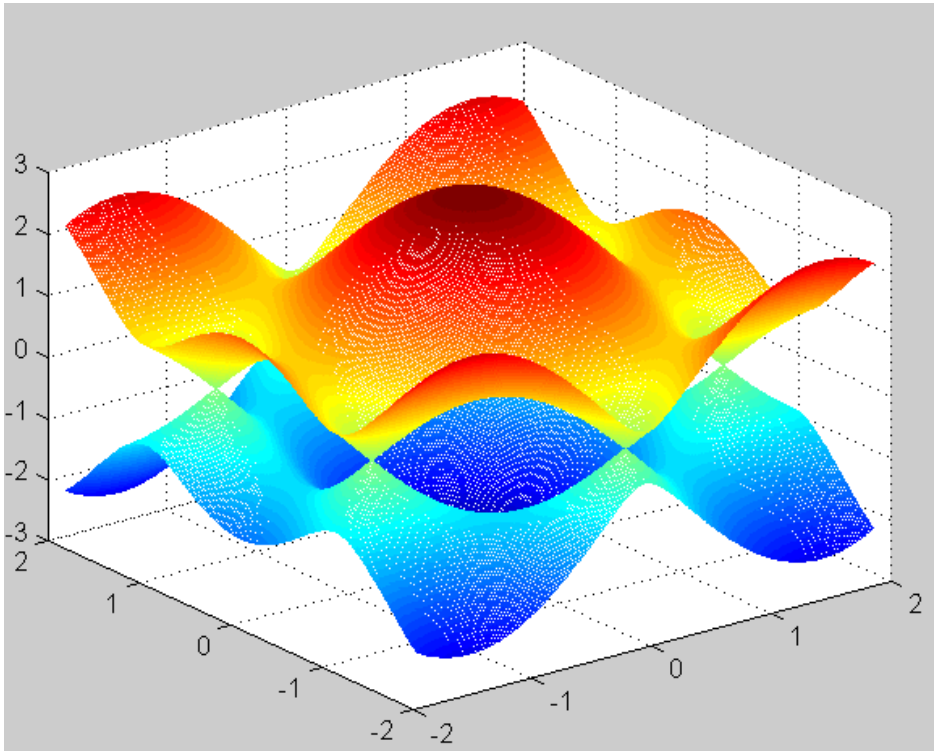
The + gives the bonding π band and the ¡ gives the anti-bonding π band. Imposing s = 0 and e_f = 0, one gets:

$$E_f(\bar{k}) = \pm\gamma_o \sqrt{1 + 4\cos\left(\frac{k_x a\sqrt{3}}{2}\right)\cos\left(\frac{k_y a}{2}\right) + 4\cos^2\left(\frac{k_y a}{2}\right)}$$

The above relationship represents the dispersion equation for a graphene sheet and is plotted in Figure 1.

In [1] we have reported the Matlab code, based on the proposed model, which allows to avoid any convergence and overflow problem, with a computational time almost instant.

In order to perform all the simulations we have used a common Windows-based PC, equipped with a Pentium IV CPU and main memory of 1 Gbyte.



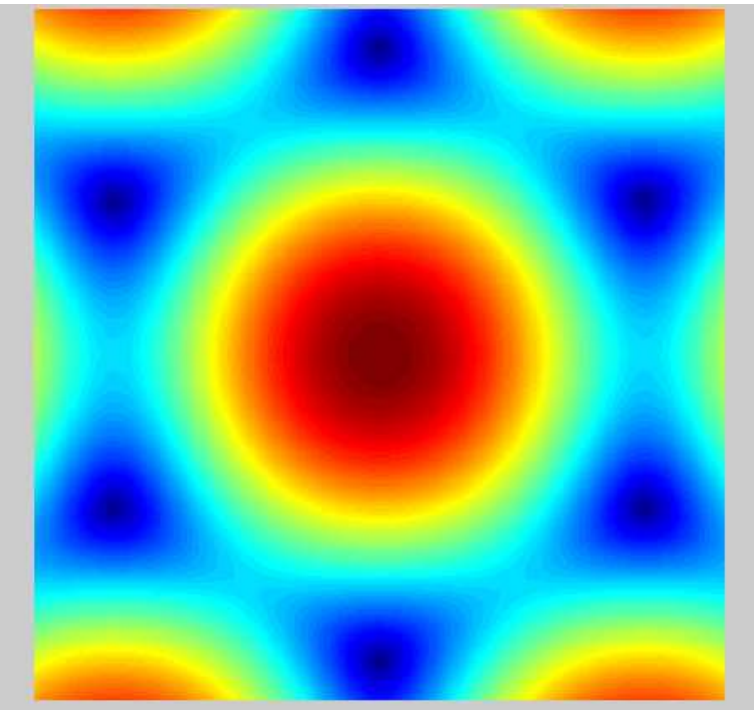


Figure 1. *Diagram of the dispersion equation for a graphene sheet.*

4. CONCLUSION

In this paper we have presented a procedure to determine the dispersion relationship of CNT. As the tight binding approximation and the LCAO represent useful tools to investigate the electronic properties of this class of materials, the proposed method is based on the application of both of them with a few seconds (2÷3) of CPU time less than the one of other methods proposed in literature [16-18], without losing in accuracy.

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DECLARATIONS

Ethical Approval. The authors declare that there are no animal studies in this work.

Conflict of Interest. The authors declare that they have no conflict of interest.

Author Contributions. R.M. gave the first idea of investigation, concept and modeling. The methodology has been done by the A.G.P., which also wrote the paper.

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