

Propriedades Eletrônicas do Grafeno investigada pelo modelo Tight Binding

Electronics Properties of graphene by Using of Tight Binding Model

Pablo Ribeiro Alves de Oliveira^{1*}, Sandra Cristina Ramos¹⁺, Jorge Anderson Paiva Ramos^{1#}

¹Universidade Estadual do Sudoeste da Bahia - UESB, Departamento de Ciências e Tecnológicas - DCET, 45083-900, Vitória da Conquista-Bahia, Brasil. e-mail: *pablo_oliveira@yahoo.com.br, +sandraramos@uesb.edu.br; #jorge@uesb.edu.br

Resumo

Alguns estudos teóricos são desenvolvidos a partir da resolução da equação de Schrodinger e de outra forma, utiliza-se o teorema de Bloch para descrever o movimento dos elétrons em um potencial específico, resolvendo o Hamiltoniano adequadamente. Aplica-se um potencial simétrico e esférico, que resulta em uma estrutura de bandas de energia para os elétrons da rede cristalina. No entanto, há determinado formalismo teórico cuja investigação das propriedades eletrônicas sejam válidas apenas para estruturas simétricas. Neste trabalho, mostra-se o desenvolvimento de um formalismo analítico que permite estudar qualquer material com determinada simetria, desde uni (1D) e bidimensionais (2D), usando Tight Binding Model (TB) para investigação das propriedades eletrônicas. Nesse sentido foi usado o teorema de Bloch e a estrutura recíproca do vetor de ondas de um determinado material cristalino, com geometria espacial confinada à Primeira Zona de Brillouin. A solução da equação de Schrodinger independente do tempo foi aplicada a uma destas estruturas, a do grafeno, para examinar suas propriedades eletrônicas. A aplicação do modelo TB apresentou resultados importantes, como a obtenção dos seis pontos de Dirac para o grafeno, que são regiões de estudos para o entendimento de suas propriedades de condução eletrônica.

Palavras-chave: Cone de Dirac, Relação de Dispersão, Grafeno, Modelo Tight Binding

Abstract

Some theoretical studies have been developed in order to solve Schrodinger equation. By Bloch's theorem has been possible to make some approach in the Hamiltonian, such as regard electrons in a specific potential, or in a spherical symmetric potential, that lead an energy bands structure study. However, there is no theoretical formalism that leads to investigate electronic properties of that structure. This paper brings the development of analytical formalism that allows to study any materials, in one (1D) and two-dimensional (2D), by using Tight Binding Model (TB). In this way, it was used the Bloch's theorem and wavevector reciprocal lattice of desire in the First Brillouin Zone. The solution of time independent Schrodinger equation was applied to graphene structure to examine its electronic properties. The TB approach has presented results, as the six points of Dirac, which has provided greater emphasis to that region than another research.

Keywords: Dirac Cone, Dispersion Relation, Graphene-Like Structure, Tight Binding Model

Introduction

The solution of Schrodinger's equation independent of time has dependence the kind of potential that is working. Since 1960, when Density Functional Theory has developed some of researches are able to conclude about the properties that didn't know yet [1]. Hence the interest in numerical methods to find the eigenstates of Schrodinger's equation have been grown, what results in new methods like Wannier Function and Ab initio [2,3]. Other approaches have been used like Hartree Fock approach [4,5] that considers the electrons influence by spherical symmetric potential and leads a research about energy levels of some atoms like carbon. It was studied the electrons of some structure that took its electrons in a weak potential. Nevertheless, this study should not conclude about energy relation in the lattice, even being a common method to solve Schrodinger equation.

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However, an attempt to develop the Tight Binding formalism leads besides simulation studies, an investigation from electronic properties of materials 1D and 2D, and an analytical result about this kind of material. The interest in theoretical models which allow to study electronic materials properties was potentialized upon graphene discovery [7]. That material is the most interesting among two-dimensional ones, due to its potential for application in several areas, such as electronic, and some peculiarities as specific singularities in regions known as well Dirac cones [8,9]. That region provides to graphene semiconductor properties, although it has a null gap [10]. This can be explained by the arrangement of its structure in a honeycomb lattice, due to hybridization sp^2 of the carbon atoms on it[6]. However, there is no analytical formalism to investigate the electronic behavior of graphene and any other materials one-dimensional or two-dimensional. The wave function eigenstates describe the lattices electrons and allows to verify some experimental features, as the six specific points and Dirac cones region of graphene electronic surface. Tight Binding model includes a potential term in the Hamiltonian. By that model it is possible to elaborate a new formalism analytical to investigate the eigenstates of any structure once the analytical term was developed.

The wave function as solution of Schrodinger's equation leads to the Bloch conditions and brings terms that is linear combination of atomic orbital that is well defined. Therefore, it is possible to get the eigenstates as function of the lattice wave vector only. The network eigenstate as function of the lattice wave vector can be find properly [11,12]. The model outed the superposition integral is obtained thus the formalism analytical that allows a theoretical study about electronic properties of structure and materials one and two-dimensional.

Model and Calculations

In order to obtain the mathematical Tight Binding formalism was taken the structure's electrons of a general structure with a strong bond. Therefore, we assume in Schrodinger equation a term from potential in the Hamiltonian, that nominated here as strong potential, that allow to write the Hamiltonian H as:

$$H = H_{at} + \Delta U \quad (1)$$

Next, it takes in the primitive vectors that gives rise to the structure mesh in study as vectors in reciprocal lattice, since it's possible to confine theses vectors in specific space, the Vigner-Seitz primitive cell called first Brillouin Zone.

In this way, it was applied the Bloch's theorem to propose as solution Schrodinger's equation, a function wave that need be written as a product cross plan wave and a periodic function, whose period is in Bravais lattice (in this case, specifically on reciprocal lattice) , that is:

$$\sum_R e^{i\vec{K} \cdot \vec{R}} \phi(\vec{r} - \vec{R}) \quad (2)$$

Hence, notice that the function ϕ in (2) should be expanded as linear combination of atomic orbitals, there is a possible description to the electrons near of its reliable position, in (3).

$$\phi(\vec{r}) = \sum_N b_n \psi_n(\vec{r}) \quad (3)$$

Thus, (3) looks for the eigenstates that is function wave associated. Therefore, seeks to solve the independent of time Schrodinger's equation for the energy in wave vector dependence that gives the material parameter base as in (4).

$$H\psi = E\psi \quad (4)$$

Results and Discussion

The formalism applied to 1D lattice structure

In order to apply the formalism that was obtained to 1D structure, it considered an periodic lattice, with vector wave parameter it is concerned on. We have assumed the interaction of the electron to the left occurs in the same way with the right electron and so on, as shown in the Figure 1:

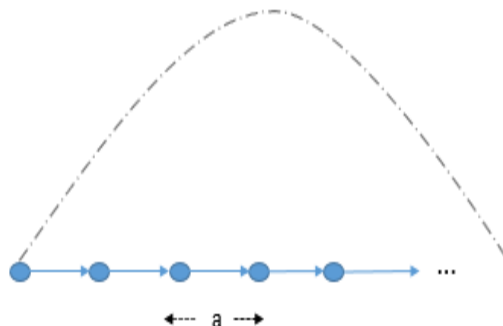


Figure 1: Arrangement atomic of the lattice periodic.

This formalism is focus the electrons on interactions, that can be described by interaction of potential. The possibilities are the linear combinations of the primitive vectors of the reciprocal lattice of their structure. The wave vectors of the reciprocal lattice are confined into Brillouin Zone (FBZ) for $\mathbf{k}$ wave vector reciprocal. For one dimensional -1D study should be considered the wave vectors $\sim \mathbf{k}$ as the K points of the FBZ.

$$k \in [0, \frac{\pi}{a}] \quad (5)$$

We can assume an arbitrary variations $\mathbf{R}$ of the lattice that can be written, for the 1D as the product of the n constituents of their structure and the lattice parameter. In module, that can write:

$$\vec{R} = n\vec{a} = na \quad (6)$$

The superposition integral can be simplified in the Tight Binding model in the 1D lattice by using $\vec{k} \cdot \vec{R} = nka$, n represents the number of elements along the 1D lattice. Thus, assuming that the potential interaction of this structure is constant, the formalism is simplified for the expression

$$E(k) = \epsilon_0 + \sum_n e^{inka} \langle \psi^* / \psi(x - na) \rangle \quad (7)$$

For $n = 0$ and $n = 1$, we get the equation.

$$E(k) = \epsilon_0 + \langle \psi^* / \psi(x) \rangle + e^{inka} \langle \psi^* / \psi(x - a) \rangle \quad (8)$$

And thus:

$$E_0 = \epsilon_0 + \langle \frac{\psi^*}{\psi(x-a)} \rangle \quad (9)$$

$$t = -2 \langle \psi^* / \psi(x - a) \rangle \quad (10)$$

For $n = 0$ and $n = 1$ is due to the lattice periodicity. As the analytical formalism obtained considers that the constituents of the mesh interact in the same way, by considering successive ' n ' just leads an extension of the lattice size, and other structure analysis at different points within the first Brillouin Zone in the interval described by equation (20).

This fact also justified the term '2' that appears in (25): to avoid computing the

interaction of the electron n with the electron $n + 1$ and the electron $n-1$, multiplies by 2, once the interaction occurs in the same way. Therefore, by using (24) and (25) in (23) and utilizing the Euler relation it obtained the expression.:

$$E(k) = E_0 - 2(\cos(ka) + i \sin(ka))t \quad (11)$$

The eigenstates are related to energy, which is an. Since an observable magnitude must be real, we neglect the complex part of (26), what lead us to obtain the follow Equation:

$$E(k) = E_0 - 2\cos(ka) t \quad (12)$$

From the can be obtain the Figure 1 for 1D structure periodic. In despite of can be observed the electrons of the conduction and valence bands of materials electronic structure like graphene.

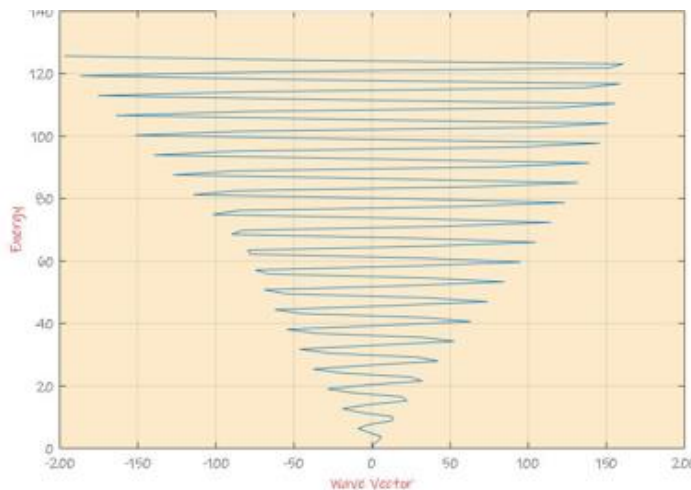


Figure 2: Dispersion Relation from 1D lattice

The formalism applied to graphene structure

As can be shown the tools that will use, it can afford to examine analytically the model. So, it will be used the Dirac notation to simplify the expressions shown in (5).

$$\langle \phi_a | \phi_b \rangle = \int_{-\infty}^{+\infty} \phi_a^* \phi_b dr \quad (13)$$

Using (1) in (4), the Schrodinger's equation can be written as in (6):

$$(H_{at} + \Delta U)\psi_n = E_n \psi_n \quad (14)$$

Multiplying the Schrodinger's equation by the complex function wave $\psi_m(\vec{r})$ and integrate over all space follow the equation (7).

$$\langle \psi_m | H_{at} | \psi_n \rangle + \langle \psi_m | \Delta U | \psi_n \rangle = E(\vec{k}) \langle \psi_m | \psi_n \rangle \quad (15)$$

Note that from a free particle the Schrodinger's equation results in (8)

$$H_{at}\psi_m = E_m\psi_m \quad (16)$$

Hence, using (8) and (6) that came from (7), it has (9).

$$E_m \langle \psi_m | \psi_n \rangle + \langle \psi_m | \Delta U | \psi_n \rangle = E(\vec{k}) \langle \psi_m | \psi_n \rangle \quad (17)$$

That means the equation

$$(E(\vec{k}) - E_m) \langle \psi_m | \psi_n \rangle = \langle \psi_m | \Delta U | \psi_n \rangle \quad (18)$$

Once regard the interactions contributions of some part of the lattice and electrons interactions at some directions, into linear combinations the lattice primitive vectors, it's proposed as Schrodinger's equation solution.

The solution is a wave function that is sum of (3) and a function wave that brings the cited features together, that is (11) and (12)

$$\psi = \phi + \psi' \quad (19)$$

Where,

$$\psi' = \sum_n \sum_R b_n e^{i\vec{k} \cdot \vec{R}} \psi_n(\vec{r} - \vec{R}) \quad (20)$$

The wave function (11) is also a Schrodinger's equation solution. However, the proposed sum has a term that can be evaluated as electrons interactions in all $\vec{R}$ possible directions inside the lattice. From this, in the structure region as function of its wave vector arise a region that regarded as Dirac cones. It's near of regions that appears a no-continues points that is well known as Dirac points. Hence, some semiconductors properties is allowed to study.

Therefore substituting (15) and (16) in (14), follow that (13)

$$(E(\vec{k}) - E_m) \sum_n b_n \langle \psi_m | \psi_n \rangle = \alpha - \gamma + \tau \quad (21)$$

Where:

$$\alpha = \sum_n b_n \langle \psi_m | \Delta U | \psi_n \rangle \quad (22)$$

$$\gamma = (E(\vec{k}) - E_m) \sum_n \sum_R b_n \langle \psi_m | e^{i\vec{k} \cdot \vec{R}} | \psi_n(\vec{r} - \vec{R}) \rangle \quad (23)$$

$$\tau = \sum_n \sum_R \langle \psi_m | \Delta U | \psi_n(\vec{r} - \vec{R}) \rangle \quad (24)$$

At (22) left inside the ensemble has been $\delta_{n,m}$. So, take $n=m$ and consider all sum as b_m as constant lead to rewrite the follow equation (25).

$$(E(\vec{k}) - E_m) b_m = \alpha - \gamma + \tau \quad (25)$$

In γ arise a term that is periodicity related, which is $e^{i\vec{k} \cdot \vec{R}}$. Therefore, it has allowed to conclude about the eigen states as vectors of reciprocal lattice function, that satisfy the reciprocal mesh conditions as in (18).

$$e^{i\vec{k} \cdot \vec{R}} = e^{i\vec{k} \cdot (\vec{R} + \vec{r})} \quad (26)$$

In the other side, τ has the expression (19).

$$\langle \psi_m | \psi_n(\vec{r} - \vec{R}) \rangle \quad (27)$$

It is well-known as superposition integral, who has an important role in magnetism theory. The Tight Binding model [19] explore these integrals meaningless.

The model validity can be verified by using the Ninith software. This software allows geometric building of carbon nanostructure as Carbon Nanotube (NTC) and Graphene. It's possible to obtain the electronics surfaces of these structures too. For this, the Ninith software

leads the length carbon bonds control, the transferred energy in the interaction and an approximate value to the superposition integral, that is denoted by “Overlap Integral” in that platform. The developed formalism can be applied to Graphene that is a pure two-dimensional structure. It was obtained with Ninithi the Graphene electronical surface shown in Figure (2).

As can be showed, the Figure 2 brings two different characters to material graphene surface. In Figure 3, it's shown the natural surface, that it did not take approaches to the superposition integral value. The space between the bonding and anti-bonding is showed too.

An important region of graphene was obtained. That region is interface of conduction band and valence band it's known as gap energy zone. The difference of the higher occupied energy level and the less energy level non-occupied take the Fermi levels. These levels concern the semi-conductors' properties to some materials. However, Graphene don't have a Fermi level, even though verification these features, experimentally [8] and moreover as super conductors [9]. Hence, these facts awake the researcher interest to specify the study about graphene and its electronical properties.

The reason of these facts can be explained in the region where the surfaces appear to touch it. This region is recognized as Dirac cones [18]. The superposition integral meaningless imply a larger gap, what get emphasis the Dirac point, as showed by Figure 3:

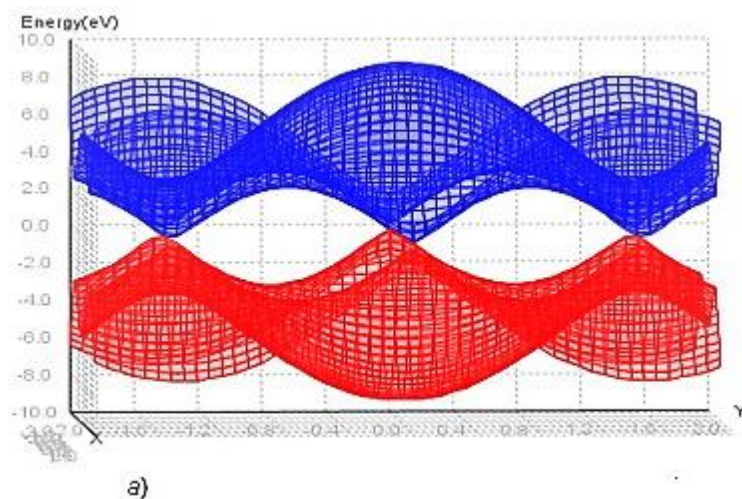


Figure 3. The graphene electronic surface bands.

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integral meaningless imply a larger gap, what get emphasis the Dirac point, as showed by Figure 2. Once the C-C length still the same, this fact can be explained by the superposition integral meaningless. Therefore, the mathematical formalism developed in this paper, beyond to verificated the data that brings from the literature, it could be used as parameter to study a structure 1D and 2D, leading more consistent researches about electronical properties of this materials, especially as graphene [19-21]

Conclusion

In this work was developed an analytical method to understand some crystalline structure (1d and 2D lattices) with its correlated properties electronic, as in order to study graphene electronics properties. The formalism obtained has allowed to obtain the energy states values that gives an enhanced Dirac points which show different energy level of crystalline structure. In the specific case, the electronic properties graphene was analyzed.

Their properties depending on kind of structure, such as, zig-zag or armchair that bring the atoms combining into graphene lattice. The formalism developed here promoting this discussion by assumption that some medication on the base wavevector lattice of graphene obtained analytically give their electronic properties by tight binding model consideration.

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REFERENCES

- [1]Novoselov, K.; Geim, A.; Neto, A.H.C; Guinea, F. The electronical properties of graphene. Reviews of Modern Physics, v.81,2009.
- [2]Dalpian, G.; Fazzio, A.; Pontes, R.B. Barrier-free substitutional doping of graphene sheets with boron atoms: Ab initio calculations. Physical Review B, v.79 ,2009.
- [3]Papaconstantopoulos, D.A.; Mehl, J.A. The Slater–Koster tight-binding method: a computationally efficient and accurate approach. journal of physics: condensed matter. USA. v.15, 3 Mar.2003.
- [4]Liu, J; Zhang,Z.H; Deng,X.Q; Fan,Z.Q; Tang,G.P. Electronic structure and transport properties of armchair Graphene nanoribbons by ordered doping. Organic Electronics, 2015.

- [5] Fuchs, J.N.; Goebirg, M.O. Introduction to the Physical properties of Graphene-Lectures Notes. 2008. Available in: http://web.physics.ucsb.edu/~phys123B/w2015/pdf_CoursGraphene2008.pdf>. Access in: Mar 14 of 2018.
- [6] Novoselov, K.S, Geim, A.K et al. Electric field effect in atomically thin carbon films. Science, 306(5696):666–669, 2004.
- [7] Asano, K.; Hotta, C.; Designing Dirac points in two-dimensional lattices. Condensed Matter Review, v.2, 2011.
- [8] Chen, Y.; Fan, Z.; Two-Dimensional Metal Nanomaterials: Synthesis, Properties, and Applications. Chemical Reviews, 2018
- [9] Uchoa, B.; Neto, A.H.C. Superconducting states of Pure and doped Graphene. Condensed Matter, v.3, Abril de 2007.
- [10] Zarneia, A.M; Chaves, A; Farias, G, A; Peeters, F.M. Energy levels of triangular and hexagonal graphene quantum dots: A comparative study between the tight-binding and Dirac equation approach, Physical Review B, v.89, 2011.
- [11] Jung, J.; Macdonald, A.H. Tight-binding model for graphene π -bands from maximally localized Wannier functions. Physical Review B, v.87, 2013
- [12] Hove, V.L. The Occurrence of Singularities in the Elastic Frequency Distribution of a Crystal. Physical Review, v.89, 1953.
- [13] Yang, Q.; Jieyang, W.; vertically-oriented graphene nanowalls: Growth and application in Li-ion batteries. Diamond And Related Materials, v.6, 2018.
- [14] Ashcroft, N.W.; Mermin, N.D. Solid State Physics. Cengage Learning, 2011.
- [15] Pise, P. J., 1982, Laterally loaded piles in a two-layer soil system., J. Geotech. Engrg. Div., 108(9), 1177–1181.
- [16] Hao, J.; Huang, C.; A promising way to open an energy gap in Bilayer graphene. Nanoscale, v.7, 2015.
- [17] Ramos, S.C., Lobo, A., Antunes, E., Corat, E.; Influence of polar groups on the wetting properties of vertically aligned multiwalled carbon nanotube surfaces. Theoretical Chemistry Accounts, v.130, 2011.
- [18] Asano, K; Hotta, C. Designing Dirac points in two-dimensional lattices. Journal of Condensed matter , vol.2 , 2015
- [19] Asano, K; Hotta, C. Designing Dirac points in two-dimensional lattices. Journal of Condensed matter , vol.2 , 2015

[20] L. D. Landau, and L. M. Lifshitz, Quantum Mechanics Non-Relativistic Theory, Butterworth-Heinemann, 3rd edition, (1981) Section 79.

[21] Kuhl, U.; Barkhofen, S. Dirac point and edge states in a microwave realization of tight-binding graphene-like structures. Physical Review B , v.82, 2010.