

## **ANALYTICAL DESCRIPTION FOR THE IMPLEMENTATION OF NUMERICAL MODELS APPLIED TO THE STUDY AND DETERMINATION OF THE *BANDGAP* OF SEMICONDUCTOR MATERIALS**

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**Abstract:** An analytical description for implementing numerical formalism, such as; *Tight Binding Model* (TBM) and Density Functional Theory (DFT) was performed to understand the semiconductor properties of graphene and Gallium Arsenide (GaAs). Such numerical models (TBM and DFT) were implemented to solve the time-independent Schrodinger equation, with the application of concepts about the Dirac points and Fermi levels of the graphene structure, in addition to the use of the Bohr-Oppenheimer approximation, which provided basis for considering the effects of minimizing the core-core and electron kinetic energy, in obtaining the “bandgap” of the investigated materials. The Hartree-Fock method was also used to solve the Slater – Koster matrix to evaluate the electron-electron interaction, in the interaction model for each electron with an electron cloud in the DFT. By implementing the models, reduced configurations of the “bandgap” of Graphene and AsGa were obtained.

**Keywords:** Graphene, AsGa, bandgap, Semiconductor, Numerical Models.

## INTRODUCTION

Graphene is a material consisting of carbon atoms arranged in a hexagonal structure. Bonding carbons share their 4 outer shell electrons through covalent and polar bonds. The energy bands associated with the bonds (sigma and pi) represent the bound and unbound electrons in the graphene structure. For graphene,  $sp^2$ -type hybridization is the one that confers electronic transport properties, as it has lower energy levels. Graphene presents a typical zero-gap semiconductor behavior, since the Density of States (DOS) is zero at the K point, which is the specific point of high symmetry in the Brillouin Zone (ZB). At low energies its dispersion versus momentum relationship is linear for a specific point of

high symmetry in the ZB. At that point, the electrons behave like fermionic particles and obey the Dirac equation [1].

The most interesting electronic properties in graphene are at and around the K point, where the conduction band touches the valence band. At other points the energy values of the bands are different. For low temperatures, the electrons obey the Dirac Hamiltonian, which behave like Dirac fermions, with zero effective mass. Graphene is a two-dimensional material with a peculiar dispersion relation:  $\epsilon(k) = \pm \hbar v F k$ . This particular dispersion is valid only for low energies and has a physical aspect very similar to quantum electrodynamics for massless fermions, since the Dirac fermions in graphene move with Fermi velocity in the order of 106 m/s. [2].

Dirac fermions behave differently when compared to the ordering of electrons subject to magnetic fields, leading to new physical phenomena such as plateaus in the quantum hall effect, giving rise to the anomalous quantum hall effect in graphene, due to the appearance of quasi-particles, which can be measured experimentally. Another interesting fact about Dirac fermions is that they are not modified due to the presence of an external electrostatic potential, due to the Klein paradox phenomenon [2,3]. And the fact that Dirac fermions present unusual behavior in the presence of barrier potentials, leads to the Zitterbewegung phenomenon [2,4] which is an unstable movement of the wave function of the Dirac problem due to the confinement of the Dirac electrons in a certain region.

## NUMERICAL MODELS

### TIGHT BINDING MODEL

The Tight-Binding (TB) approximation describes crystal lattices considering the superposition of the wave functions of atoms, without taking into account the atomic description of the system [5]. In graphene,

the electrons participating in bonding have a completely full valence band, and therefore do not contribute to conduction. The free carbon electron will only experience slight perturbations from its neighbors. This allows us to carry out an expansion of the wave function in terms of linear functions of atomic orbitals [6] with a specific description for the Hamiltonian, as already developed by Ribeiro et al [7], in which he presents the Dirac point using the model TB.

## DENSITY FUNCTIONAL THEORY

Density Functional Theory (DFT) has been the main model for calculating the electronic structure of materials. It is a widely used technique in the calculation of molecular structure, as it has a low computational cost [8]. It is a useful technique for investigations of medium and large molecular systems, describing the reality of the electronic properties of atoms, organic and inorganic molecules, metals and semiconductors. The central focus of the DFT is the electron density for the description of the  $\Psi$  wave function. The electron density is a much simpler function than the wave function, because the electron density depends on the coordinates of only one electron, while the wave function depends on the coordinates of  $N$  electrons. DFT requires concepts from the theorems proposed by Hohenberg and Kohn [9].

## ANALYTICAL DESCRIPTION

The Hamiltonian applied in the description of the Tight Binding numerical model for graphene must consider the crystal as a collection of neutral atoms with weak interactions. It consists of an approximation model of allowed energies (or bands) for particles in the material in which, in graphene, we take a given fixed atom in a sublattice A or B and its close neighbors through their covalent bonds where the

shared electron performs jumps between the two neighbors A and B. These jumps are energetically represented by the Hopping parameter, which contributes energetically to the bands [10,11]. The energy bands close to one of the Dirac points can then be obtained, as follows:

$$E(k) = \pm t [2 \cos(ka) + 4 \cos(kb)] \quad (1)$$

As observed in equation (1), the spectrum is symmetric around zero energy if  $t' = 0$ . For finite values of  $t'$  ( $t$  represents is the hop energy of the neighbor in the same sublattice given by the Hopping parameter ) the symmetry of the electron hole is broken and the bands become asymmetric. This dispersion can be obtained by expanding the full band structure next to the vector  $K$  (or  $k'$ ), as  $k' = K + q$ . The chemical bond of each carbon atom in graphene can be represented with a wave function. When we add two symmetric functions we will have a region with a greater probability of finding the electron. A very schematic and probabilistic model is to think that each carbon atom forms a potential well. When we approach two wells, the wave function ceases to be an eigenstate and starts to combine symmetrically and anti-symmetrically in the solution. And the symmetrical combination is the one that has the lowest energy and lowest momentum. By joining three wells, we can write the wave function as the combination of each of these wells which can be written according to equation (2).

$$\psi(x) = \pm\psi_1(x) \pm \psi_2(x) \pm \psi_3(x) \quad (2)$$

The three independent functions of each energy level and each well will originate the three energy levels, and by joining infinite energy levels we will obtain the origin of an energy band. For a chain of  $N$  atoms, an energy band is expected to appear. With a large number of atoms, there is little difference if you place one more node, as the energy of

the states will be closer to each other. The gap between energy levels will give rise to energy gaps, which is the bandgap. In this structure, a definition of energy bands with a limit of investigation called Fermi levels is then presented. The Fermi level energy is defined as the energy of the highest occupied level. Thus, all levels with energy less than the energy of the Fermi level would be occupied and all levels with energy above, unoccupied, for systems at 0 K. In systems with non-zero temperatures, there is no longer an abrupt transition of the probability of occupation, but a probability given by the Fermi-Dirac distribution [10,11].

According to Fermi's studies and statistics, less energetic states are more likely to be occupied than more energetic states. This way, when a system has several electrons, these will occupy higher energy levels as the lower levels are filled. In solid state physics the Fermi surface is the surface in momentum space at which the total excitation energy equals the Fermi energy. This surface can have a non-trivial topology. It can be said that the Fermi surface divides the electronic states occupied from those that remain free. This concept has many applications in the theory of atomic orbitals and in the behavior of semiconductors. Specifically, for the Graphene bilayer, the Fermi level coincides with the Dirac point, which is the point where the valence band touches the conduction band. For low energies the energy dispersion as a function of momentum is linear, which differs from other semiconductors, with Dirac fermion-type excitations for a point of high symmetry in the First Brillouin Zone (ZB). To understand the functioning, behavior and electronic structure of the nucleus and the electron, in a crystalline lattice, the time-independent Schroedinger equation represented in equation (3) is developed:

$$H\psi = E\psi \quad (3)$$

Substituting the hamiltonian of the crystal, we obtain equation (4) :

$$\left\{ \sum_i \left( \frac{-\hbar^2}{2m} \nabla_i^2 \right) + \sum_\alpha \left( \frac{-\hbar^2}{2m} \nabla_\alpha^2 \right) + \frac{1}{2} \sum_{i,j} \left( \frac{e^2}{4\pi\epsilon_0 r_{i,j}} \right) + v(\vec{R}_1, \dots, \vec{R}_N) + u(\vec{r}_1, \dots, \vec{r}_N, \vec{R}_1, \dots, \vec{R}_N) \right\} \psi = E\psi \quad (4)$$

The contribution of the kinetic energy of the nucleus can be neglected in the Hamiltonian, which is the Born-Oppenheimer approximation [12]. Furthermore, they assume that the nuclei are fixed and the coordinates  $R_1 \dots R_N$  are points of the crystalline lattice and are invariable, thus  $v(R_1, \dots, R_N)$  is constant. We assume that the potential energy of interaction between the nuclei is zero. This way we can write the simplified Hamiltonian, as the kinetic energy of the electron, the potential energy of electron-electron interaction and the energy of electron interaction with the nucleus.

Equation (4) describes the movement of electrons in a lattice, considering the nuclei at rest. For the second term of the expression that represents the electron-electron repulsion, we will use the Hartree-Fock method [13] to represent this interaction by another path, presented in equation (6),

$$\frac{1}{2} \sum_{i,j} \left( \frac{e^2}{4\pi\epsilon_0 r_{i,j}} \right) = \sum_i \Omega_i(r_i) \quad (5)$$

where  $\Omega(r)$  is called a self-consistent field, in electronic correlation we consider that an electron has its repulsions and properties generated by its interaction with an average of the field generated by other electrons. This method does not consider the one-to-one interaction. And for the third term we can do something similar, presented in equation (6),

$$\frac{1}{2} \sum_{i,j} \left( \frac{e^2}{4\pi\epsilon_0 r_{i,j}} \right) = \sum_i \Omega_i(r_i) \quad (6)$$

where  $U(r)$  is the potential energy of the  $i$ -th electron in a field of all nuclei. Rewriting equation (5) we get:

So the Hamiltonian of the  $i$ th electron is:

$$\widehat{H}_i = -\frac{\hbar^2}{2m} \nabla_i^2 + \Omega_i(r_i) + U_i(r_i) \quad (7)$$

So, we can finally write the Schroedinger equation as:

$$\left( \sum_i \widehat{H}_i \right) \psi_e = E \psi_e \quad (8)$$

It follows that electrons move independently of one another in a potential field. This allows us to consider the electrons in the crystal as a system of non-interacting particles. Next, we will use the approximation that the global wavefunction of the crystal is nothing more than the product of the mono-electronic wavefunction.

$$\Psi_e(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \psi_1(\vec{r}_1) \psi_2(\vec{r}_2) \dots \psi_N(\vec{r}_N) = \prod_i \psi_i \quad (9)$$

And the total energy of the system is expressed by:

$$E = E_1 + E_2 + \dots + E_N = \sum_i E_i \quad (10)$$

We can write the product of the wave eigenfunctions as:

$$\prod_i \psi_i = \Psi_1 \Psi_2 \dots \Psi_N \quad (11)$$

Writing the Schroedinger equation for each electron in the crystal, and dividing all sides of that equation by the factor  $\prod \Psi_N$ , we can write.

$$\begin{aligned} \frac{1}{\psi_1} H_1 \psi_1 + \frac{1}{\psi_1} H_1 \psi_1 + \dots + \frac{1}{\psi_1} H_1 \psi_1 &= E_1 + E_2 + \dots + E_N \\ H_1 \psi_1 &= E_1 \psi_1 \\ H_2 \psi_2 &= E_2 \psi_2 \\ H_N \psi_N &= E_N \psi_N \end{aligned} \quad (12)$$

Considering that each term of Equation 14 depends on the coordinates of each electron independently and therefore, the Hartree-Fock method reduces the Schroedinger equation, for many particles, to a single electron equation, that is:

$$\begin{aligned} \widehat{H}\Psi(\vec{r}) &= E\Psi(\vec{r}) \\ \left\{ \frac{-\hbar^2}{2m} \nabla^2 + V(r) \right\} \Psi &= E\Psi \quad (13) \\ V(\vec{r}) &= V(\vec{r} + \vec{R}) \end{aligned}$$

The eigenfunctions of the wave equation for a particle subjected to a periodic potential are the product of a plane wave  $e^{i(k \cdot r)}$  by a periodic function defined  $u_k(r)$  with the periodicity of the crystal lattice. Bloch's function can be written as a sum of traveling waves[7,13].

Since  $H$  is the free Hamiltonian and  $V$  is the potential generated by the lattice, in general when using perturbation theory we want  $V$  to be very small so that we can only write a few terms of the expansion, but in this problem the solution can be written in perturbative series even if we have to keep infinite terms, and the potential is not small. Since  $|n(0)\rangle$  is an eigenfunction  $H$ , we can obtain an eigenfunction of  $H$  in the form of a series  $|n\rangle = |n(0)\rangle + \lambda|n(1)\rangle + \lambda^2|n(2)\rangle + (16)\dots$  writing the perturbed ket as a function of the unperturbed  $|n(0)\rangle$  and the  $|n(1)\rangle$  which is the first-order correction given by the perturbation theory given by this summation:

$$|n(1)\rangle = \sum_{k \neq n} k^{(0)} |V|n(0)\rangle \frac{1}{E_n^{(0)} - E_k^{(0)}} |n(0)\rangle$$

$$|n^{(1)}\rangle = \sum_{k \neq n} k^{(0)} |V|n^{(0)}\rangle \frac{1}{E_n^{(0)} - E_k^{(0)}} |n^{(0)}\rangle \quad (14)$$

$|k(0)\rangle$  arises in the perturbative correction as long as the potential is able to connect the  $|n(0)\rangle$  with the  $|k(0)\rangle$ , that is, we start from a known solution that is  $|n(0)\rangle$  when we turn on the perturbation the  $|n(0)\rangle$  is no longer the hamiltonian eigenfunctions, but we can write these hamiltonian eigenfunctions with a sum over the unperturbed kets.

In the correction of  $|n(0)\rangle$ , only the  $|k(0)\rangle$  will appear in the first order as long as the potential is able to connect  $|k(0)\rangle$  with  $|n(0)\rangle$ . In second order, the expression takes the form:

$$\begin{aligned} |n^{(2)}\rangle &= \sum_{k \neq n} \sum_{l \neq n} |k^{(0)}\rangle \frac{k^{(0)} |V|n^{(0)}\rangle l^{(0)} |V|n^{(0)}\rangle}{(E_n^{(0)} - E_k^{(0)})(E_n^{(0)} - E_l^{(0)})} - \sum_{k \neq n} \\ &|k^{(0)}\rangle \frac{n^{(0)} |V|n^{(0)}\rangle k^{(0)} |V|n^{(0)}\rangle}{(E_n^{(0)} - E_k^{(0)})^2} \\ &- \left(\frac{1}{2}\right) |n^{(0)}\rangle \sum_{k \neq n} n^{(0)} |V|n^{(0)}\rangle k^{(0)} |V|n^{(0)}\rangle \frac{1}{(E_n^{(0)} - E_k^{(0)})^2} \\ |n^{(2)}\rangle &= \sum_{k \neq n} \sum_{l \neq n} |k^{(0)}\rangle \frac{k^{(0)} |V|n^{(0)}\rangle l^{(0)} |V|n^{(0)}\rangle}{(E_n^{(0)} - E_k^{(0)})(E_n^{(0)} - E_l^{(0)})} - \\ &\sum_{k \neq n} |k^{(0)}\rangle \frac{n^{(0)} |V|n^{(0)}\rangle k^{(0)} |V|n^{(0)}\rangle}{(E_n^{(0)} - E_k^{(0)})^2} \\ &- \left(\frac{1}{2}\right) |n^{(0)}\rangle \sum_{k \neq n} n^{(0)} |V|n^{(0)}\rangle k^{(0)} |V|n^{(0)}\rangle \frac{1}{(E_n^{(0)} - E_k^{(0)})^2} \end{aligned} \quad (15)$$

$|k(0)\rangle$  and  $|l(0)\rangle$  are eigenvectors of  $H_0$  different from  $|n(0)\rangle$ . For the  $|k(0)\rangle$  to appear in second order it is necessary that the potential connects the  $|k(0)\rangle$  with  $|n(0)\rangle$  in second order in perturbation theory, so that they are connectable from an intermediate state, given by:

$$\begin{aligned} \psi(k) &= Ae^{ik.r} + \sum_{k' \neq k} c_{k'} e^{ik'.r} \\ \psi(k) &= Ae^{ik.r} + \sum_{k' \neq k} c_{k'} e^{ik'.r} \end{aligned} \quad (16)$$

For  $k'$  is present it is necessary that the potential connects  $k'$  with  $k$ . In first order perturbation theory the potential  $V$  connects a potential  $k$  with  $k'$  only if the Laue condition is satisfied:

For  $k'$  to be connected with  $k$  in second order of perturbation theory, in this case there has to be a  $k''$  such that the potential connects  $k'$  with  $k''$  and connects  $k''$  with  $k$ , also in first order, so this is possible due to Laue's condition.

$$k' = k'' + K_1 \quad e \quad k' = k'' + K_2 \quad (17)$$

The sum of vectors of the reciprocal lattice is also a vector of the reciprocal lattice, this stems from the fact that the reciprocal lattice is a Bravais lattice, that is, the fact that the potential is periodic, shows that to connect  $k$  with  $k'$  satisfying the condition of Laue, this works for any order, for the tenth order the argument is valid. Only with the Laue condition can we guarantee that the only  $k'$  that will appear in the summation are the  $k'$  that differ from  $K$  only by a vector of the reciprocal lattice, this is the essence of Bloch's theorem, because precisely the summation can be written as an integral and we can have any  $k'$ , but only  $k'$  will remain such that  $k'-K$  is a vector of the reciprocal lattice [13] and this way solving the equation gives us energy levels for the periodic crystal.

$$\begin{aligned} \psi_k(r) &= Ae^{ik.r} + \sum_{k' \neq k} c_{k'} e^{ik'.r} \Rightarrow \psi_k(r) = \\ &Ae^{ik.r} + \sum_{K \neq 0} c_{k+K} e^{(ik+K).r} \\ \psi_k(r) &= Ae^{ik.r} + \sum_{k' \neq k} c_{k'} e^{ik'.r} \Rightarrow \\ \psi_k(r) &= Ae^{ik.r} + \sum_{K \neq 0} c_{k+K} e^{(ik+K).r} \end{aligned} \quad (18)$$

## METHODOLOGY

In this article, an analytical description was developed with the application of the Tight Binding model to investigate the properties of graphene and GaAs semiconductor materials. The behavior of a potential perpendicularly applied to the plane of the two-dimensional lattice parallel to the graphene  $\pi$  band as well as the effect of this compared to the type of electronic doping modifies its band structure. The effect of this behavior is studied by *Density Functional Theory* (DFT). This model was used to model the energy dispersion through an electronic state density function for the GaAs semiconductor material. The figures were plotted using the free software Octave 6.2.0.

## RESULTS AND DISCUSSIONS

In the *Tight-Binding* model, crystals are considered as a collection of weakly interacting neutral atoms, this is assumed because there are several solids whose atoms have relatively large potentials, so that electrons are mostly bound to nuclei, as in semiconductors and insulators. It is assumed then that the state of the electron in the crystal differs little from its isolated or neutral state, so the perturbation theory considering the Hamiltonian of the crystal as the atomic Hamiltonian one more correction to be implemented. For the one-dimensional chain, with independent electrons, using the Bohr Oppenheimer approximation we have:

A single electron in the presence of a one-dimensional chain, the Hamiltonian will be composed of the kinetic energy of the electron plus the potential energy of interaction of the electron with each of the atoms. So we will have N terms of potential energy. It is an approximation in which we can write the wave function written as a function of only the fundamental level of each of the atoms.

The electron wave function is described as a summation of N terms, where n is the number of atoms surrounding the self state that we would have if there was only atom i in the world and there were no atoms:

$$H = K + \sum_{i=1}^N V_i \quad (19)$$

When we evaluate only one carbon atom, we have an associated fundamental energy level, for two atoms we will have two energy levels and for n atoms, we have functions described by the eigenvalues  $\phi$ , which correspond, to solve an eigenvalue equation for a Hamiltonian ( $n \times m$ ). This way, the following form can be written in terms of components:

$$\sum_m H_{nm} \phi_m = E \phi_n \quad (20)$$

$$H_{nm} = n|H|m$$

There is also the need to express the Hamiltonian matrix. In this approach, the self ground state of atoms is described by a matrix derived from the Hamiltonian. This is described in terms of the kinetic energy plus the potential interaction energy with the n ion plus the remainder of the matrix interaction.

$$\langle n|H|n \rangle = \langle n|K + V_n|n \rangle + \sum_{i \neq n} \langle n|V_i|n \rangle \quad (21)$$

$$H_{nn} = E_{atômico} + V_0 = E_0$$

Equation 21 expresses the Atomic Energy for all atoms added to the term taking  $V_0$ . And the sum of the two terms is called  $E_0$ , applying to the lattice symmetry for all diagonal elements.

And, for the off-diagonal elements ( $m \neq n$ ), we have:

$$n|H|m\rangle = n|K + V_n|m\rangle + \sum_{i \neq n} n|V_i|m\rangle \quad (22)$$

Which corresponds to taking the matrix elements of H between the n state and the m state, again one can write the hamiltonian this way by separating the kinetic energy of the electron plus the potential energy n, plus the potential due to the other atoms. Note that this first term of the expression on the right K + Vn is the Hamiltonian due to the atom n, which in terms of Energy comes:

as  $m \neq n$ , we only have the sum:

$$\langle n|H|m\rangle = \sum_{i \neq n} \langle n|V_i|m\rangle \quad (23)$$

In equation 30, the term  $\sum \langle n|V|m\rangle$ ; ( $m \neq n$ ), the  $V_{n-1}$  represents the potential due to the atom n - 1, in one dimension and the Coulomb potential is given by:

$$V = -\left(\frac{1}{4\pi\epsilon_0} \frac{Q}{x}\right) \quad (24)$$

where x is the position relative to the potential due to the position of the n - 1 atom, and the summation for all  $i \neq n$ . In this case, there will be a well of potential in each of them, except for the one that is not included in this sum. Taking that matrix element means computing the integral of:

$$\sum_{i \neq n} \langle n|V_i|m\rangle = \int \psi_n^* \left( \sum_{i \neq n} V_i \right) \psi_m dx \quad (25)$$

$\psi^*$  is the eigenstate of n alone,  $\psi$  is the eigenstate of the atom m, so we assume that the m,n are very nm far apart, this means that the superposition of the  $\psi_m$  is almost zero, the places it finds -if the atoms in the  $\psi_m$  function make it impossible to find an electron of  $\psi_n$ , which means taking in the expression above,

null value, if m is far from n. Only for the first approximation there are possible values, if m is next to n, then it is said that this sum will tend to zero, if n is not next to m and n, otherwise, if  $m=n \pm 1$ .

It is defined that this matrix element is -t, which by symmetry will be the same whenever the first neighbors, so this t is called the hopping term, or Hopping parameter, which measures how much the electron can jump from one atom to a neighboring atom. The most rigorous would be to take into account that there is a coupling, albeit small or short-range, with other sites, but this is a first approximation, thus the off-diagonal term is -t only when the first neighbor is different from zero :

$$h_{nm} = -t(\delta_{m,n+1} + \delta_{m,n-1}) \quad (26)$$

Obtaining the eigenstate of this Hamiltonian will allow determining what are the possible energies, as well as what are the eigenvectors. From then on, linear combinations are obtained, which will show the eigenstate of the problem within this approximation, since the eigenfunction is a linear combination of the lowest energy eigenstates of each atom separately, as assumed at the beginning.

Specifically, for graphene, we use a wave function  $\varphi(k,r)$ , as the sum over the atomic wave function  $\varphi(r - R)$  over site j:

$$\phi(k,r)_j = \frac{1}{(\sqrt{N})} \sum_{R_j} e^{ik \cdot R_j} \varphi(r - R_j) \quad (j = 1, \dots, n) \quad (27)$$

Where  $R_j$  is the position of the atom and N is the number of unit cells, so the above equation satisfies Bloch's theorem. In a solid, the eigenfunction  $\psi(k,r)_j$  is defined as a linear combination of Bloch functions [13]:



$$\psi(\underline{k}, \underline{r})_j = \sum_{j'=1} C(\underline{k})_{jj'} \cdot \phi(\underline{k}, \underline{r})_{j'} \quad (28)$$

Where the  $C$  are the coefficients to be determined.

The eigenvalues  $E(k)$  are given by the ratio between the transfer matrix, which represents the transition of electrons in the state between the different carbon atoms of the crystal lattice, and the matrix  $S_{[jj]}$ .

$$E(k)_j = \frac{\langle \psi_j | H | \psi_j \rangle}{\langle \psi_j | \psi_j \rangle} = \frac{\int \psi_j^* H \psi_j d\tau^3}{\int \psi_j^* \psi_j d\tau^3} \quad (29)$$

Substituting the wave function, we define as the transfer integral matrix

$$H_{[jj]}(k) = \langle \phi_{[j]} | H | \phi_{[j]} \rangle$$

and

$$S_{[jj]}(k) = \langle \phi_{[j]} | - | \phi_{[j]} \rangle$$

overlapping integral matrix :

$$HC_{[i]} = E_{[i]}(k) SC_{[i]} \quad (30)$$

We only have a non-zero solution when,  $\det[H - E(k)iS] = 0$ . The secular equation, which is used to find the electronic structure of a hexagonal lattice, whose vectors of the triangular sublattices of atoms A and B they are:

$$a_1 = \left(\frac{a}{2}, \frac{\sqrt{3}a}{2}\right), \quad a_2 = \left(\frac{a}{2}, -\frac{\sqrt{3}a}{2}\right) \quad (31)$$

The electronic and transport properties are due to the  $\pi$  orbital lying perpendicular to the plane:

$$H_{AA} = \langle \phi_A | H | \phi_A \rangle = \frac{1}{N} \sum_{RA=R'A} \langle \phi(r - R_A) | H | \phi(r - R_A) \rangle = \epsilon_{2P} \quad (32)$$

The same procedure can be applied to  $H_{BB}$ . For other elements it can be calculated as follows:

$$H_{AB} = \langle \phi_A | H | \phi_B \rangle = \frac{1}{N} \sum_{RA=R'A} e^{-ik \cdot (R_A - R_B)} \langle \phi(r - R_A) | H | \phi(r - R_B) \rangle$$

$$H_{AB} = (e^{i\delta_1} + e^{i\delta_2} + e^{i\delta_3}) \langle \phi(r - R_A) | H | \phi(r - R_B) \rangle$$

$$H_{AB} = \left[ e^{-ik_y \cdot \frac{a}{\sqrt{3}}} + 2e^{ik_y \cdot \frac{a}{\sqrt{3}}} \cos\left(\frac{ka}{\sqrt{3}}\right) \right] (-V_{pp\pi})$$

$$H_{AB} = -g(k)V_{pp\pi}$$

(33)

Where we define  $g(k) = e^{-ik \cdot (a/\sqrt{3})} + 2e^{ik \cdot (a/\sqrt{3})} \cos((k_x a)/\sqrt{3})$  like the geometric factor and  $-V_{pp\pi} = \langle \phi(r - R_A) | H | \phi(r - R_B) \rangle$  as the hopping parameter between  $\pi$  orbitals of the A and B sublattices.

Writing the matrix of  $H$  knowing that  $H_{[BA]} = H_{[AB]}^*$  and for the overlap matrix elements, we have  $S_{[AA]} = S_{[BB]} = 1$ , diagonalizing the last expression, we obtain the dispersion relation:

$$E_{\pm} = \frac{\epsilon_{2p} \pm V_{pp\pi} \omega(k)}{1 \pm S_{pp\pi} \omega(k)} \quad (34)$$

where we define  $\omega(k)$  as:

$$\omega(k) = \sqrt{|g(k)|^2} = \sqrt{1 + 4\cos\left(\frac{\sqrt{3}k_y a}{2}\right) \cos\left(\frac{k_x a}{2}\right) + 4\cos^2\left(\frac{k_x a}{2}\right)} \quad (35)$$

To simplify the analytical calculations, the  $S$  matrix is used as a unitary matrix, that is, an orthogonal Tight Binding model. And the last equation becomes:

$$E_{\pm} = \epsilon_{2p} \pm V_{pp\pi} \omega(k) \quad (36)$$

Using the equation  $H = -g(k)V$  and we expand the wave vector  $k$  around the points  $k$  and  $k'$ , because when the system is excited, the electrons leave the valence band and occupy the available states in the conduction band. These states are located very close to the states

$$E = \pm v_F |P| \quad \frac{\partial^2 E}{\partial^2 |k|} = \frac{\hbar^2}{4\pi^2 m}$$

$$v_F = \frac{\sqrt{3}a}{2\hbar} V_{pp\pi} \approx 0,03c \quad (37)$$

It is proved that the electrons in graphene near the Dirac point behave like massless Dirac fermions [11].

Once the parameters of equation 39 are applied to the TB model, Figure 1 is plotted. This graph provides the behavior of electrons in graphene close to the Dirac point. This behavior shows that graphene in its hexagonal form behaves as a zero-gap conductor. With this result it becomes evident that graphene presents a density of states that, particularly at this point (center of the band) tends to zero. On the other hand, graphene may have its properties inherent to the modification of this density of states. This way, the desirable semiconductor property for graphene can be leveraged to a non-zero gap outside the band center, which depends on the different values for the electron k-wave vectors.

As the electron-atom interactions are taken as evidence, one can evaluate the bandgap of graphene, and this way, evaluate its semiconductor properties. It is verified that electronic conduction [10,14] through electronic doping [12] are situations that potentiate these interactions, and therefore expand the bandgap gap. In these cases, other methods and models are used, such as the Density Functional Theory (DFT), which is one of the most used methods for description and modeling used to find the energy dispersion of function materials and electronic state density theory [ 15,16].

To validate the model, a DFT study was investigated for a semiconductor material - Gallium Arsenide (GaAs) - and later apply it in the investigation of doped graphene. The DFT model was first applied in the investigation of that structure. AsGa features arsenic atom

ligand, which has 5 electrons in the last layer known as pentavalent element and trivalent gallium. The electronic structure of the AsGa crystal is known as a zinc blend and the atoms form a covalent bond. [15]. The DFT Model presented for AsGa starts from the solution of the Kohn-Sham equations, which describe the behavior of electrons and nuclei of the AsGa crystal, which is associated with the resolution of the time-independent Schroedinger equation, as described in previous sections.

This allows evaluating the variation of the bandgap. It must be noted that instead of calculating the energy through the wave function, the charge density or electronic density was used, which deals with the Hamiltonian of many interacting bodies, thus making it possible to obtain energy through the electronic density, as well as the square of the wave function.

Figure 2 shows the bandgap for AsGa, obtained by the DFT model. The gap for the AsGa structure is around 1.5 eV. Therefore, AsGa has a semiconductor character with the presence of a direct gap at this point. This result is in agreement with that obtained in the literature [15]. This way, the model developed for AsGa allows its application to the structure of modified graphene.

Figure (2b) shows the scheme of the valence band with direct and indirect gap. These are the characteristics of a semiconductor like AsGa crystals, InS, from group III-V [1], typically a behavior of semiconductors with small gap, that is, the valence bands (below the gap) are completely occupied by electrons, while the conduction bands (above the gap) are completely empty. Thus, semiconductors must have zero conductivity at zero temperature. For direct semiconductors, the top of the valence band and the bottom of the conduction band occur on the same K-wave vector, in the case of GaAs, and the indirect, the top of the valence band and the bottom of

# Graphene dispersion energy

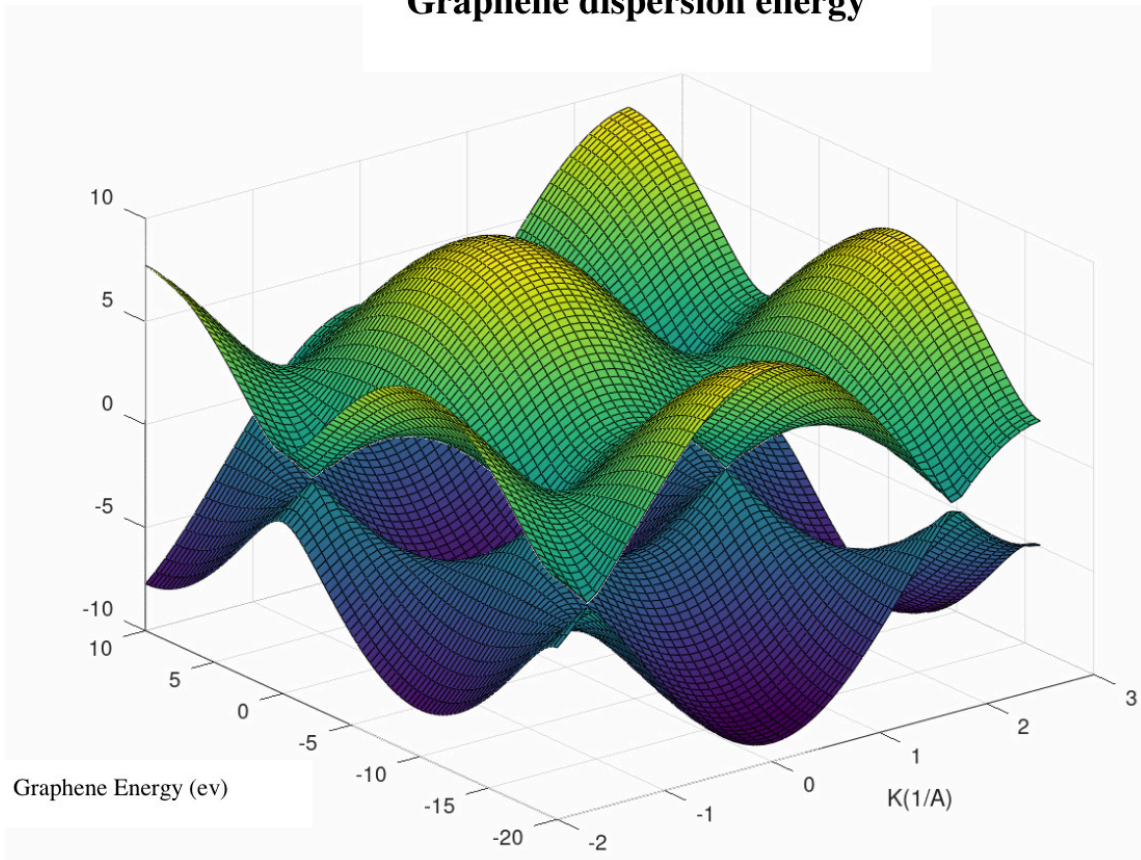
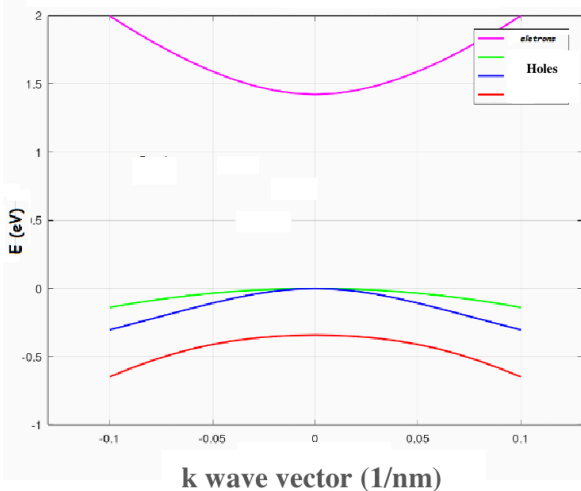
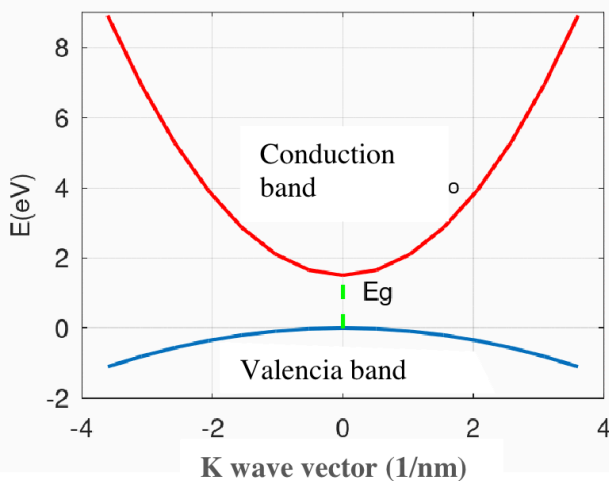


Figure 1: Graphene band structure,  $E(\text{eV}) \times k$ . Highlight the points (Dirac points) where the energy is zero.

Dispersion Energy for AsGa – DFT: Energy Levels



Dispersion energy for AsGa - DFT



(a) gap around 1.5 eV; (b) energy levels for different hole locations.

Figure 2: Energy Band for AsGa obtained by the DFT model.

the conduction band occur on points distinct from  $k$  distinct, in the case of other types of semiconductors with modified structure.

With this approximate calculation of free electrons in which the density of states decreases with the cube root of the energy, we can represent the band structure as a parabola, Figure 2 (a) and (b). In semimetals and insulators this dependence is more complicated. This result helps understanding how to control the charge carrier density in a two-dimensional layer of semiconductor materials, such as graphene, where the levels of occupied states close to the Fermi level and the gap opening between the conduction band and valence can be manipulated, such as the effect of the electric field, which causes the opening of the gap and displacement of the Fermi energy [18,19]. In intrinsic semiconductor crystals, for example, the Fermi level is located approximately in the center of the gapband. Doping is one of the known ways to modify the concentration of carriers, and consequently the position of the Fermi level. This modification can take place in two independent ways.

## FINAL CONSIDERATIONS

This work presents an analytical description for the implementation of the Tight Binding model and the Density Theory Functional. Numerical models have their peculiarities and are great tools for analyzing electronic properties of materials, especially 3D materials. For graphene that present electrons almost insensitive to disorders, electron-electron interactions, very long mean free paths; these two tools presented analysis contributions in two aspects: In the first one, the TB model was used to evaluate how electrons behave at points of high symmetry in the graphene structure, which configured in a region where the valence band touches the band of conduction, with

a zero gap configuration (Dirac points) and the second is that the structure of the energy bands for graphene can be modified under the effect of doping, by the application of electric and magnetic fields, addition of layers, control of its geometry and chemical doping. This behavior approximates the characteristics of this modified graphene to the band structure of AsGa. As a result of these modifications, there is a change in the structure of the graphene bands and, therefore, in its density of states (DOS). To evaluate this behavior, it is necessary to investigate other models, such as the one used for the structure of AsGa, which is the DFT. With this, it is feasible to create a set of many-body effects that can be induced by dopants and new characteristics for graphene will be explored by applying concepts and descriptions of different numerical models in obtaining and understanding these behaviors.

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