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Department: Material sciences

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Thesis

Option : Condensed Matter Physics

Topic:

Development and implementation of computational code for studying the electronic properties of graphene nanostructure

Presented by:

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Abstract:

Graphene is two-dimensional material with attractive electronic properties that have been successfully integrated into nanotransistors. However, it still has some issues due to its metallic nature. One way to solve this problem is by nanostructuring it. To better understanding the effect of nanostructuring on graphene, we need to solve the Schrodinger equation: if we use the tight-binding model, the solution of this equation is simply a linear combination of atomic orbital of these nanostructures. If you need the energy spectrum of graphene quantum dots with precise shape and edges, you need to construct a Hamiltonian matrix based on your input data: unit cell, hopping integral, shape and size. In this master thesis, we provide an easy way for writing a code that can generate a Hamiltonian matrix for finite size.

Résumé:

Le graphène est un matériau bidimensionnel doté de propriétés électroniques intéressantes qui ont été intégrées avec succès dans des nanotransistors. Cependant, sa nature métallique pose encore quelques problèmes. L'un des moyens de résoudre ce problème consiste à le nanostructurer. Pour mieux comprendre l'effet de la nanostructuration sur le graphène, nous devons résoudre l'équation de Schrodinger : si nous utilisons le modèle de liaison fortes, la solution de cette équation est simplement une combinaison linéaire des orbitales atomiques de ces nanostructures. Si vous avez besoin du spectre énergétique des nanostructures de graphène avec une forme et des bords précis, vous devez construire une matrice hamiltonienne basée sur vos données d'entrée : cellule unite, intégrale de transfert, la forme et la taille. Dans ce mémoire de Master, nous proposons une méthode simple pour écrire un code capable de générer une matrice hamiltonienne pour une taille finie.

الملخص

الجرافين مادة ثنائية الأبعاد ذات خصائص إلكترونية جذابة تم دمجها بنجاح في الترانزستورات النانوية. ومع ذلك ، لا يزال لديها بعض المشكلات بسبب طبيعتها المعدنية. تتمثل إحدى طرق حل هذه المشكلة في هيكلتها النانوية. لفهم تأثير البنية النانوية على الجرافين بشكل أفضل ، نحتاج إلى حل معادلة شرودنجر: إذا استخدمنا نموذج شديد الإرتباط ، فإن حل هذه المعادلة هو ببساطة تركيب خطي من الدوال الذرية لهذه الهياكل النانوية. إذا كنت بحاجة إلى طيف الطاقة لنقاط الجرافين الكمومية ذات الشكل والحواف الدقيقة ، فأنت بحاجة إلى إنشاء مصفوفة هاملتون بناء على بيانات الإدخال الخاصة بك: خلية الوحدة ، الشكل الأبعاد. في هذه الأطروحة ، نقدم طريقة سهلة لكتابة برنامج يمكنه إنشاء مصفوفة هاملتون .

Contents

DEDIC
ATION

I dedicate this work to the soul of my late father, Mohammed, may he rest in peace, and to my mother, siblings, and sisters. I also dedicate it to the children of my siblings and the children of my sisters, especially the little darling Hoyam, daughter of Aouatef. In addition, to the entire family and relatives.

Nabila REDJEM

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Our thanks and deep gratitude go to :

Mr. ***T. KIROUANI*** *for supervising this work, for his assistance, advice, and patience.*

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Mr. ***SAOUANE Azzeddine*** *for accepting to examine and evaluate this work.*

These acknowledgments would not be complete without the teachers of the Department of Material Sciences, for their encouragement, trust, and moral support they have shown throughout these past years.

General introduction:

Science is always at the service of human beings, with researchers from all over the world work together to solve the challenges and problems facing our society today.

These problems are interdisciplinary, such as the increase in computer speed, for example, which requires electronic engineers to invent new circuits and computer scientists to optimize programs, and physicists to discover and create new materials

As physicists, we understood that the new family of materials (two-dimensional) has a huge role to play in tomorrows technological that's why we decided to carry out this study.

This manuscript is structured around 3 chapters:

In the first chapter, we discussed the limitations that prevent the development and nano-fabrication of electronic components, and proposed a solution: two-dimensional materials,

This chapter concludes with applications of these materials in the field of nanoelectronics and optoelectronics.

In the second chapter, we discussed the application of tight binding model in infinite and finite size then we proposed an easy way to find hamiltonian matrix of graphene nanostructure.

In the last chapter, the details of code are given and we validate our results with literature.

Chapter 01: art of work

1.1 Introduction:

The world has witnessed a series of major industrial revolutions, each marked by significant technological advancements. The first of these, the mechanical revolution, was characterized by the invention of machines such as the steam engine and the mechanical loom. The energy revolution that followed was made possible by the invention of electricity, which transformed the way we produce and use energy.(4)

However, the true electronic revolution only occurred after the discovery of semiconductors, materials with incredible electro-optical properties. This discovery enabled the creation of a series of inventions in the field of electronics, such as transistors and diodes, which led to the appearance of electronic products in our daily lives, such as phones, televisions, computers, etc. (15)

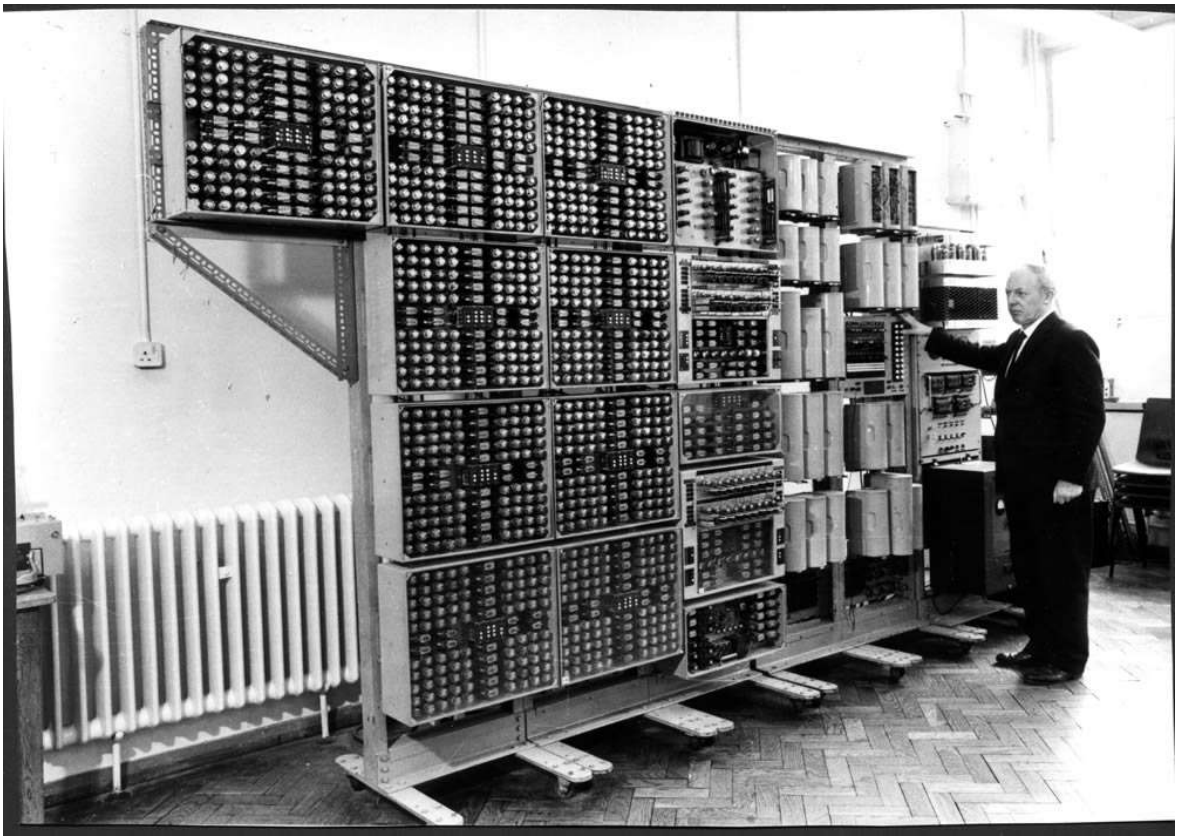


Fig 1.1: Witch is an ancient British computer of the 1950s [01]

The transition between the electronic revolution and the digital revolution was ensured by ingenious inventions of semiconductor-based electronic components. Powerful calculating machines were thus created, capable of quickly and efficiently processing information. This

transition led to the creation of more sophisticated and powerful electronic devices, such as laptops and tablets. (03)

It should be noted that the first calculating machine was invented in the 17th century, but it was limited in its capabilities. In 1944, computers weighed 30 tons and consumed around 150 kW to perform simple calculations. Today, a tablet weighs only 700g with a powerful microprocessor and incredible features, demonstrating the speed and extent of technological evolution in the field of electronics and semiconductors.(11)

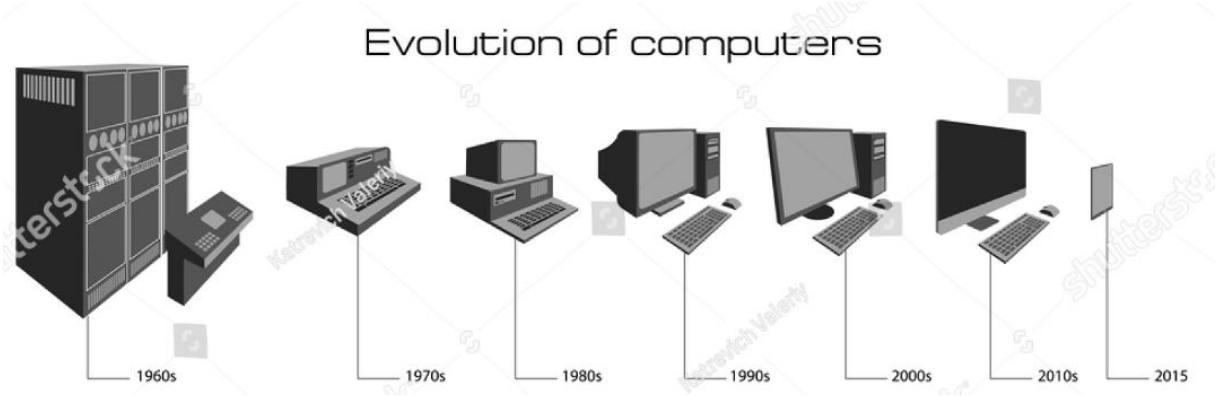


Fig 1.2: evolution of computers

How was it possible to create such an advanced tablet? What is the secret of its production?

The answer is simple: the miniaturization of electronic components. The most crucial electronic component in digital electronics is the transistor. It is used to perform numerical calculations and works with low electrical voltages. Researchers have succeeded in reducing the size of transistors and interconnecting them in millions or even billions in an integrated circuit, which has made it possible to create increasingly powerful processors. This miniaturization of electronic components is therefore the secret of the creation of the tablet and other advanced electronic products that we use today. (08)

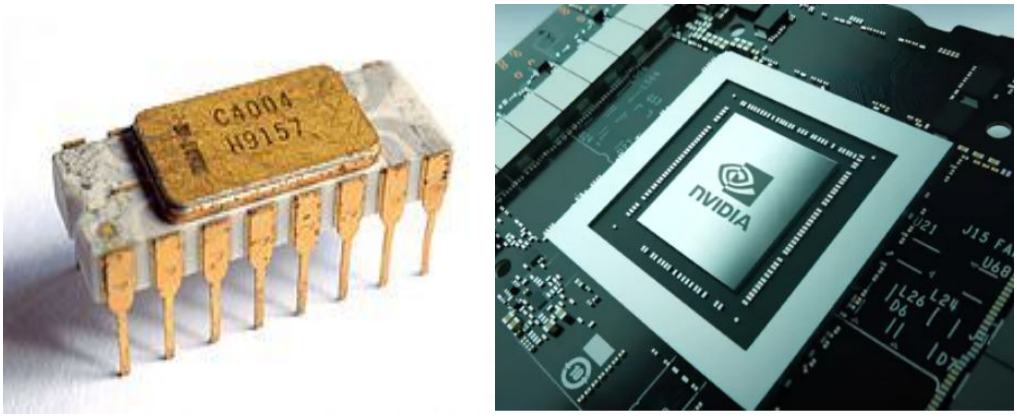


Fig 1.3) : Intel 4004 contain 2300 transistors in 1971 [02], b) NVIDIA flagship contain75 billions transistors in 2022 [03]

What are the major consequences of the reduction in the size of electronic components?

Firstly, the decrease in the size of electronic components leads to a significant reduction in manufacturing costs, as fewer raw materials is required to produce a larger number of electronic components. (06)

Secondly, this size reduction also leads to a reduction in power consumption, as smaller components require less energy to operate. This is particularly important in portable electronic products such as smartphones and tablets, which require high battery autonomy. (19)

Finally, the reduction in the size of electronic components allows for an increase in the operating speed of electronic devices and the creation of incredible computing power. In 1965, Moore's Law was stated, which stated that the number of transistors integrated on a chip could double every 18 months. This observation has been respected over the years, and the capacity of processors has been multiplied by 10,000,000 since 1971, as shown in Fig 1.4. This increase in computing power has enabled the development of new technologies and applications, such as artificial intelligence, virtual reality and many others. (12)

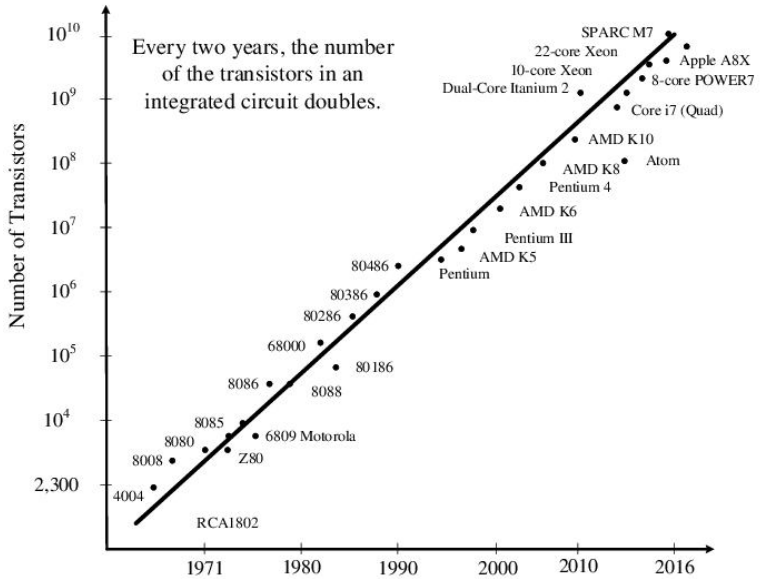


Fig 1.4 Moore's Law [04]

To answer the question of whether Moore's Law will remain valid in the world of nanoelectronics and whether the race for miniaturization has an end, current research trends must be taken into account. Laboratories and companies working in the field of miniaturization dedicate considerable budgets to making electronic components smaller and reaching sizes of tens of nanometers. (01)

However, there are limitations that slow down the nanoelectronics industry. Firstly, the number of dopant atoms in semiconductors decreases with the reduction in the size of the transistor, which leads to the appearance of logical errors and electrostatic discharges. Additionally, cooling the devices is very difficult to achieve, and the reduction in the size of electronic components can lead to the appearance of quantum phenomena such as the tunneling effect.(18)

Finally, mass production of microprocessors and other nanoelectronic components is limited by lithography techniques and masks. Despite these limitations, researchers continue to work on solutions to overcome these obstacles and advance in the miniaturization of electronic components. (21)

In conclusion, Moore's law can continue to hold true in the world of nanoelectronics, but current limits of electronic component miniaturization and technical challenges must be overcome to continue this trend. (16)

The most commonly used semiconductors in electronic component microfabrication are silicon and GaAs. However, researchers are planning to replace silicon with new materials that have interesting electrical and optical properties, especially for nanofabrication. Two-dimensional materials (*2D*) are one of these materials, with monoatomic thickness and innovative properties that could be promising for nanoelectronics. (07)

1.2. Definition of 2D materials:

In the bulk, free electrons make random movements in three dimensions, meaning that electrons have three degrees of freedom.

If one of dimension of the material is nanometric in size, electrons move freely in two dimensions, in which case they have two degrees of freedom.

If both dimensions of the material are nanometric in size, electrons have only one degree of freedom, meaning they can move freely in a single direction.

If all three dimensions of the material are nanometric in size, the electron is completely confined and has 0 degrees of freedom.

Therefore, nanomaterials can be classified based on the degrees of freedom of their electrons, as shown in the following table: (05)

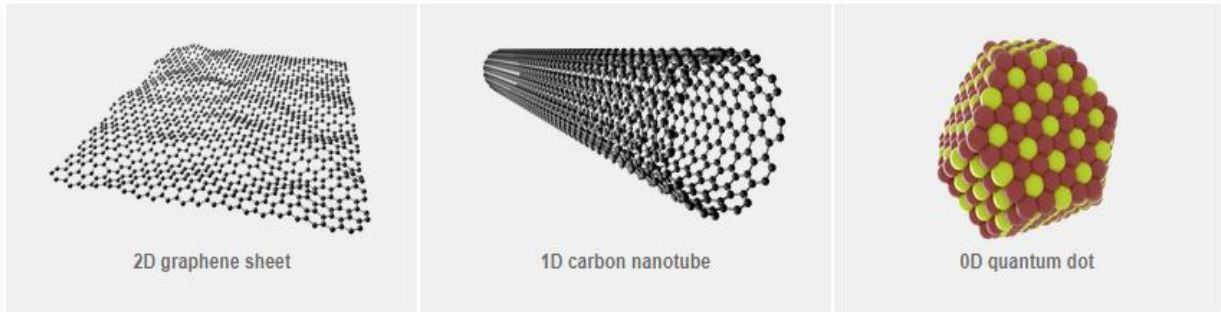


Fig 1.5 a) *2d* material b) *1d* material c) *0d* material

A two-dimensional material is a 2D material whose thickness is very thin, on the order of a nanometer.

Based on their planar structures, they can be easily integrated into electronic devices and make contacts, unlike the integration of carbon nanotubes or fullerene C60, which is difficult.

These *2D* materials can be integrated with semiconductors such as silicon or GaAs. The electronic properties can be modified, and the Eg (bandgap) can be tuned, which allows for the control of the frequency of the emitted light.

The power consumption of the integrated circuit can be reduced, and the information processing speed and computing capacity can be increased. (22)

The conversion efficiency of electric-light or vice versa can be increased in optoelectronic devices. (06)

1.3 Graphene:

Graphene is a two-dimensional material with a hexagonal crystal structure, as illustrated in Fig 1.6. It is widely recognized as one of the stiffest materials and is also considered the best conductor of electricity and heat among all known materials. Additionally, graphene is transparent, making it interesting for applications in the fields of optics and electronics. (13)

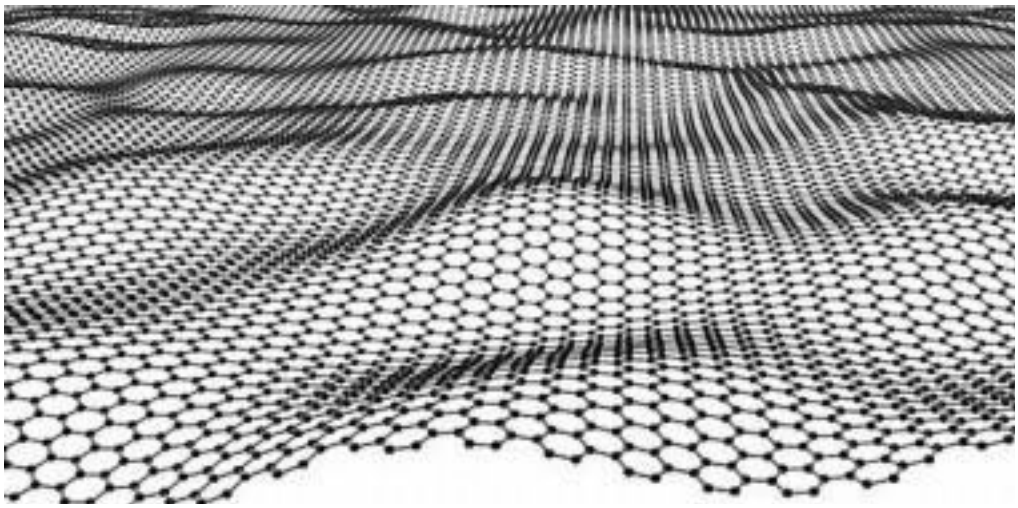


Fig 1.6 shows the nano-sized deformations that provide stability in the structure of grapheme

André Geim and Konstantin Novoselov [05] discovered graphene for the first time in 2004, and they received the Nobel Prize in Physics in 2010 for this discovery. By using adhesive tape (Scotch tape), thin graphite sheets were isolated from a graphite, as shown in Fig 1.7. The repetition of folding these sheets leads to thinner graphite flakes. These flakes are deposited on a SiC or SiO_2 substrate, and graphene is identified using an optical microscope. (14)

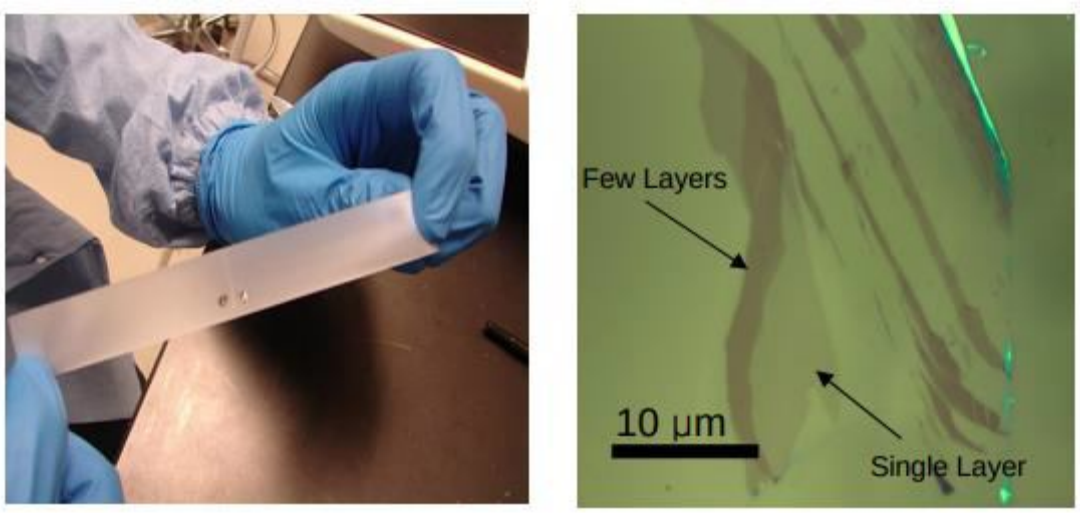


Fig 1.7 a) Adhesive tape with graphite, b) Image obtained by optical microscope of graphene deposited on an SiO_2 substrate.[06]

The electronic configuration of carbon is $1s^2\ 2s^2\ 2p^2$, so it has four valence electrons. Hybridization between the $2s$ and $2p_x$ and $2p_y$ orbitals forms three orbitals called sp^2, which are oriented at 120° in the plane, as shown in the following figure. (20)

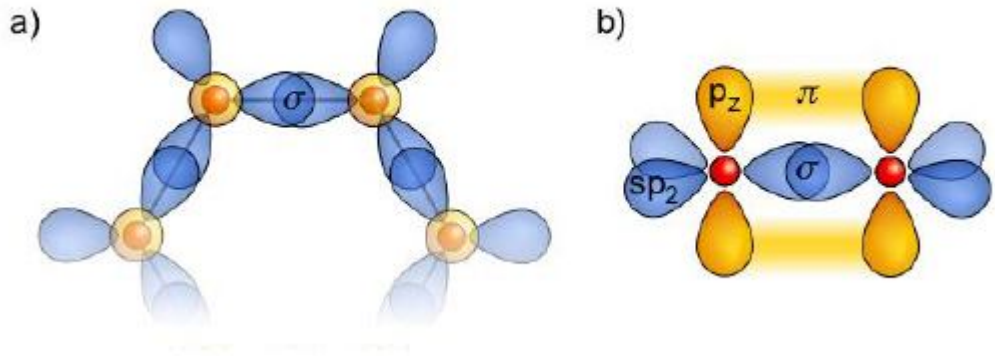


Fig 1.8 hybridation *sp2*

There are two types of bonds in graphene:

The sigma **σ** bond: Each carbon atom is covalently bonded to three neighboring carbon atoms through sp^2 orbitals. The carbon atoms are arranged in an ordered manner on a hexagonal lattice, which gives graphene exceptional rigidity due to these **σ** bonds. (04)

The π bonds: formed by overlapping of p_z orbitals, which are perpendicular to the graphene plane.(09)

What are the reasons for the high electron mobility in graphene?

There are two main reasons for this:

1. Ballistic transport: The classical Drude model for describing electric current in solids, where electrons undergo many collisions to move, does not always apply to two-dimensional materials such as graphene, as electrons undergo very few collisions [07].
2. This is due to the strong (sigma) bonds between carbon atoms, which make graphene very rigid and significantly reduce the number of scatterers. (10)

1.4 Applications:

The field of two-dimensional materials is a relatively new area of research, but it is very promising, as evidenced by the large number of scientific articles and patents filed since 2004 concerning graphene. It is worth mentioning that the global graphene market was estimated at 150 million dollars in 2020. (17)

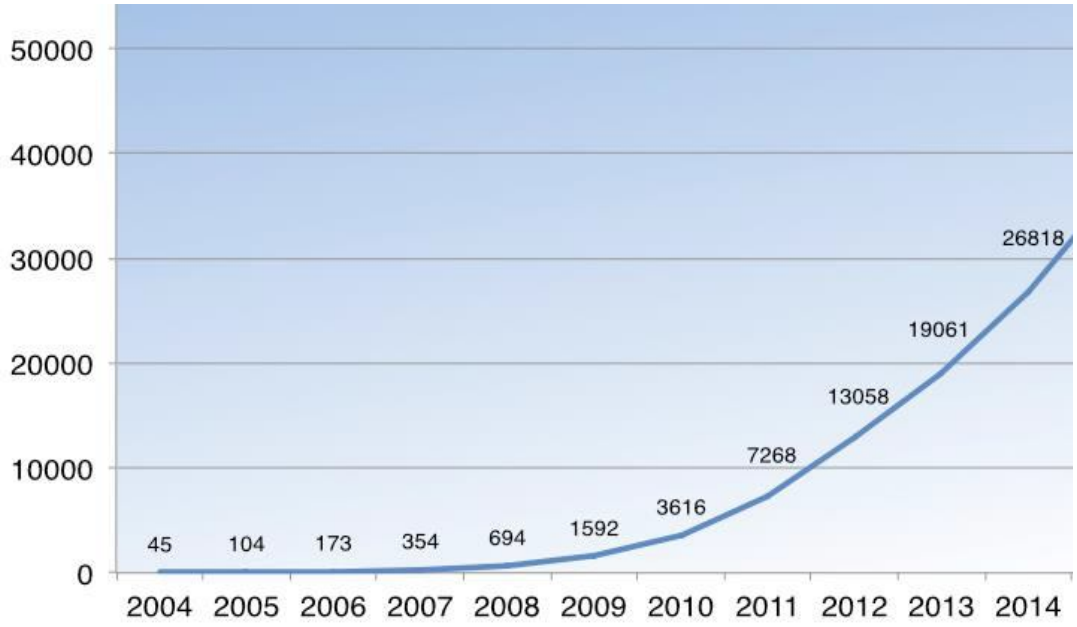


Fig 1.9: number of patents on graphene that have been filed since the year of its discovery until 2014 [08]

Researchers have successfully incorporated two-dimensional materials such as graphene into various electronic components such as transistors, sensors, photodetectors, and electrodes. The integration of these materials into technological applications is interesting for two main reasons. First, materials with atomic thickness have unique and highly attractive properties such as charge mobility in the case of graphene, making them in high demand. In addition, the geometry and architecture of nano-electronic components are mainly based on planar structures, such as stacking layers . (22)

In the following, we will present some research work that has been carried out in laboratories to integrate graphene into nanocomponents. (07)

1.4.1 Field Effect Transistor (FET) based on graphene

A field effect transistor is an electronic component that has three electrodes, as shown in Fig 1.10: (01)

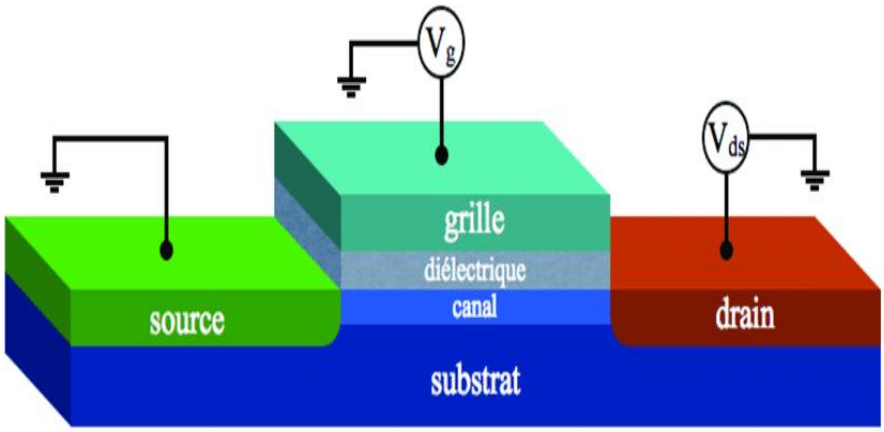


Fig 1.10 Transistor FET

1. The source and drain
2. The gate, which is placed above the device
3. The channel
4. The dielectric that separates the channel from the gate.

Electric current flows between the source and drain. However, this current can be regulated by applying a voltage to the gate [09]. When the voltage applied to the gate is high enough, it creates an electric field that allows control of the current flow between the source and drain. Thus, current flow can be allowed or blocked depending on the voltage applied to the gate. (15)

In electronics, transistors are often used to create logic circuits, it can be used to represent a data bit, where I_{off} corresponds to the value 0 and I_{on} corresponds to the value 1. By combining multiple transistors, more complex circuits can be created to perform logical operations, calculations, and data processing. (13)

The channel length of the transistor plays an important role in the transport of electrons through the channel. When the channel length is long, electrons move by diffusion, which means they undergo collisions with the atoms of the material constituting the channel. These collisions have the effect of slowing down electrons and reducing their speed. In this case, Ohm's law can be used to describe the behavior of the transistor. (20)

On the other hand, when the channel length is very short, on the order of a few tens of nanometers, the transport of electrons through the channel becomes ballistic. This means that electrons move at a constant speed without undergoing significant collisions with the atoms of the material. (22)

If we fabricate a nano FET transistor and integrate graphene as a channel [10], we will have enormous advantages:

1. The time required to traverse the channel is too short, about 0.1 picoseconds (10^{-12} s), as electrons move with ballistic manner over distances of around 0.3 microns at room temperature.
2. The speed of electrons is high, as electrons travel the same distance a hundred times faster in graphene than in silicon and gallium arsenide (*GaAs*).

We recall that the front gate allows controlling the flow of electric current from the source to the drain by systematically measuring the electrical conductivity (resistance) as a function of the gate voltage Vg. (08)

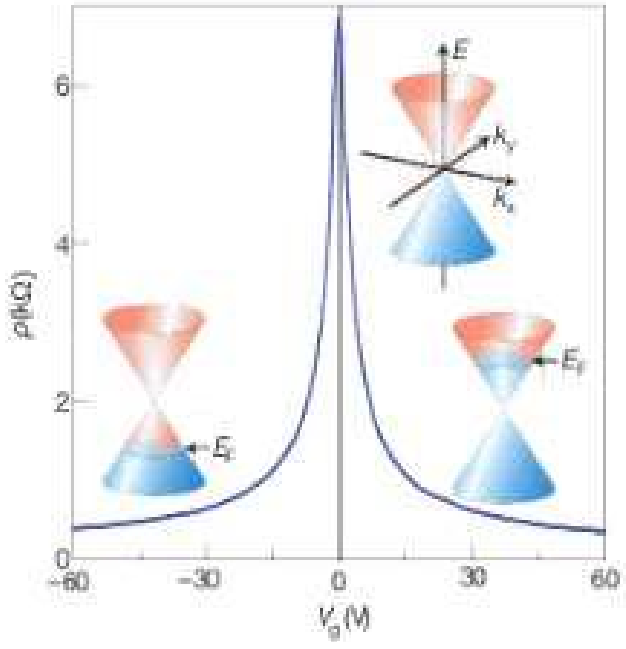


Fig 1.11 the resistivity as a function of the gate voltage $\mathbf{V_g}$ [11]

From the semi-classical theory of electron transport, we know that electrical conductivity is proportional to the density of charge carriers. Therefore, from the curve, we can deduce the following information:

- If we apply a positive gate voltage $Vg > 0$, the Fermi energy of graphene shifts towards the conduction band, that increases the density of charge carriers (electrons) and thus increases conductivity.
- If we apply a negative gate voltage $Vg < 0$, the Fermi energy of graphene shifts towards the valence band, that increases the density of charge carriers (holes) and thus increases conductivity.
- If we apply zero gate voltage $Vg = 0$, the conductivity of graphene is very low but never vanishes due to the absence of a bandgap. (09)

Therefore, if we apply a high gate voltage Vg, we can pass an electric current Ion from the drain to the source because if Vg is zero, the current I_{off} is very low, but it does not become zero. (19)

Graphene has a zero bandgap, and it exhibits a too low I_{on}/ I_{off} ratio due to the reason mentioned above. This ratio is unfavorable for the operation of a transistor. (12)

1.4.2 Sensors

Sensors are devices capable of converting a physical quantity into an electrical signal, and they are widely used in many technological and industrial applications. The design of innovative sensors at competitive prices requires the integration of new materials such as graphene. The integration of graphene into sensors is promising because this material has attractive mechanical properties such as rigidity and flexibility, in addition to being transparent, making it the ideal material for this type of application. Moreover, the best sensors on the market are those that exhibit high sensitivity, meaning that a small variation in the detected physical quantity will cause a considerable change in the electrical signal and in this context; graphene-based sensors show significant sensitivity. (20)

Masses or molecules can also be detected mechanically by a nanoelectromechanical (*NEM*) sensor based on graphene. Fig 1.12 represents a nanomechanical resonator (a mechanical structure that vibrates periodically and also has a natural frequency). (03)

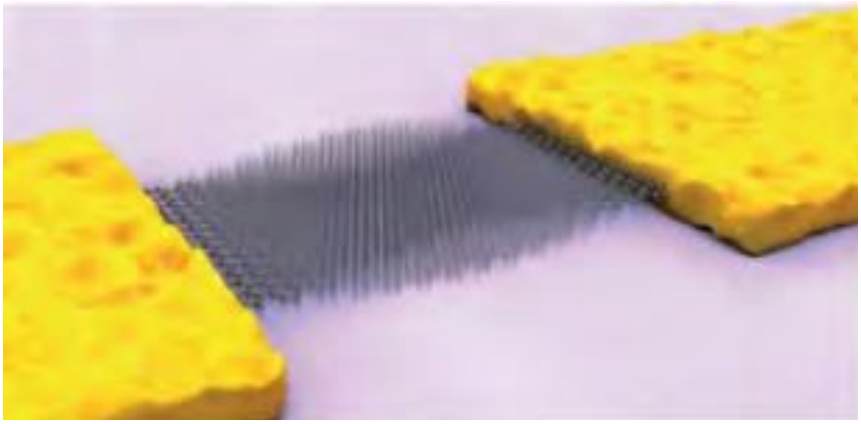


Fig 1.12 Nano-electromechanical sensor contains a graphene that connects to the two electrodes [13]

When a molecule attaches to the graphene, it leads to a modification of the mass and natural frequency of this resonator. Consequently, this also leads to a modification of the detected electrical signal. (04)

1.4.3 Photodetector

A photodetector is an electronic device designed to detect and convert light into an electrical current. This process occurs through the absorption of photons by the photosensitive material. Photodetectors are used in several inventions such as remote controls, *DVD* players, and *DVDs*. (09)

The graphene-based photodetector is an example of a modern photodetector. As illustrated in Fig 1.13, it generates an electrical current when exposed to light. This current is produced by the energy transition of electrons from the valence band to the conduction band, which is caused by the absorption of photons. This process also results in the creation of charge carriers, namely electrons and holes. (14)

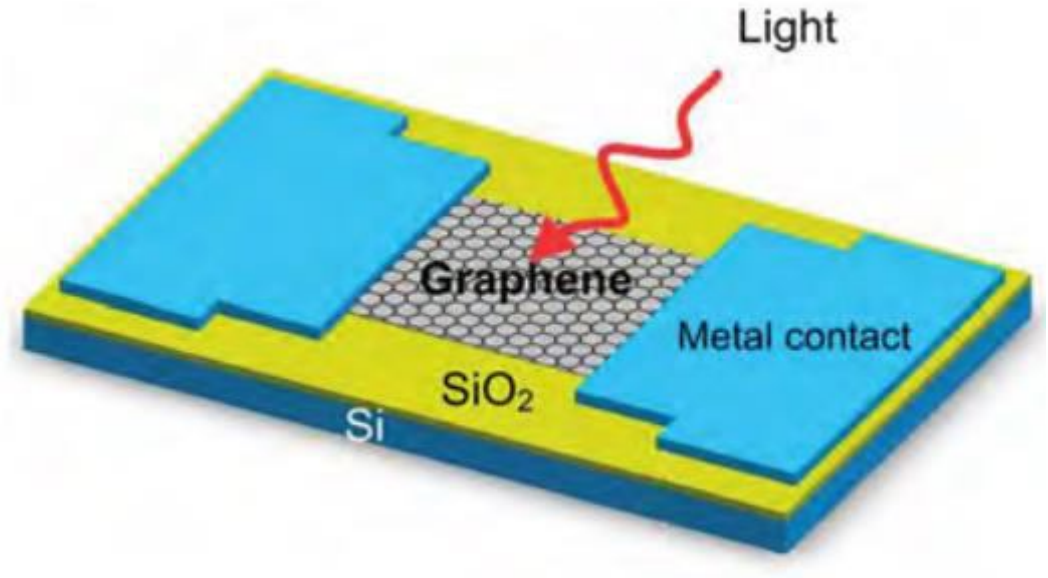


Fig 1.13 shows a photodetector based on a simple architecture (graphene-metal-metal)[14]

The graphene-based photodetector works over a wide range of wavelengths because the dispersion relation (E as a function of k) is linear around the Fermi energy and the bandgap is zero, so all photons with different frequencies can generate charge carriers, unlike other semiconductor-based photodetectors where the frequency of the incident photons must be greater than E_g/h.*(20)*

The integration of graphene into photodetectors is a promising because:

1. Due to the planar geometry of this material, integrating it into photodetector architecture is easy and straightforward.
2. The response time (the time required to generate a photocurrent) is related to mobility, and graphene has high mobility, and their electrons move with a Fermi velocity V_F of 10^6 m/s, making the response time too short.
3. The possibility of detecting any high wavelength of electromagnetic wave ,this ability is due to the absence of a bandgap in this material. (21)

Graphene is an atom-thick material that absorbs almost 2.3% of incident light, which is less favorable for optoelectronic applications. Therefore, it is necessary to improve their light absorption, and researchers have recently succeeded in increasing absorption by incorporating nanoparticles with graphene into the photodetector . (15)

1.4.4 Transparent electrode:

To manufacture electronic devices such as OLED screens, touch-screens, or photovoltaic cells, require materials for electrodes which can pass the electric current and light simultaneously. Among the materials used for this purpose, ITO (indium-tin oxide) is widely used due to its high electrical conductivity and optical transparency. However, it has undesirable mechanical properties such as fragility and limited flexibility. In the future, it is desired to replace ITO with graphene, as this material has advantages such as chemical and thermal stability, transparency, high electrical conductivity, flexibility, and strength superior to that of steel. In addition, it is easy to achieve ohmic contact with graphene because its work function is similar to that of ITO. (21)

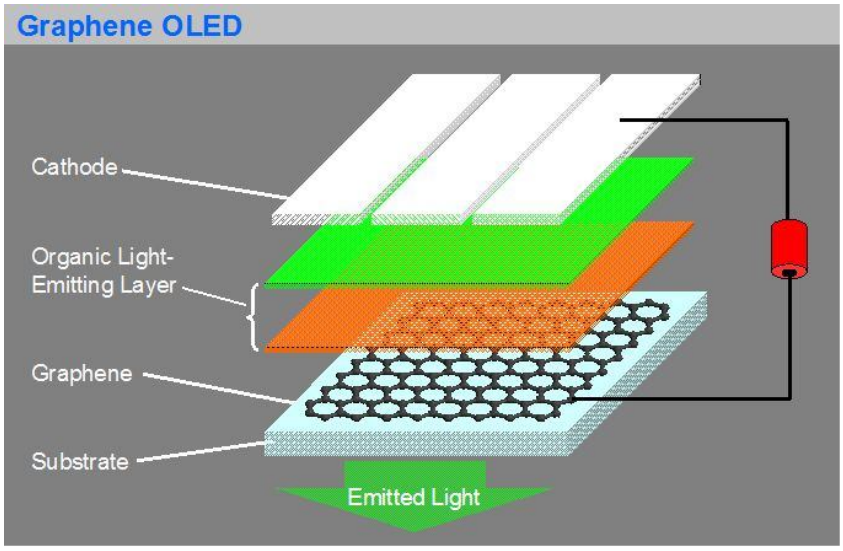


Fig 1.14: graphene *OLED* [16]

1.5 Conclusion:

As mentioned earlier, laboratory-scale electronic devices based on graphene and other two-dimensional materials such as nanotransistors have already been manufactured. Scientists are now seeking to commercialize them by moving from the fabrication of a single nanotransistor to that of a billion transistors on a chip. However, this requires mastering and developing new miniaturization techniques as well as the ability to manufacture these materials on a large scale, with high quality and at a lower cost. This is the current main challenge in the research field of two-dimensional materials. (16)

Chapter 02: Tight binding model

2.1. **Introduction:**

To understand the behavior of electrons in the solid, physicists have proposed several models, which are based mainly on approximations and simplifications of the Schrödinger equation such as the free electron model (17), which neglects all kinds of interactions and it takes into account only the kinetic energy of an electron. However, this model has limitations because it cannot explain the difference between a metal and an insulator. (18)

There are other correct models such as tight binding model. The idea behind it is the following: the Schrodinger equation in solid is a complicated differential equation and an exact analytical solution is not always available, one way to solve it is to suppose that the solution can be written as the linear combination of orthogonal functions that belong to the Hilbert space, if we want more precise solution and make a better approximation of the exact solution, the most accurate choice of these orthogonal functions are atomic orbital functions.
The name of this model "tight binding" comes from the choice of atomic orbital; these functions are almost localized in the centers of their nuclei (18).

2.2 **Tight-binding model for infinite dimensions:**

Application the tight binding model in infinite dimensions monolayer material requires several assumptions and simplifications like

1. The monolayer material is perfect and does not contain any defects.
2. Coulomb interactions between electrons are negligible.
3. The monolayer material is crystal, it has a periodicity and symmetry then it can be described by a Bravais lattice with base.

-One the most important consequence of this assumption is that potential is just periodic function which has the same periodicity of the Bravais lattice or the potential is identical on all Bravais nodes.

4. The wave function is constructed as a linear combination of all atomic orbitals found in the monolayer material and then it will be re-written in simple form by application of Bloch's theorem (19).
5. While solving the Schrodinger equation, we discover integrals called hopping energy and we assume that the values of these integrals are important only for the near neighbors.

-This study is useful for finding the dispersion relation and it help us to **determine the exact values of the hopping energy** (20).
The value of hopping energy of graphene for first near neighbors is -2.8 ev (05).

2.3 Tight-binding model for finite size:

Bloch's theorem only applies when we imposed symmetry and periodicity in our system, this approach is an efficient and fast way to reduce mathematical calculations. However, in cases where the system does not have symmetry, such as a system that contains defects or it is a nanostructure, we can always **apply the tight binding model** but we will not be able to use the Bloch's theorem. (19)

The purpose of this chapter is built a code that helps us to construct Hamiltonian matrix of graphene nanostructure. (20)

First, let's explain the theoretical aspects behind this code, the wave function of an electron with energy ***E*** is linear combination of all atomic orbital found in our nanostructure

$$\psi(\vec{r}) = \sum_{\mu}^{m} \varphi(\vec{r} - \vec{R_\mu}) c_\mu$$

Now, we need to know the exact values of coefficient c_μ by following these steps:

1. We put these previous solutions in Schrodinger equation $H|\psi\rangle = \sum_{\mu}^{m} H|\varphi_\mu\rangle c_\mu$

2. We can obtain a system of linear equations by multiplying previous equation by $\langle\varphi_s|$

Where $s=1, \ldots, \boldsymbol{m}$; ***m:*** total number of atomic orbital in our nanostructure

$$\langle\varphi_1|H|\psi\rangle = \sum_{\mu}^{m} \langle\varphi_1|H|\varphi_\mu\rangle c_\mu = c_1 H_{1,1} + c_2 H_{1,2} + \ldots + c_m H_{1,m} = E c_1$$

$$\langle\varphi_2|H|\psi\rangle = \sum_{\mu}^{m} \langle\varphi_2|H|\varphi_\mu\rangle c_\mu = c_1 H_{2,1} + c_2 H_{2,2} + \ldots + c_m H_{2,m} = E c_2$$

.....

$$\langle\varphi_{m-1}|H|\psi\rangle = \sum_{\mu}^{m} \langle\varphi_{m-1}|H|\varphi_\mu\rangle c_\mu = c_1 H_{m-1,1} + c_2 H_{m-1,2} + \ldots + c_m H_{m-1,m} = E c_{m-1}$$

$$\langle\varphi_m|H|\psi\rangle = \sum_{\mu}^{m} \langle\varphi_m|H|\varphi_\mu\rangle c_\mu = c_1 H_{m,1} + c_2 H_{m,2} + \ldots + c_m H_{m,m} = E c_m$$

These linear equations can be written in matrix form

$$\begin{pmatrix} H_{1,1} & .. & .. & H_{1,m} \\ . & . & & . \\ . & & . & . \\ H_{m,1} & .. & .. & H_{m,m} \end{pmatrix} \begin{pmatrix} c_1 \\ . \\ . \\ c_m \end{pmatrix} = E \begin{pmatrix} c_1 \\ . \\ . \\ c_m \end{pmatrix}$$

In this study, it is assumed that the overlap integrals are negligible, which makes the atomic orbital an orthogonal basis. (22)

The diagonal element $H_{i,i}$ represents onsite energy of an electron in orbital ***i***

The non-diagonal element $H_{i,j}$ equals zero if orbital ***i*** is not near neighbor of orbital ***j***

3. The problem has now become purely numerical, where we need to find the eigenvalues (energies) and the eigenvectors (coefficients c_i) of the Hamiltonian matrix. (17)

2.4. **Tight-binding model for graphene nanostructure:**

The fast way to obtain the Hamiltonian matrix of graphene to assume that the wave function of graphene can be written as follows

$$|\psi\rangle = \sum_{i}^{N}\left(c_{A,i}|\varphi_{A,i}\rangle + c_{B,i}|\varphi_{B,i}\rangle\right) \quad (19)$$

Which $|\varphi_{A,i}\rangle$ represents the atomic orbital $2p_z$ of carbon atom denoted ***A*** in unit cell ***i.***

And $|\varphi_{B,i}\rangle$ represents the atomic orbital $2p_z$ of carbon atom denoted ***B*** in unit cell ***i.***

N is total number of unit cells in nanostructure

Let's start with a simple example and we choose ***N=4***. In this case, the wave function is

$$|\psi\rangle = c_{A,1}|\varphi_{A,1}\rangle + c_{B,1}|\varphi_{B,1}\rangle + c_{A,2}|\varphi_{A,2}\rangle + c_{B,2}|\varphi_{B,2}\rangle + c_{A,3}|\varphi_{A,3}\rangle + c_{B,3}|\varphi_{B,3}\rangle + c_{A,4}|\varphi_{A,4}\rangle + c_{B,4}|\varphi_{B,4}\rangle$$

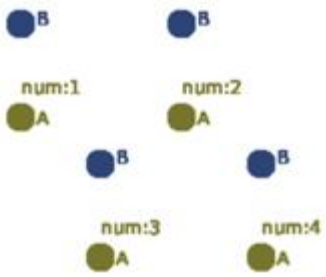


Fig 2.1: simple case

The following equations are obtained by projection of atomic orbital of unit cell ***i*** ($\langle\varphi_{A,i}|$ and $\langle\varphi_{B,i}|$) in Schrödinger equation (15)

$$c_{A1}\langle\varphi_{Ai}|H|\varphi_{A1}\rangle + c_{B1}\langle\varphi_{Ai}|H|\varphi_{B1}\rangle + c_{A2}\langle\varphi_{Ai}|H|\varphi_{A2}\rangle + \ldots + c_{B4}\langle\varphi_{Ai}|H|\varphi_{B4}\rangle = Ec_{Ai}$$

$$c_{A1}\langle\varphi_{Bi}|H|\varphi_{A1}\rangle + c_{B1}\langle\varphi_{Bi}|H|\varphi_{B1}\rangle + c_{A2}\langle\varphi_{Bi}|H|\varphi_{A2}\rangle + \ldots + c_{B4}\langle\varphi_{Bi}|H|\varphi_{B4}\rangle = Ec_{Bi}$$

Previous equations can be rewritten in matrix form

$$\begin{pmatrix} \langle \varphi_{Ai} | H | \varphi_{A1} \rangle & \langle \varphi_{Ai} | H | \varphi_{B1} \rangle \\ \langle \varphi_{Bi} | H | \varphi_{A1} \rangle & \langle \varphi_{Bi} | H | \varphi_{B1} \rangle \end{pmatrix} \begin{pmatrix} c_{A1} \\ c_{B1} \end{pmatrix} + \begin{pmatrix} \langle \varphi_{Ai} | H | \varphi_{A2} \rangle & \langle \varphi_{Ai} | H | \varphi_{B2} \rangle \\ \langle \varphi_{Bi} | H | \varphi_{A2} \rangle & \langle \varphi_{Bi} | H | \varphi_{B2} \rangle \end{pmatrix} \begin{pmatrix} c_{A2} \\ c_{B2} \end{pmatrix} + \ldots.$$

$$+ \begin{pmatrix} \langle \varphi_{Ai} | H | \varphi_{A4} \rangle & \langle \varphi_{Ai} | H | \varphi_{B4} \rangle \\ \langle \varphi_{Bi} | H | \varphi_{A4} \rangle & \langle \varphi_{Bi} | H | \varphi_{B4} \rangle \end{pmatrix} \begin{pmatrix} c_{A4} \\ c_{B4} \end{pmatrix} = E \begin{pmatrix} c_{A1} \\ c_{B1} \end{pmatrix}$$

If we denote the following submatrix

$$\begin{pmatrix} \langle \varphi_{Ai} | H | \varphi_{Aj} \rangle & \langle \varphi_{Ai} | H | \varphi_{Bj} \rangle \\ \langle \varphi_{Bi} | H | \varphi_{Aj} \rangle & \langle \varphi_{Bi} | H | \varphi_{Bj} \rangle \end{pmatrix} = h_{i,j}$$

This example leads us to assume that Hamiltonian matrix can be rewritten by submatrix $\boldsymbol{h_{i,j}}$ ***(12)***

$$H = \begin{pmatrix} h_{1,1} & .. & h_{1,N} \\ . & . & . \\ h_{N,1} & .. & h_{N,N} \end{pmatrix}$$

2.5. Construction of the Hamiltonian matrix:

The simplest shape of graphene nanostructure to start with is parallelogram (09)

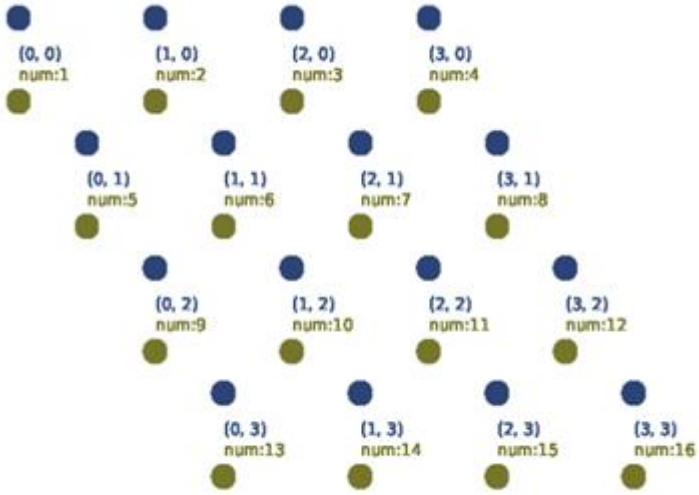


Fig 2.2: labeling the unit cells

Some remarks can help us in coding

1. Each unit cell has own index ***(iu, ju)*** and it has its own number ***num*** Fig 2.2
2. The relation between number of unit cells and their indices is ***num= iu+1+(ju*nx).***

Where ***nX*** is total number of unit cells along ***x*** direction and ***nY*** is total number of unit cells in ***y*** direction.

3. From Fig 2.3, we can deduce the formulas that help us calculate the numbers of first nearest neighbors.

   The number of downright nearest neighbor can be calculated by

   *numdoR= iu+1+((ju-1)*nX)*

   The number of down left nearest neighbor can be calculated by

   *numdoL= iu+2+((ju-1)*nX)*

   The number of upper right nearest neighbor can be calculated by

   *numupR= iu+1+((ju+1)*nX)*

   The number of upper left nearest neighbor can be calculated by

   *numupL= iu+((ju+1)*nX)(16)*

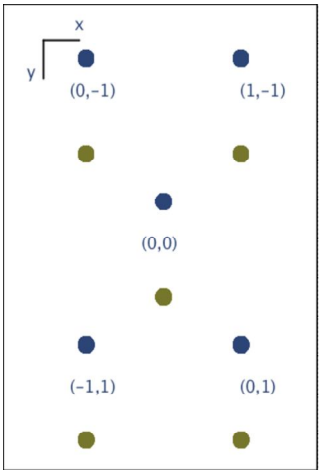


Fig 2.3: index of nearest neighbor

4. Assuming we have two cells, the first unit cell with ***num*** =***k*** and the second one with ***num***= ***s*** then the diagonal sub-matrices

$$h_{k,k} = \begin{pmatrix} \varepsilon & t \\ t & \varepsilon \end{pmatrix}$$

Where t is hopping energy and ε is onsite energy; it is conventionally assumed that ε equals *0* ev

5. If the unit cell ***k*** is nearest neighbor of unit cell ***s***, then

$h_{k,s} = \begin{pmatrix} 0 & t \\ 0 & 0 \end{pmatrix}$ if ***s*** equals *numdoR* or *numdoL*.; $h_{k,s} = \begin{pmatrix} 0 & 0 \\ t & 0 \end{pmatrix}$ if ***s*** equals *numupL* or *numupR*.

6. If unit cell ***s*** is not a nearest neighbor of unit cell ***k*** then $h_{k,s} = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}$

7. Each projection of ($\langle \varphi_{A,k} |$ and $\langle \varphi_{B,k} |$) in Schrödinger equation yields a row of sub-matrix

$$L = \begin{bmatrix} h_{k,1} & h_{k,2} & h_{k,3} & \dots & h_{k,N} \end{bmatrix} \quad (13)$$

Chapter 03: Coding and validation

3.1 Coding section:

This code is written in Python, and we need import tow libraries: Numpy and Matplotlib

```
import numpy as np
import matplotlib.pyplot as plt
```

we start writing a class ***cellunit*** for unit cell, the goal of this class is to collect information about the indices and number of current unit cell and the number of their first nearest neighbors. (14)

class cellunit:

```
    def __init__(s, i, j, nX, nY):
        s.nX= nX
        s.nY= nY
        s.iu= i
        s.ju= j
        s.Eonsite= 0
        s.t= -2.8
        s.numupL, s.numupR, s.numdoR, s.numdoL= 0, 0, 0, 0
        s.num= (s.iu+1)+s.nX*s.ju
```

When constructor of this class is executed; the number of unit cell s.num is calculated based on the equation mentioned in remark 02. (06)

The numbers of the first nearest neighbor unit cells are initialized as zero but we must create a Method called ***neigbN*** in this class that allows us to calculate them based on remark 3.

Before that, we must verify if the nearest neighbor with indices ***(iu, ju)*** are inside our shape or not. if this condition is satisfied $0 \leq iu \leq nX$, $0 \leq ju \leq nY$

```
def isinside(s, i, j):
        d=(i>=0 and j>=0 and i<=s.nX-1 and j <= s.nY-1)
        return d
def neigbN (s):
         i= s.iu
         j= s.ju+1
        if (s.isinside(i, j)):
                s.numupR= (s.iu+1)+s.nX*(s.ju+1)
        i=s.iu-1
        j=s.ju+1
```

```
if(s.isinside(i, j)):
        s.numupL= (s.iu)+s.nX*(s.ju+1)
 i=s.iu
 j=s.ju-1
 if (s.isinside(i, j)):
        s.numdoR= (s.iu+1)+s.nX*(s.ju-1)
 i= s.iu+1
 j= s.ju-1
if (s.isinside(i, j)):
        s.numdoL= (s.iu+2)+s.nX*(s.ju-1)
```

In this class, we define a new method ***Looknei*** which receives an object of class *cellunit* ***b*** and it compares the numbers between ***b.num*** and ***num*** of current unit cell and it will return a sub-matrix $h_{i,j}$ based on the remarks (5 , 6, 7) (11)

```
def Looknei (s, b):
        Ediag= np.array ([[s.E, s.t], [s.t, s.E]])
        tup=   np.array ([[0, s.t], [0, 0]])
        tdown=   np.array ([[0, 0], [s.t, 0]])
        zero=    np.array ([[0, 0], [0, 0]])
        if (s.num== b.num):
                return Ediag
        elif (b.num == s.numupLorb.num == s.numupR):
                return tup
        elif (b.num == s.numdoRorb.num == s.numdoL):
                return tdown
         else:
                return zero
```

Next, we write new class called "***nanostructure"***, in the constructor of this class we define total number of unit cell along ***x***-direction (*nX)* and along ***y***-direction (*nY)* as well as the total number of unit cells in our nanostructure ***N=nX*nY (08)***

When the constructor of this class executed, a list called "***nanos***" will be created and it will contain ***N*** objects of class *cellunit,* each object has own indices and own number

```
class nanostructure:
    def __init__(s, nxx, nyy):
        s.nX= nxx;
        s.nY= nyy;
        s.N= s.nX*s.nY;
```

```
s.nanos= []
for j in range(s.nY):
        for i in range(s.nX):
            s.nanos.append(cell(i, j, s.nX, s.nY))
```

In this class, we define a method named *neig(s)*, the main goal of this method is to perform calculation of the numbers of first near neighbors for each declared unit cell ***nanos[i]***

```
def neig(s):
    for i in range(s.N):
        s.nanos[i].neigbN()
```

The sub-matrix $h_{2,3}$ for example can be constructed by calling the following method *s.nanos[2].Looknei(s.nanos(3))*

if we want to construct the following row of sub-matrix: $L = \begin{bmatrix} h_{2,1} & h_{2,2} & h_{2,3} & \dots & h_{2,N} \end{bmatrix}$

- Iterate over ***i*** from 1 to ***N*** for obtaining all elements of the row L .
- Call function *np.append(L, u, axis=1)* from numpy library which allows to append matrix to actual submatrix $\begin{bmatrix} h_{21} & h_{22} & h_{23} \end{bmatrix} + h_{24} \rightarrow \begin{bmatrix} h_{21} & h_{22} & h_{23} & h_{24} \end{bmatrix}$

We define a method called "***MakeLine"*** that allows us to construct a row of sub-matrix

```
def MakeLine(s, numL):
    L= np.array(s.nanos[numL].Looknei(s.nanos[0]))
    for i in range(1, s.dim):
        u= s.nanos[numL].Looknei(s.nanos[i])
        L= np.append (L, u, axis=1)
    return L
```

In this stage, we can call ***MakeLine(s, 1)*** to generate the first row of submatrix

$H = \begin{bmatrix} h_{1,1} & h_{1,2} & h_{1,3} & \dots & h_{1,N} \end{bmatrix}$

if we call it again ***MakeLine(s, 2)*** it will return to us the second row of the submatrix

$L = \begin{bmatrix} h_{2,1} & h_{2,2} & h_{2,3} & \dots & h_{2,N} \end{bmatrix}$

if we use the append function *H= np.append(H, L, axis=0)* we obtain

$$\begin{bmatrix} h_{1,1} & h_{1,2} & h_{1,3} & \dots & h_{1,N} \\ h_{2,1} & h_{2,2} & h_{2,3} & \dots & h_{2,N} \end{bmatrix}$$

Now, if we want to obtain the entire Hamiltonian matrix, we must iterate over ***i*** from 1 to ***N***

```
def MakeHamiltonian(s):
```

```
H=  s.MakeLine(0)
for i in range(1, s.N):
    L= s.MakeLine(i)
    H= np.append(H, L, axis=0)
return H
```

Finally, we obtain the entire Hamiltonian matrix when the method ***MakeHamiltonian()*** is executed The constructed matrix is **Hermitian** and its **eigenvalues** are real.

The dimension of ***H*** is ($2N*2N$) because we have N unit cells, and each unit cell contains two atoms

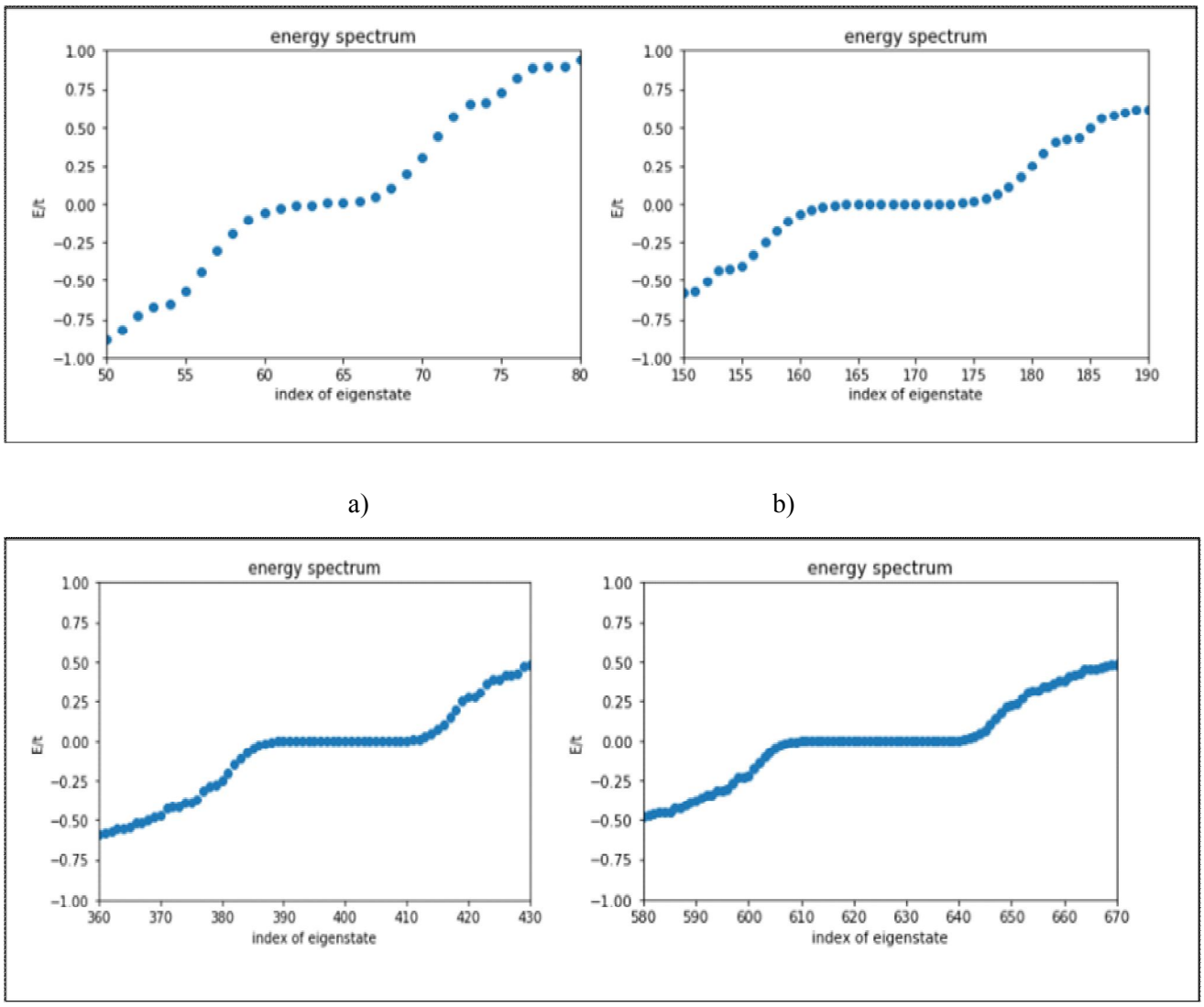
The hopping energy is only significant for first nearest neighbors. If N is large the resulting matrix becomes sparse matrix, and there are specific numerical methods available for finding eigenvalues and eigenvectors of this kind of matrix, such as *eigh()* from Scipy.library.

In our nanostructure class, we can import Scipy library and define method ***solve ()*** as follows (02)

```
import scipy as sc
  def  solve(s, H):
       return sc.eigh(H)
```

3.2. Results and validation:

In this section, we present the results obtained from our code where the energy spectrum is calculated for different size of graphene nanostructures as shown in Fig 3.1 (19)



a) b)

c) d)

Fig 3.1: Comparison between energy spectrums of four nanostructures. a) 128 atoms, b) 338 atoms, c) 800 atoms, d) 1250 atoms

The application of tight-binding model for nanostructure which owns a shape mentioned in Fig 3.1 give us the following informations: (22)

1. The appearance of two energy bands: conduction band and valence band
2. A discrete energy spectrum for small sizes and a continuous energy spectrum for large sizes
3. The appearance of degeneracy at the Fermi level

4. The degenerate energy states increase with size of nanostructures

Our nanostructure contains zigzag edges; this edge is responsible of the observed degeneracy. This result has been confirmed through calculation of local density of state (21).

We can create a graphene nonoribbon with an armchair edge configuration by putting ***nY>> nX***. This is because, as shown in Fig 2.2, the armchair edge appears in the x-direction (22)

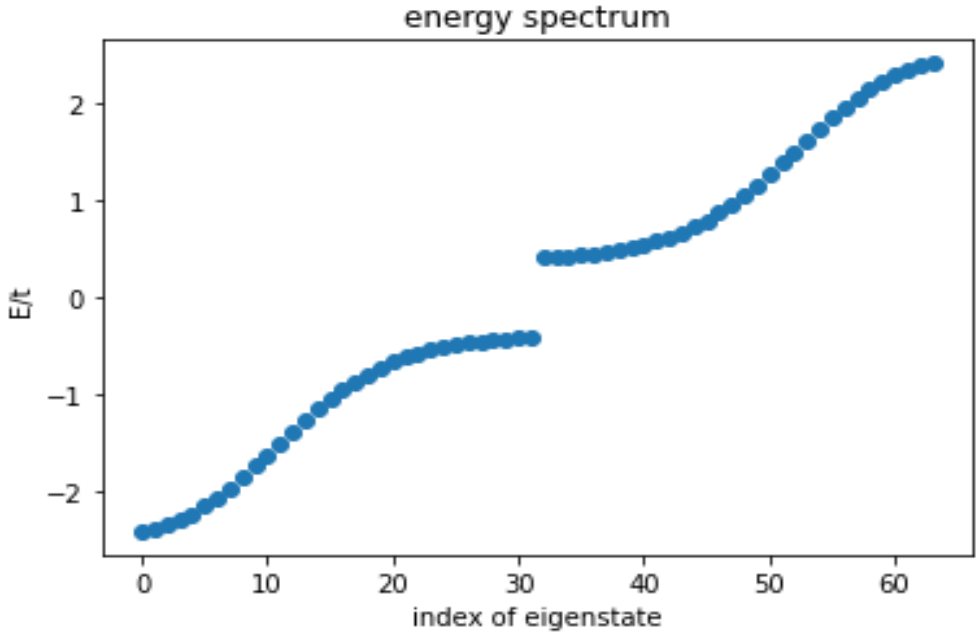


Fig 3.2 energy spectrum for graphene nanoribbon with *nX*=16 and *nY*=2

In Fig 3.2: we demonstrate that our code successfully predicts the **band gap opening** in graphene nanoribbon with armchair edge (22).

General Conclusion

The code developed in this study serves as a fundamental building block for finding the Hamiltonian matrix for more complex shapes of graphene nanostructure. It can also be used for calculating the local density of states or studying quantum transport in this material.

In addition, we can explore the outcomes of our code, as they contribute to the estimation of electron probabilities at specific locations with corresponding energy levels Based on our results, we can conclude also that the electronic properties of the nanoribbon are significantly influenced by its edge configuration

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