



# Treball Final de Grau

**On the possibility to identify N dimers in N-doped graphene by means of X-Ray Photoelectron Spectroscopy.**

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*Els impossibles d'avui seran possibles demà.*

Konstantin Tsiolkovsky

No us podeu imaginar la estona que porto intentant trobar la forma més adequada d'escriure aquestes línies, no hi ha manera, quan per fi em semblar que he donat amb la resposta, una altre idea se m'apareix i m'obliga a reescriure-ho tot de dalt a baix, fins i tot per un moment he pensat que el Treball de Fi de Grau de seixanta pàgines en anglès havia estat més fàcil d'escriure que aquestes poques línies, però després d'aquest moment de desconcert ho he vist clar, totes les formes que he imaginat d'escriure aquestes línies tenien un fet en comú, el que volia transmetre era el mateix, agraïment, agraïment al Francesc per haver-me guiat en aquest llarg camí així com per la paciència que ha demostrat al explicar-me una i altre vegada aquells conceptes que no entenia, agraïment a la Noèlia per una paciència il·limitada i una ajuda incondicional sense les que no hauria pogut tirar endavant aquest treball i per últim agraïment a la meua família i amics que m'han recolzat i escoltat atentament les meves elucubracions derivades del TFG, de les que sense cap mena de dubte no entenien res però tot i així s'interessaven i preguntaven.

Estic segur de que podria haver escrit aquestes línies de vint maneres més, però el missatge hauria estat el mateix, per tot el que heu fet per mi, gràcies.



# REPORT





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# 1. SUMMARY

Graphene is a material with unique properties not seen yet in other compounds. In fact, this is the reason behind everyone talking about it. In the last years, the possible applications of this compound have been studied extensively due to its unexpected and exotic properties. Nowadays, the number of applications of graphene based devices and systems is ever growing. The present work focuses in one of these possible applications.

Graphene has the capacity to behave like a metal, this is because some special features of its electronic structure; namely the absence of a band gap. This provides a great capability to act as an electrical conductor. In fact, graphene conductivity can overcome that of metallic compounds such as copper, one of the best electrical conductors. This property is worthy in itself but also implies some drawbacks in possible applications in electronics. Doping, as in the case of classical semiconductors based in Si and largely used in transistors and other electronic devices, offers the possibility to engineer the band gap of graphene as well. In fact, doping with nitrogen has been successfully achieved and the resulting system behaves effectively as an n-doped semiconductor. The problem of doping is, however, the lack of control in the synthesis and, depending on the method used, the nitrogen atoms introduced in the graphene network can occupy different sites resulting in different advantageous or undesired properties. The first step towards a control of the doping at an atomic level requires identifying the sites where the N atoms are located. In addition, N atoms in the graphene network may cluster in dimers which have been suggested to introduce a structural instability.

The main aim of the present work is to investigate whether the presence of N dimers in the graphene networks can be identified through X-ray photoelectron spectroscopy (XPS), one of the most broadly used techniques in materials science. XPS provides the binding energy (BE) of core electrons that depends essentially on the ionized atom but also and its surroundings. Following, previous work on the theoretical study of the core level binding energy (CLBE) of isolated N atoms at distinct sites of the graphene network, we analyze different models for N dimers on graphene and inspect the corresponding N(1s) CLBE to provide information on

whether these structures can be resolved by XPS. This is accomplished by the help of theoretical calculations based on Density Functional Theory (DFT), which allowed us to accurately determine the N(1s) CLBE and to, hence, to provide information regarding possible spectroscopic differentiation of the different possible atomic arrangements. The results are conclusive, the existence of near neighbour (n,n) dimers lead CLBEs different enough so as to unambiguously identify them. On the other hand, next near neighbour (n,n,n) dimers cannot be detected using XPS because the (n,n,n) dimer signal is too close to the isolated nitrogen signal.

**Keywords:** Graphene, XPS, N-dimers, binding energy, DFT.

## 2. RESUM

El grafè és un material amb propietats que fins ara no s'havien pogut observar en cap altre compost, de fet és precisament per aquest motiu que està en boca de tots. En els últims anys s'han estudiat extensivament les possibles aplicacions d'aquest compost, que degut a les seves propietats, han acabat essent molt extenses, si bé és cert que aquest treball només està relacionat amb una d'aquestes d'aplicacions.

El grafè té la capacitat de comportar-se com un metall degut a que la seva estructura electrònica no presentar banda prohibida, fet que li atorga una gran capacitat com a conductor elèctric, tan és així que la seva conductivitat arribar a superar la d'elements amb un comportament pròpiament metàl·lic com ara el coure, considerat un dels millors elements conductors que es coneixen. Aquesta capacitat per si sola ja és digne d'esment, però en aquest treball anirem una mica més lluny, perquè si bé és cert que una conductivitat superior pot obrir moltes oportunitats aquest jove material, la capacitat d'emprar-lo per a substituir els components electrònics produïts fins ara a partir del silici, aportant una miniaturització i un augment significatiu de la eficiència pot representar una revolució en molts àmbits de la nostra societat.

Hom pot haver pensat, encertadament, que el silici no és pas un material conductor, comportament que acabem d'atribuir-li al grafè. Concretament, el silici pertany al grup dels semiconductors, i és precisament aquest caràcter intrínsec de la seva naturalesa que, convenientment dopat, és emprat en la fabricació de transistors i així formar part dels components electrònics. Doncs bé, el grafè també pot comportar-se com a semiconductor, però per això cal generar una banda prohibida, que s'aconsegueix dopant-lo, per exemple amb nitrogen. El problema del dopatge és la manca de control, a nivell atòmic, dels llocs que el N ocupa a la xarxa bidimensional de grafè. En funció del mètode de síntesi utilitzat, els àtoms de nitrogen poden veure's afavorits a ocupar diferents posicions que podem trobar en la estructura del grafè, a saber: nitrogen piridínic, pirrolic i grafitic i les seves combinacions dos a dos.

Per tal de determinar on s'ha realitzat el dopatge una de les tècniques que es podrien emprar és la espectroscòpia fotoelectrònica de raigs-x (XPS) que es permet mesurar les energies de lligadura (BE) dels nivells interns (CLBE de l'anglès “*core level binding energy*”), que depenen essencialment del àtom que ha estat ionitzat però també del seu entorn. Seguint treballs previs centrats en l'estudi teòric dels CLBEs d'àtoms de N aïllats en la xarxa de grafè, en el present treball s'analitzen i interpreten els valors corresponents a les CLBEs de N(1s) per tal de determinar si aquestes estructures es podrien resoldre emprant XPS. Això s'aconsegueix mitjançant l'ajut de càlculs teòrics basats en la teoria del funcional de la densitat (DFT) que ens ha permès determinar de manera acurada les CLBE dels N(1s) i així aportar informació sobre la possible diferenciació de les estructures atòmiques que contenen dos àtoms de N. Els resultats són concloents, l'existència de dímers de tipus veí proper (n,n) es pot resoldre atès que presenten CLBEs prou diferents. D'altra banda, en cas de segons veïns no es pot resoldre ja que les CLBEs són molt properes a la dels àtoms de N en l'estructura de grafè aïllats.

**Paraules clau:** Grafè, XPS, dímers de N, energia de lligadura, DFT.

### **3. INTRODUCTION**

There is a new world coming, the technological advances promoted by science are changing our life style. In one hundred years the way in which mankind has lived has changed so much that probably our predecessors would feel lost in our time. But what technological advance has provoked this change? The answer of this question is not easy and concrete but probably the electronic devices have had a great impact in this society transformation. The capacity to connect each other in different parts of the world practically instant or the possibility to know everything with a few clicks, that of course has changed us, but the really fact that is behind these developments are the instruments that have the capacity to transmit electrical pulses at an incredible speed, the capacity to change that signals and the size that they need to do it, in other words, electronic microchips. These little electronic compounds are the basis of the current world, every electronic device has electronic microchips, and if we observe our environment we will see that we use so many objects based on electronics, so we can say that our world is governed, indirectly, by microchips.

Since the beginning of electronics all the microchips used are made of silicon, a semiconductor material capable to do all the functions named before, but recently, a group of scientists discovered an incredible material, graphene, this surprising material has some qualities that make him awesome. If we search information of graphene we will find a great quantity of articles explaining their exceptional properties, but to relate graphene with microchips only two of this properties are needed. Graphene has an incredible capacity to conduct current, two hundred times more than copper, this happens because graphene behaves as a metal, concretely, graphene has some points on its electronic structure where there is not band gap, electrons can pass from valence band to conduction band without a need of an energy input, this makes it a great substitute to all integrated circuits in electronic devices, and this is an incredible advance, but not the only one.

The second property and probably the more important is that graphene can substitute silicon as the principal compound of microchips, but how? I have mentioned that silicon can do what it does because it is a semiconductor, it has a band gap that confers to it this capacity, and I also have commented that graphene does not have it, so how is that possible? It is true that pure graphene can't act as a semiconductor but if we dope it, for instance with nitrogen, things change, nitrogen opens a band gap and this makes graphene able to substitute silicon and at the same time provides some advantages like the reduction of the size, more speed of transmission of electrical pulses and the decrease of the fragility of the microchip.

But in this life nothing is as simple as it seems. When N-doped graphene is generated, isolated nitrogen atoms can be placed in three different positions into the graphene structure, namely, graphitic nitrogen, pyridinic nitrogen and pyrrolic nitrogen. Moreover, groups of N atoms can be present on the doped sample and it is important to know where these atoms are placed because this will determine the efficiency of graphene acting as a semiconductor, and not only this, also the defects that are generated by doping graphene are related to the concentration of nitrogen and where is it placed<sup>1</sup>. To know where nitrogen is placed one of the most recurrent used technique is X-ray photoelectron spectroscopy (XPS), this technique help us to determine the structure of graphene using the Core Level Binding Energy (CLBE) or the Core Level Binding Energy Shifts (CLBE shifts). Both, the XPS and the BE's, will be explained hereinafter but, what is interesting now is that these energies are different in function of the nitrogen type we have and the environment of these atoms, so we can define how is graphene network or how nitrogen atoms are placed into the network.

### **3.1. GRAPHENE<sup>2</sup>**

At the beginning of 20<sup>th</sup> century, two scientists called Landau and Peierls argued that 2D crystals were impossible to find or synthetize because they are thermodynamically unstable, well now we know that this is not true, the proof: graphene. It was not until 2004 that two scientists named Andre Geim and Konstantin Novoselov found a method, known as mechanical exfoliation, to synthetize graphene, this discovery made them deserve the Nobel Prize in physics in 2010.



Graphene is and allotrope of carbon densely packed in two dimensions that form six-membered rings and is, at the same time, the studied object in this work. Recently, this material has taken importance because of its incredible properties that we will see forward and also because of its honeycomb structure is the basis of other carbon allotropes, like carbon nanotubes or fullerene.

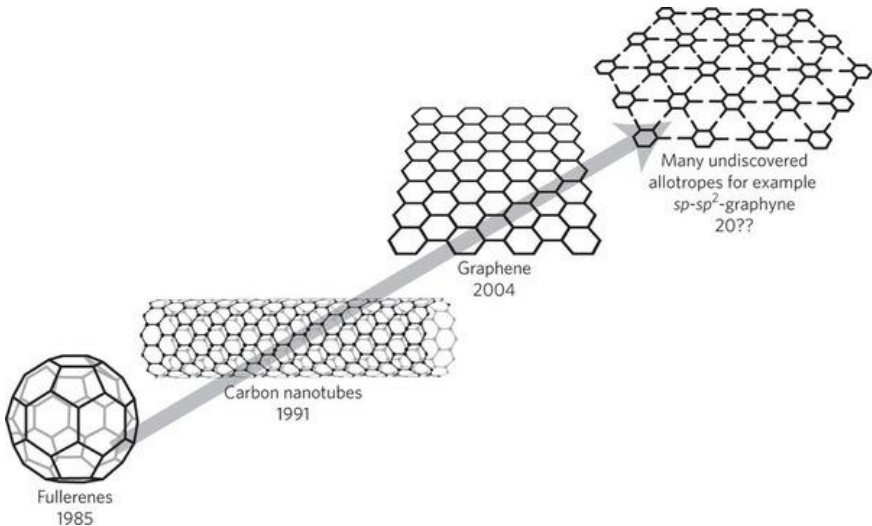


Figure1. Different allotrope structures of carbon

(Andreas Hirsch. *The era of carbon allotropes. Nature Materials* 9, 868-871 (2010))

It is possible to define three types of graphene in function of number of layers that form it, namely: single-layer graphene (SG), bi-layer graphene (BG) and few-layer graphene. Probably the most important of these three types is the first one, the single-layer graphene, but this fact is not only related with its properties, that are different from the other types, the most important fact is that there is not a well-defined procedures to synthetize graphene with the desired number of layers, and if there is not, all the possible applications for this other types of graphene are useless. It is important to note that the  $p_z$  orbitals of graphene (also called  $\pi$  orbitals) are not completely filled and also less weakly attached than the electrons forming  $\sigma$  bonds, these two features combined with honeycomb structure are the reason that gives graphene a special electronic band structure. This electronic band structure explains why graphene act like a metal, as explained above, in some points called Dirac points<sup>2</sup>, valence band and conduction band are

overlapping, and this gives to graphene the status of semiconductor of zero-gap. Close to Dirac points, electrons behave as massless charge carriers with an incredible speed<sup>2</sup> ( $10^6\text{m/s}$ ), more than any other material.

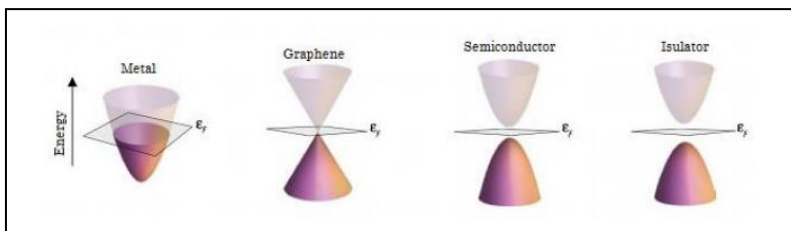


Figure 2. Different electronics band structures near Fermi level. Note that graphene seems a metal with a negligible density of states at Fermi level.

(Victor Manuel Freire Soler. *Fabrication and characterization of macroscopic graphene layers on metallic substrates*. Universitat de Barcelona. 2014.)

### 3.2. X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

Even from the beginning, in 1956, X-ray Photoelectron Spectroscopy is one of the most employed experimental techniques in chemistry and physics. This technique has a wide range of applications in different fields like in chemistry analysis for atoms, molecules and condensed phases, and even more, also is a surface sensitive technique. To understand why this technique is a good choice to study molecules surface is indispensable to know how it works. Mainly, this technique is based on Einstein's explanation of the photoelectric effect, whereby photons can induce electrons emission from the surface of the solid because these photons give their energy to the electrons ( $h\nu$ ), but not any energy is enough to reach this purpose, the energy needed has to be greater than or equal to the energy of the work function<sup>3</sup> (defined as the minimum energy required to remove an electron from the highest occupied energy level in the solid to the vacuum level, it is usually given the symbol  $\phi$ ). The vacuum level, named in the definition of the work function, is the necessary energy given to an electron to reach vacuum far from the interaction with other particles (zero potential energy) and at the same time, this electron will have zero kinetic energy, it will be at rest.

In XPS, a monochromatic beam of X-ray is emitted on the surface causing the photoemission to the atom, and the instrument is capable to measure the extra kinetic energy that the electrons that exceed the vacuum level have, if there is an electron with only the vacuum level energy this photon will not be detected by the instrument, so we can define

vacuum level as an “energy zero”. All the electrons can be affected by the incident ray, valence electrons and core electrons. Core electrons are the key to identify what element we have, so studying their Binding Energy, a new concept that will be explained below, we will be able to get information about the chemical environment or the oxidation state of the atom.

### 3.2.1. Binding Energy and Binding Energies shifts

For a molecule, the binding energy is defined as the energy needed to remove one electron from a system in its ground state; this is to move one electron from the system to the vacuum. Note, however, that in the case of a condensed matter system it is necessary to consider the surface work function  $\phi$ . In the XPS technique, an X-ray ionizes the sample (core and valence) electrons and measures the kinetic energy of the ejected electrons when they arrive to the detector. The overall effect is closely related to the photoelectric effect and, hence, one can just use the Einstein famous equation as

$$E_{kin} = h\nu - (E_B + \phi) \quad (1)$$

where  $E_{kin}$  is the kinetic energy,  $h\nu$  is the energy of the photon,  $E_B$  is the binding energy and  $\phi$  is the work function. If we know the work function is trivial to convert  $E_{KIN}$  into BE and that's what plot the instrument of XPS.

$$E_B = h\nu - E_{KIN} - \phi \quad (2)$$

XPS focuses on the core level binding energies (CLBEs) which are characteristic of each chemical element. Hence, the ensemble of CLBEs obtained from the XPS peaks, ordered in function of the BE, fully determines the chemical composition of a molecule ( $\phi=0$ ) or a solid. CLBEs provide also useful information regarding the environment, chemical interactions and chemical bonding, of the core ionized atom. In that case the important quantity is not the CLBE but the shift with respect to a given reference, these are referred to as Core Level Binding Energies Shifts ( $\Delta$ CLBEs), this is the difference between two CLBEs of a given atom in different systems.

The ionization of a core level is an extremely fast process and, hence, one can argue that the information regarding the environment of the ionized atom is already present in the neutral, unionized system. This is usually referred to as initial state CLBEs and can be obtained from the wave function (or electron density) of the neutral system. Clearly, the ionization process is not infinitely fast and, therefore, final state effects where the wave function of the cation is

considered need to be taken into account. For a given core in different environment,  $\Delta$ CLBEs are usually determined by initial state effects. Nevertheless, in some cases final state effects are predominant as in the case of satellites that are an integral part of XPS spectra and often difficult the separation of the main line from the satellites. It is worth pointing out that satellites are not involved in the systems studied in the present work.

Once we have obtained the BE shifts, calculated from the experimental BEs, we have to appreciate how this shifts are related with features like the chemical or physical environment and the chemical bonding and, comparing to theoretical calculation as those describes in the forthcoming sections, whether they are essentially dominated by initial state effects. Several main mechanisms are known to contribute to the BE shifts. The first and most important mechanism is the charge transfer to or from the core ionized atom, a second mechanism is related to the electrical field caused by charges that are located around the atom. Other, mechanisms that contributes to BE shift are coordination and hybridization.<sup>5</sup>

## **4. OBJECTIVES**

- The principal objective of this work is to determine if it is possible to differentiate N atoms in nitrogen dimers placed in different positions in the graphene structure using their experimental Core Level Binding Energy that we will be approach from theoretical calculations.
- Acquire knowledge on computational methods of calculation as well as new quantum chemistry concepts.
- Better understanding of all the concepts related to XPS.

## 5. THEORETICAL FRAMEWORK

### 5.1. HARTREE-FOCK METHOD

The Hartree-Fock method approximates the wave function and the energy of the electronic ground state of a quantum system of electrons based on the variational principle that, in turns follows from the variational theorem. The variational theorem states that, for a given system described by the exact ( $\hat{H}$ ) Hamiltonian, the expectation energy obtained from a well behaved trial wave function ( $\Psi$ ) is always higher than the exact ground state energy ( $E_0$ ) corresponding to the exact ground state wave function ( $\Psi_0$ ), that is

$$\langle \Psi | \hat{H} | \Psi \rangle = E \geq E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle \quad (3)$$

It is generally impossible to obtain  $E_0$  from trial wave functions even when applying the variational principle. Moreover, the choice of the trial function already entails some approximations. A first usual approximation is to assume that electrons do not interact with each other. This, allows one to express the N-electron wave function ( $\Psi$ ) as a product of individual one-electron wave functions ( $\phi$ ) called orbitals. Also, to fulfil the Pauli principle, it is required to introduce the spin electron concept that assigns a particular spin state,  $\alpha$  or  $\beta$ , to individual electrons. Hence, the one-electron functions, generally termed as spinorbitals, are the result of the product of spatial orbitals and of the spin function  $\sigma(s)$ , the latter being either  $\alpha(s)$  and  $\beta(s)$  with  $s$  defining a generic spin coordinate. Thus, spinorbitals take the form

$$\chi_1^\alpha(\vec{x}_1) = \phi(\vec{r}_1) \alpha(s_1) \quad (4)$$

$$\chi_1^\beta(\vec{x}_1) = \phi(\vec{r}_1) \beta(s_1) \quad (5)$$

Since two electrons can have the same space orbital part, it is possible to write the N-electron wave function of n non-interacting electrons as:

$$\Psi = \chi_1^\alpha(\vec{x}_1) \chi_1^\beta(\vec{x}_2) \dots \chi_{\frac{N}{2}}^\beta(\vec{x}_n) \quad (6)$$

The expression above is known as a Hartree product and determinates that electron 1 is in the spinorbital  $\chi_1^\alpha$  and electron 2 in  $\chi_1^\beta$  and so on. One can argue that this equation is finally a good

candidate for the approximate wave function that a first variational estimate of the ground state energy of the system. Nevertheless, another factor should be considered, the antisymmetric principle. This principle expose that electrons, having half-integer spin, are fermions and must be described by a wave function that changes the sign under any permutation of any pair of electrons or fermions. To satisfy the antisymmetric principle V.A. Fock suggested expressing the total wave function as a matrix of  $N \times N$  spin orbitals that allow the sign change when two electrons permuted their spatial positions. The resulting wave function is called Slater determinant,  $\Phi_{SD}$ , and normally is expressed as the diagonal elements of the matrix, that define the electronic configuration.

$$\Psi \approx \Phi_{SD} = \frac{1}{\sqrt{N!}} |\chi_1(\vec{x}_1)\chi_2(\vec{x}_2) \dots \chi_N(\vec{x}_n)| \quad (7)$$

The main difference between a Hartree product and a Slater determinant is that the former defines the state of each electron (electron 1 at  $\chi_1^\alpha$ ) whereas the latter does not distinguish between electrons (one electron at  $\chi_1^\alpha$ ) thus fulfilling the basic principle of indistinguishability of electrons. Once a reasonable a physically acceptable approximation to the real wave function of the system is reached; one can proceed to calculate the minimum energy of the system using the variational method.

To reach the minimum ground state energy of the molecule using the variational method only spin orbitals can be chosen, with this in mind D.R. Hartree and V. Fock argue that with the optimum spin orbitals the minimum ground state energy will be reached, so they derived the next expression, named Hartree-Fock equation:

$$\hat{f}_i \chi_i = \varepsilon_i \chi_i \quad (8)$$

where  $\chi_i$  is the spin orbital  $i$ ,  $\varepsilon_i$  is the energy of the spin orbital and  $\hat{f}_i$  is the Fock operator. It is important to note that since there are  $N$  spin orbitals also there are  $N$  Hartree-Fock equations that have to be solved, but all are identical so solving only one is enough.

The Fock operator is defined as:

$$\hat{f} = -\frac{1}{2} V_i^2 - \sum_a^m \frac{Z_a}{r_{ia}} + V_{HF}(i) \quad (9)$$

Where the first term is the kinetic energy of the electrons, the second term is the potential energy between electrons and nucleus and the last one is the Hartree-Fock potential.

The Hartree-Fock operator looks similar to Hamiltonian operator but as the Fock equation represent a system of non-interacting electrons the term that attempts to determine the potential

energy between one electron with each one of the system in the Hamiltonian operator is omitted on Hartree-Fock operator and replaced by the Hartree Fock potential, where electron-electron interaction is described as an average effect felt by one electron due to the presence of all other electrons of the system. The difference between Hartree-Fock operator and Hamiltonian operator is the correlation operator.

The Hartree-Fock potential is described as:

$$V_{HF}(\vec{x}_1) = \sum_j^n (\hat{j}_j(\vec{x}_1) - \hat{K}_j(\vec{x}_1)) \quad (10)$$

where the first term represent the Coulomb operator,  $\hat{j}_j$ , and the second term, the exchange operator,  $\hat{K}_j$ , that take into account the spin correlation effects. Those operators depend on the spin orbitals so at this point is where the variational process begin. A set of spin orbitals,  $\chi_N(i)$ , is considered to do the calculation of the two operators described before ( $\hat{j}, \hat{k}$ ), then the Hartree-Fock potential is calculated,  $V_{HF}$ . Next the Fock operator,  $\hat{f}$ , is built using the Hartree-Fock potential for every spin orbital, and the equations are solved using the already called Fock operator. At this point a new set of spin orbitals,  $\chi_N(ii)$ , is obtained and is compared with the initial set of spin orbitals, if this new set of spin orbitals does not differ by a specified threshold from the initial set, then the iterative process concludes, if not, the process continuous and the new set of spin orbitals is used to calculate the Hartree-Fock potential and all the steps mentioned are repeated. The trial orbitals provide a potential which is consistent with them, this is usually referred to a Self-Consistent field (SCF).

$$\chi_N(i) \rightarrow \hat{j}, \hat{k} \rightarrow V_{HF} \rightarrow \hat{f} \rightarrow \chi_N(ii)$$

In practice, convergence is achieved mostly relying on the total energy and not in the difference of the spin orbitals sets.

$$\chi_N(i) \rightarrow E(i) \rightarrow \hat{j}, \hat{k} \rightarrow V_{HF} \rightarrow \hat{f} \rightarrow \chi_N(ii) \rightarrow E(ii)$$

## 5.2. DENSITY FUNCTIONAL THEORY METHOD

The Density Functional Theory (DFT) method is another option to reach the ground state energy of an electron system. This alternative method has an important difference with the already mentioned Hartree-Fock method. DFT uses the electron density,  $\rho$ , not the electronic wave functions and the Schrödinger equation to calculate the energy of a molecular system.

The electron density is defined as:



$$\rho(\vec{r}) = N \int \dots \int |\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N)|^2 d\vec{x}_2 \dots d\vec{x}_N \quad (11)$$

what this integral says is that the electron density can determine the probability to find one electron with whatever spin in a prefixed volume,  $d\vec{x}$ , irrespective of all the other electrons' positions. The use of electron density has important consequences. Using wave functions implies working with  $4N$  variables, three spatial and one spin variable for every electron of the system, but with electron density only three spatial variables are needed, this difference between the two methods makes DFT easier, at a mathematical and computational level, than the Hartree-Fock method.

The Density Functional Theory is based on two theorems; the first one represents the relation between the energy of the studied system,  $E$ , and the electron density,  $\rho$ :

$$E = E[\rho] \quad (12)$$

where the square brackets denote the functional relation. A functional is a function applied to another function that results in a scalar number. Here, an energy is obtained once a density is known and the functional is also known,  $E$ .

The second theorem is a variational principle and states that for any electron density the energy obtained, using the functional, will be higher than the ground state energy of the system,  $E_0$ .

$$E[\rho] \geq E_0[\rho_0] \quad (13)$$

These two theorems do not provide any tool or mechanism to get the  $E$  from  $\rho$ , but W. Kohn and L.J. Sham developed a way to reach our objective, and the result is really similar to the Hartree-Fock method.

This formalism is based on considering a fictitious system where electrons do not interact but that have the same density of the real system. Therefore, it is possible to describe the system as a wave function like in Hartree-Fock, concretely as a Slater determinant.

$$\Theta_S = \frac{1}{\sqrt{N!}} |\varphi_1(\vec{x}_1) \varphi_2(\vec{x}_2) \dots \varphi_N(\vec{x}_N)| \quad (14)$$

To distinguish this function of the Slater determinant it is frequent to write it with a  $\Theta_S$  and the spin orbitals as  $\varphi_1$ .

Until this moment we have done exactly the same as in the HF method, but here the difference between DFT and HF appears. As said before, to find the energy of the system,  $E$ , a functional of the density is used, but how do we get the density needed for the calculation? The

density of a system ( $\rho_S$ ) is the result of the summation of the moduli of the squared spin orbitals,  $\varphi_i$ :

$$\rho_S(\vec{r}) = \sum |\varphi_i(\vec{r})|^2 \quad (15)$$

Accordingly, we are at a similar situation as in the Hartree-Fock method, to know the ground state energy of a system,  $E_0$ , the ground state density,  $\rho_0$ , is needed and to get it the set of ground state spin orbitals has to be calculated. To obtain the appropriate set of spin orbitals a variational process is required. The variational procedure leads to the Kohn-Sham operator:

$$\hat{f}^{KS} = -\frac{1}{2}\nabla_i^2 + V_{KS}(\vec{r}) \quad (16)$$

where the first term is the kinetic energy of the electrons and the second term is the Kohn-Sham effective potential,  $V_{KS}$ ,

$$V_{KS}(\vec{r}) = \int \frac{\rho(\vec{r}')}{r_{12}} d\vec{r}'^2 - \sum_A^M \frac{Z_A}{r_{1A}} + V_{XC}(\vec{r}_1) \quad (17)$$

the first term is the Coulomb repulsion between the considered electron and the total electrons density of the system, the second term is the electron-nucleus attraction and the last one,  $V_{XC}$ , is called the exchange-correlation potential because it comprises exchange and correlation effects, in principle more accurately than in the HF method. The exact form of the exchange correlation potential involves the derivative functional of the exchange correlation energy,  $E_{XC}$ , with respect to  $\rho$ :

$$V_{XC} = \frac{\delta E_{XC}}{\delta \rho} \quad (18)$$

At this moment the variational process is almost complete. The problem is that the exchange correlation energy,  $E_{XC}$ , is a functional of the electron density that is unknown, so approximated form of it is assumed. Then an electron density is guessed,  $\rho_i$ , and we are able to calculate the exchange –correlation potential,  $V_{XC}$ . As a result, we obtain the Kohn-Sham effective potential,  $V_{KS}$ , that gives the definitive form of the Kohn-Sham operator,  $\hat{f}^{KS}$ . The Kohn-Sham equations, as in Hartree-Fock, can be solved using an initial set of spin orbitals,  $\varphi_i$ , that return another set of spin orbitals,  $\varphi_{ii}$ . This new set, leads to a new electron density,  $\rho_S$ , that is compared with the first one electron density guessed. If the difference between this two electron densities is less than a given threshold we proceed to calculate the energy of the system using the functional of the density,  $E[\rho]$ :

$$E[\rho] = T_s[\rho] + E_{Ne}[\rho] + J[\rho] + E_{XC}[\rho] \quad (19)$$

where ,  $T_s$ , is the kinetic energy of the system with non-interacting electrons,  $E_{Ne}$ , is the electron-nucleus attraction,  $J$ , is the classical Coulomb interaction and  $E_{XC}$  is the already mentioned exchange-correlation energy, that is the only term which his form is unknown.

Obviously, if the difference between the two densities is larger than the threshold then the iterative process starts again, and the new guessed density is the result from the calculation done before.

$$\rho_i, \varphi_i \rightarrow E_{XC} \rightarrow V_{XC} \rightarrow V_{KS} \rightarrow \hat{f}^{KS} \rightarrow \varphi_{ii} \rightarrow \rho_S$$

### 5.3. INITIAL AND FINAL STATE CONTRIBUTION TO BINDING ENERGIES<sup>4,5</sup>

It is possible to get a good theoretical approximation to the experimental binding energies using the following equation:

$$BE = E(\text{hole configuration}) - E(\text{ground state, Initial configuration}) \quad (20)$$

where the first term makes reference to minimum energy of the ionized molecule and the second term makes reference to the minimum energy of the neutral molecule. These two energies are obtained by a variational calculation using the Hartree-Fock or DFT methods.

Binding energies can be expressed or decomposed in two different BEs, the initial state BE, and the final state contribution to BE. The initial state BE is the difference between the total energy of the neutral molecule, at their minimum energy (SCF), and the total energy of the ionized molecule with the same orbitals variationally determined for the neutral molecule. When the same orbitals are used is said that we have a Frozen Orbital (FO) wave function or density so the initial state BE can be expressed as:

$$BE_i(\text{FO}) = \langle a_i \Psi_{\text{GS}} | \hat{H} | a_i \Psi_{\text{GS}} \rangle - \langle \Psi_{\text{GS}} | \hat{H} | \Psi_{\text{GS}} \rangle \quad (21)$$

where  $\Psi_{\text{GS}}$  is the wave function or density of the neutral molecule at equilibrium geometry and  $a_i \Psi_{\text{GS}}$  is the wave function or density of ionized molecule without one electron that is removed from the  $i$ th core orbital of  $\Psi_{\text{GS}}$ ;  $a_i$  is the annihilation operator of one electron in the  $i$ th core orbital. For DFT, one uses a FO density and thus:

$$BE_i(\text{FO}) = E_{\text{DFT}}[\rho_i(\text{FO})] - E_{\text{DFT}}[\rho(\text{GS})] \quad (22)$$

where  $E_{\text{DFT}}$  represent the energy of a given density functional,  $\rho_i(\text{FO})$  is the FO density and  $\rho(\text{GS})$  is the ground state density of the neutral molecule.

It is important to note that the initial state BE is not the approximation that we are looking, how is said above, the theoretical BE is a mixture of initial state effects and final state effects, so to reach an acceptable approximation to experimental BE is necessary take into account the final state effects that results in a final BE, but initial state effects are useful for interpretation.

The BE energy is given by the relaxation process that takes place when the other electrons that are not emitted, called "passive electrons", feel that the effective nuclear charge is increased by one ( $Z \rightarrow Z+1$ ), result of the loss of the ionized electron. In computational terms the final BE is calculated when the SCF process concludes, this process allow the orbitals to relax. So the BE, can be expressed as:

$$BE_i(\Delta SCF) = E^{N-1} - E^N \quad (23)$$

where  $E^{N-1}$  is the variational energy for the N-1 electron configuration where an electron has been removed from the  $i$ th core level, put another way, the final energy of the SCF calculation of the ionized molecule, and  $E^N$  is the energy of the neutral molecule that has the minimum energy after SCF calculation.

$$BE_i(\Delta SCF) = BE_i(\text{final}) \quad (24)$$

Now someone might notice that in fact the final BE is the same as the equation (20) BE, so the BE, the real approximation to experimental BE, is when we consider final state effects. So, why is the initial state BE calculated? First of all, but not the most important reason, is that the initial state BE is achieved easily during the calculation process of the final BE and the second reason is because the initial state BE correspond to the atom before ionization. These initial state effects are sensible to chemical environment or oxidation states, so can gives us information about where is this atom placed or how it is unit to around atoms. Also we can define final state effects that correspond to the atoms response to ionization, like that relaxation process called before.

Another important variable, is the relaxation energy ( $E_r$ ) or final state contribution, this energy can be described as the difference between FO and final  $\Delta SCF$  values and has the following equation:

$$E_r = BE_i(\text{FO}) - BE_i(\Delta SCF) > 0 \quad (25)$$

where  $BE_i(\text{FO})$  is the initial state BE and  $BE_i(\Delta SCF)$  is the calculated BE. The value of the relaxation energy can never be less than zero, this is totally logical because the final BE is

always smaller than the initial state BE, to justify this sentence we only have to think about the meaning of the BEs. The BEs are the energy difference between GS molecule, the most stable electronic structure, and the ionized molecule relaxed and not relaxed, the relaxation process will bring the ionized molecule to a more stable electronic structure that is the same as saying less energy difference with the GS molecule, and this less energy difference is the final BE.

It is possible to determine whether effect, initial or final, contributes in major proportion to the final BE, and this fact is related to  $E_r$ . As is said above the final state effects correspond to the relaxation process that happens when the “passive electrons” feel the absence of the emitted electron like a greater effective nuclear charge, this relaxation process is reflected in the relaxation energy,  $E_r$ . Therefore, in conclusion, the final state effects are reflected in the  $E_r$  and as we will see the value of the  $E_r$  represent a very small part of the final BE, therefore we can truly say that, at least, in the studied models the final state effects have lesser importance or, put in another way, the BE is essentially due to the initial state effects.

## 6. COMPUTATIONAL STUDIES

It is known that only pyridinic nitrogen can be identified using XPS<sup>6</sup> because the BE shift between graphitic and pyrrolic nitrogen is overly similar. As it is said in the objectives section N-dimer CLBE will be calculated from different positions in a simple model that tries to represent a graphene flake, coronene. However, also pyridine and pyrrole have been studied to have a good approach to the procedure needed to do calculations in GAMESS, General Atomic and Molecular Electronic Structure System. Several different positions for the N-dimer will be studied and explained.

## 6.1. METHOD

The method used to achieve the theoretical initial and final BE might seem simple and fast, only one optimization and single point energy calculations are made, but as all in this life, anything is easy until you have to do it. As it is said, first a geometry optimization for the studied model is done, this calculation gives the ground state energy and also the orbitals of the molecule, that represents the contribution from all the atomic orbitals to every molecular orbital that are needed to continue with the process, the term atomic orbital will be explained below.

Once the ground state energy of the system is reached we proceed to do the calculation of the ionized system, to do it, only a single point energy calculation specifying the new charge of the molecule (+1) is needed, but doing this, the program (GAMESS) will ionize the electron that is in the HOMO orbital, if it is filled, or the SOMO orbital, if it is half filled, and this is not what we are looking for, we want to calculate the CLBE, so the electron that we want to be ionized has to come from the core level, and to do it a “trick” is employed. The molecular orbitals are known as and influence of the different atomic orbitals, and there is an option provided by the program that allow to fixing the molecular orbitals at the position where we want them, the option is called RSTRCT.

Now, it is just needed to do the orbitals rearrangement to put the molecular orbital with more contribution of the core level (1s) atomic orbital of the desired atom to the HOMO/SOMO position and makes the energy calculation of the ionized molecule. The energy of the first iteration will be the energy of the ionized molecule with the same orbitals of the neutral molecule, and the difference of this energy and the GS energy is the same as saying the initial state BE, and when the iterative process concludes the final energy will be the energy of the ionized molecule where the relaxation process has been done, and the difference of this energy and the GS energy is the same as saying the final BE.

### 6.1.1 Basis sets<sup>7</sup>

Throughout this work, in some sections the term atomic orbitals has appeared. This term is related to the LCAO approximation, introduced by Roothaan in 1951, that eases considerably the calculations used in the two methods exposed above (DFT and HF) simplifying the spin orbitals or molecular orbitals functions. This approximation is based on an alternative to describe the spin orbitals,  $\chi_i$ , as linear combinations of atomic orbitals:

$$\chi_i = \sum_{\mu=1}^L c_{\mu i} \eta_{\mu} \quad (26)$$

where  $c_{\mu i}$  are linear coefficients and  $\eta_{\mu}$  are the atomic orbitals, also called, basis functions. After several steps, which will not be detailed here, one can determine the linear coefficients which are the only unknown to be determined, but if we think about it is totally logical, as the molecular orbitals are a combination of basis functions that we choose, the only parameter that can change to get a new set of spin/molecular orbitals are these linear coefficients, the iterative process remains equal but it will be made from a different perspective, focusing on the already mentioned, linear coefficients.

The basis functions selected to build the molecular orbitals are called as “basis set”, and they are spatially localized functions centered on the atoms that have a radial part and an angular part, like hydrogen-like atomic orbitals.

There are two different types of basis functions, Slater Type Orbitals (STO) and Gaussian Type Orbitals (GTO). For computational convenience a GTO basis is used here.

At this point, after having decided the type of function that will be used, the most important factor is the quality of the basis (number of functions) to be used. The smallest number of functions possible is called a minimal basis set, where only one basis function is used to describe an atomic orbital, for example, for the second row elements of the periodic table only two s-functions (1s and 2s) and one set of p-functions (2p<sub>x</sub>, 2p<sub>y</sub> and 2p<sub>z</sub>) are used, but this set of basis do not describe properly the real system, and the results differ from experimental data. So to overcome this obstacle an incredible variety of sets have been proposed, only few of them, used in our calculations will be explained.

The first minimal basis set used is STO-3G, where three Gaussian functions form one CGF (Contracted Gaussian Function) that describe one atomic orbital. Another set type is 6-31G, that means that 6 primitive Gaussian functions form one CGF for every core orbital and the other two numbers mean that for the valence level we have two CGF, one with 3 primitive Gaussian functions and the other with one primitive Gaussian function, that basically it is not a CGF because it is not a combination of Gaussian functions, is directly a GTO. Also 4-31G is used, as you can imagine, the only change is the number of Gaussian functions that form the CGF for the core orbitals. The last basis set that is used only for nitrogen atoms is a “polarized valence triple zeta (pVTZ)”, where eleven primitive Gaussian functions are used to form six CGF that describe the core orbitals, six primitive Gaussian functions contracted to three CGF to describe the

valence orbitals and one GTO to describe a “d” orbital that allow a possible polarization of the “p” orbitals. The triple zeta sets are used to describe better the electron distribution that it is different in the different directions.

## 6.2. PYRIDINE

The pyridine molecule is taken as a simple model to help to understand how the pyridinic nitrogen is placed in graphene surface and also how the different basis sets affects at the accuracy of calculated energies.

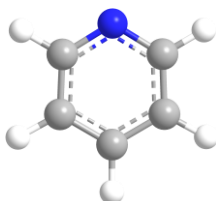


Figure 3. Pyridine molecule

The pyridine molecule contains eleven atoms, 5 carbons, 5 hydrogens and 1 nitrogen in an aromatic ring where nitrogen contributes with one electron to the  $\pi$  system. The molecule derives from benzene by changing the nitrogen atom for a carbon-hydrogen group, and this is how pyridinic nitrogen placed in a graphene surface can be understood, as the substitution of a C-H group by a nitrogen atom.

For the pyridine molecule different CLBE calculations have been done, but not in different positions, since all the atoms are equivalent, therefore, the calculations differ on the basis set used and how this affect to the result, and not only this, for every basis set both studied methods have been used (DFT-HF). As it is explained in the method section, firstly we have to know the ground state energy doing a geometry optimization, followed by the rearrangement of the molecular orbitals. To carry out the geometry optimization some guidelines must be used, the multiplicity and the charge. In this type of system the multiplicity is easy to know as all the molecular orbitals are occupied by two electrons, then if the total number of electrons is pair the multiplicity is one, and for those systems with odd number of electrons, the multiplicity will be two, because one molecular orbital will have only one electron. For every system, not only pyridine, the multiplicity will be displayed because it is important in the energy calculation. The



charge is also easy to define because all the studied systems are neutral, charge=0, before the ionization and after the charge will be +1 since only one electron is removed.

<b>Pyridine before ionization/neutral</b>	
<b>Total number of electrons</b>	42
<b>Multiplicity</b>	1
<b>Charge</b>	0

Table 1. State description of pyridine molecule before ionization.

<b>Pyridine after ionization</b>	
<b>Total number of electrons</b>	41
<b>Multiplicity</b>	2
<b>Charge</b>	+1

Table 2. State description of pyridine molecule after ionization.

When the total energy of the optimized molecule is obtained and the orbitals of the neutral molecule are displayed, the next step is do the single point energy calculation with the rearranged orbitals, in this case we have 42 electrons, consequently 21 molecular orbitals are occupied, and the HOMO, Highest Occupied Molecular Orbital, is the 21. Then the molecular orbital with more contribution of the N(1s), normally the first one, has to be placed above the already mentioned HOMO orbital, then the orbitals scrolling to their new position, the second molecular orbital will be the first one, and the old twenty one orbital will be the twentieth. With the already mentioned RSTRCT function, we are able to find the initial state BE and when the process ends also the final BE.

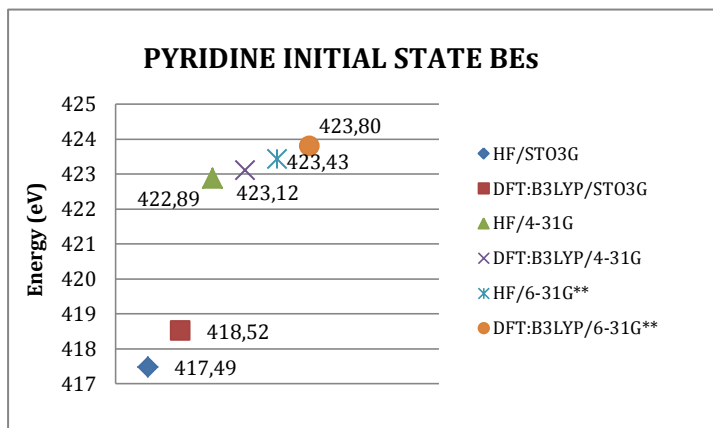


Figure 4. Plot of initial state CLBE of pyridine with different basis and methods.

In the graphic are represented all the initial state BEs calculated for pyridine, in three different basis and with the two method (DFT and HF). It is important to note the influence of basis and the method used, as you can see, there is an ascendant progression correlated with both parameters, since more complex is the basis higher are the energies and for DFT and HF we have something similar, DFT always gives higher energies than HF, but as the initial state BE is not obtained experimentally, we cannot know if this progression takes us to a more accurate result, because we cannot prove it, but as we know from other sections of this work, the final BE is achieved when the relaxation process occurs and this final BE is an approximation to the energy measured experimentally, so probably the answer will be given by the next graphic and the experimental value<sup>8</sup>.

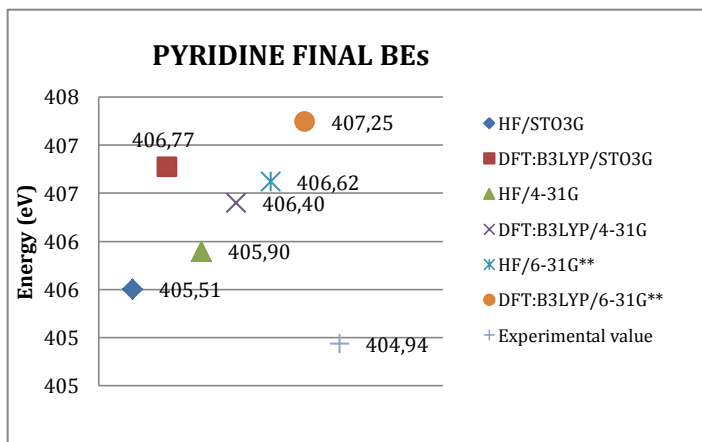


Figure 5. Plot of final CLBE of pyridine with different basis and methods.

Theoretically, better basis defines better the reality, complex basis, made from an increased number of Gaussian functions leads to more accurate results of the variational process because you will have more values (coefficients) to optimize. Analysing the obtained results (Appendix 2) leads us to think otherwise, the most complex basis 6-31G\*\* also gives the most incorrect result, the farthest result from the experimental value. It is true that 6-31G\*\* is the most complex basis used, but even so it is a simple basis compared with the pVTZ, so to demonstrate that the complexity of the basis (number of GTO used) really affects to the accuracy this complete basis is used.

Pyridine (pVTZ for nitrogen)	Final BE (eV)
HF	404,60
DFT	404,81

(a)pVTZ basis only used in nitrogen, for all other atoms 6-31G\*.

Table 3. Final BE of pyridine using pVTZ basis.

If we compare the results from the table 3 with the experimental value (404.94 eV) is possible to assure that effectively the quality of the basis matter and not only this, DFT has a better result than HF, although is early to determine that DFT is better to make this type of calculations, but with the next molecule, pyrrole, probably we will be able to determine that effectively DFT can obtain better results.

Another interesting fact is disclosed if we compare the initial and final state contributions. As is defined in section 5.3 the initial state contribution is achieved with the initial state BE, and the final state contribution is achieved with the relaxation energy, so if we compare those two values we will be able to know which one is the most important effect/contribution. To reach this objective the basis that has better accuracy is used, and as it is seen a few lines above is the pVTZ basis. Again, it is obvious, that the method that will be used will be that one which gives better results comparing to the experimental value and it is better theoretically grounded, this is, more exact, and in this case it is the DFT method. Er is achieved using the equation 25.

$$Final\ state\ contribution(\%) = \left( \frac{E_r}{BE(\Delta SCF)} \right) * 100 = 4,61\% \quad (27)$$

The result is conclusive, the final state effects only contributes a little less than 5% to the BE, so in conclusion, we can determine that for this system, and all others studied system, the BE is essentially due to initial state effects, therefore, the oxidation state, the electronegativity of surrounding atoms, the type of bond with other atoms... that is what really defines the BE for this type of systems.

### 6.3. PYRROLE

The molecule of pyrrole is contains 10 atoms, 4 carbons, 5 hydrogens and 1 nitrogen in an aromatic ring as in the pyridine molecule, but in this case nitrogen contributes with two electrons to the  $\pi$  system. This molecule is perfect to understand how is a pyrrolic nitrogen placed in the a graphene surface, in pyridine a C-H group is changed by the nitrogen atom, but in a pyrrolic position only a carbon is changed and the hydrogen bonded to the carbon remains unchanged, so in conclusion a pyrrolic nitrogen is the same as in pyrrole but in a six membered ring.

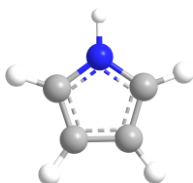


Figure 6. Pyrrole molecule

The same calculations and method used for pyridine have also been used for pyrrole, therefore, to not repeat, only pre-ionized and post-ionized states with all the results achieved will be explained. The pre-ionized state is clearly defined by the next table,

<b>Pyrrole before ionization/neutral</b>	
<b>Total number of electrons</b>	36
<b>Multiplicity</b>	1
<b>Charge</b>	0

Table 4. State description of pyridine molecule before ionization.

as in pyridine we start with an even number of electrons, so the multiplicity will obviously be 1 and the charge 0, as we are in a pre-ionized state. The post-ionized state is also really similar to the previously seen in pyridine, and it is described in the next table,

<b>Pyridine after ionization</b>	
<b>Total number of electrons</b>	35
<b>Multiplicity</b>	2
<b>Charge</b>	+1

Table 5. State description of pyridine molecule after ionization.

where all dates are easily deduced, an electron less, an odd number of electrons therefore a multiplicity equal to 2 and charge +1. But not all is the same as in pyridine; in this case the HOMO will be the eighteenth orbital because we have only eighteen molecular orbitals occupied. In the next plot all the values achieved (Appendix 2) from the initial state calculations are represented.

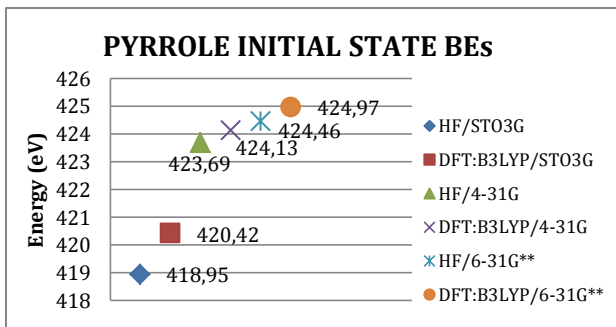


Figure 7. Plot of initial state CLBE of pyrrole with different basis and methods.

It is interesting to note that as in pyridine there is an ascendant correlation of all the values when a more extensive basis is used, and also the same pattern can be seen, DFT results are higher than HF results, this probably means that as in pyridine DFT gives more accurate results, but only comparing the experimental value<sup>9</sup> and the final BE, that is the theoretical approximation, can ensure that effectively DFT is the best option and that this is supported by theoretical arguments, i.e. DFT accounts for electronic correlation and HF does not.

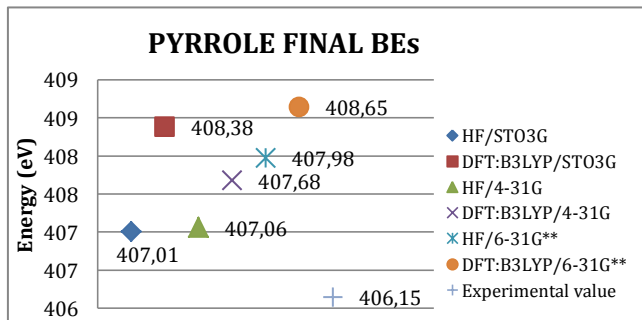


Figure 8. Plot of final CLBE of pyrrole with different basis and methods.

Again the same correlation is seen, an ascendant tendency that moves away from the experimental value in function of the complexity of the basis, consequently, the calculation with pVTZ basis is done to ensure that effectively the type of basis used affects to the accuracy.

Pyrrole (pVTZ for nitrogen)	Final BE (eV)
HF	406,07
DFT	406,34

(a)pVTZ basis only used in nitrogen, for all other atoms 6-31G\*.

Table 6. Final BE of pyrrole using pVTZ basis.

The results are conclusive, but in a different way if we compare with the pyridine case, it is true that pVTZ gives accurate results than the others basis, that as it is said above it is totally logical because this basis has more Gaussian functions to describe the orbitals and that is translated in more accuracy, but this time HF gives a better result than DFT, the difference between the HF result and the experimental value (0,08 eV) is less than the difference between the DFT result and the experimental value (0,19 eV). That does not mean in any case that HF is better than DFT, just the opposite, all this calculations are made using the B3LYP functional and in principle this functional provides in general better results than HF<sup>4</sup>. With this on mind next calculations will be done with DFT, pVTZ basis and B3LYP functional.

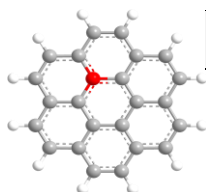
## 6.4. CORONENE

The first option considered to make the calculations was Circumcorone, a molecule that is representative of the graphene surface, but calculations for this molecule require more time that we had, so taken this into account, the final molecule used is a smaller molecule, Coronene. This molecule attempts to represent a graphene flake where the BE of different type of nitrogen can be theoretically calculated and with the results we will try to determine if effectively the N(1s) core level BE of N-dimers are enough different to be measured experimentally. First, it is important to note that one of the three basic positions of nitrogen in graphene has not still explained, the graphitic nitrogen. This type of nitrogen is described as the substitution of a carbon atom placed in the middle of the graphene surface, or in this case a flake, by nitrogen. To understand it better we will begin explaining the different positions studied related to the graphitic nitrogen on the coronene structure, the results will be plotted after.

### 6.4.1. When the graphitic nitrogen is ionized

Three different cases related to graphitic nitrogen have been studied; the first is single graphitic nitrogen and is essential to compare the N-dimers. This nitrogen increase by one the

number of electrons of the system as it is the substitution of a carbon ( $Z=6$ ) atom that have an electron less than nitrogen ( $Z=7$ ), therefore, as the total number of electrons of the system before the substitution is pair, now we have a system with an HOMO half filled (SOMO) and this means that multiplicity is increased, this new system has a multiplicity of two. This is the first case where we have a system with an odd number of electrons before the ionization and that bring to a different single point calculation (BEs calculation). When we modify the orbitals to put the one that we want to the HOMO level, SOMO in this case, is essential to take into account that when the system is ionized we will have two electrons odd, that which remain in the ionized orbital (new HOMO) and the electron of the SOMO orbital before the change, therefore, although the number of electrons is pair the multiplicity is not 1, this system will have a multiplicity equal to 3, where this two unpaired electrons are considered. It must be noted that an open-shell singlet is also possible. This has not been considered here although one can safety argue that triplet and open-shell singlet will be nearly degenerated.



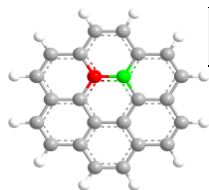
Graphitic nitrogen	Before ionization	After ionization
<b>Total number of electrons</b>	157	156
<b>Multiplicity</b>	2	3
<b>Charge</b>	0	+1

(a) red atom is the ionized nitrogen atom.

Figure 9 and Table 7. Description of the coronene system with graphitic nitrogen.

Once the graphitic case has been defined we consider other options based on the formation of graphitic n-dimer. So the first two options are precisely n-dimers where the nitrogens are all graphitic. In these cases it is important to note that we are adding two electrons so the total number of electrons before ionization is pair as in pyridine or pyrrole molecules, therefore, the multiplicity is 1, and after the ionization the multiplicity will be 2. From here all the possibilities related to the multiplicity have been explained, so for future cases, only the values will be put on the table that describe the studied system, but it will not be explained.

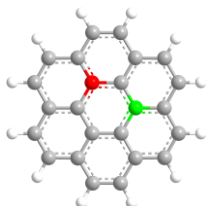




<b>N-dimer of (n,n) graphitic nitrogens</b>	<b>Before ionization</b>	<b>After ionization</b>
<b>Total number of electrons</b>	158	157
<b>Multiplicity</b>	1	2
<b>Charge</b>	0	+1

(a) red atom is the ionized one and green atom is the other nitrogen which form the dimer.

Figure 10 and Table 8. Description of the coronene system with the (n,n) dimer.

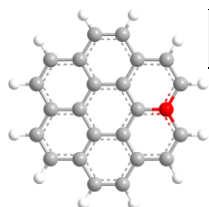


<b>N-dimer of (n,n,n) graphitic nitrogens</b>	<b>Before ionization</b>	<b>After ionization</b>
<b>Total number of electrons</b>	158	157
<b>Multiplicity</b>	1	2
<b>Charge</b>	0	+1

(a) red atom is the ionized one and green atom is the other nitrogen which form the dimer.

Figure 11 and Table 9. Description of the coronene system with the (n,n,n) graphitic dimer.

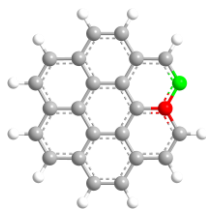
There are three possibilities more with the graphitic nitrogen that have not been considered yet. We can also find the graphitic nitrogen at the external ring of atoms where we can form n-dimers involving also pyrrolic and pyridinic atoms. These three possibilities are described below (Figures 12, 13 and 14).



<b>Graphitic nitrogen of external ring</b>	<b>Before ionization</b>	<b>After ionization</b>
<b>Total number of electrons</b>	157	156
<b>Multiplicity</b>	2	3
<b>Charge</b>	0	+1

(a) red atom is the ionized nitrogen atom.

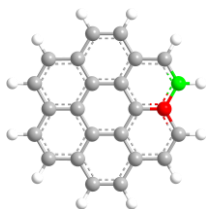
Figure 12 and Table 10. Description of the coronene system with external graphitic nitrogen.



<b>N-dimer of graphitic and pyridinic nitrogens</b>	<b>Before ionization</b>	<b>After ionization</b>
<b>Total number of electrons</b>	157	156
<b>Multiplicity</b>	2	3
<b>Charge</b>	0	+1

(a) red atom is the ionized one (graphitic) and green atom is a pyridinic nitrogen.  
 (b) note that the green atom (pyridinic) is not bonded to an hydrogen, as in pyridine.

Figure 13 and Table 11. Description of the coronene system with n-dimer formed of graphitic and pyridinic nitrogens, where the ionized one is the graphitic nitrogen.



<b>N-dimer of graphitic and pyrrolic nitrogens</b>	<b>Before ionization</b>	<b>After ionization</b>
<b>Total number of electrons</b>	158	157
<b>Multiplicity</b>	1	2
<b>Charge</b>	0	+1

(a) red atom is the ionized one (graphitic) and green atom is a pyrrolic nitrogen.  
 (b) note that the green atom (pyrrolic) is bonded to an hydrogen, as in pyrrole.

Figure 14 and Table 12. Description of the coronene system with n-dimer formed of graphitic and pyrrolic nitrogens, where the ionized one is the graphitic nitrogen.

All the different positions studied where the ionized nitrogen is graphitic have been described, therefore, just missing to plot all the results achieved and see if it is effectively possible to distinguish them. That does not mean that only those positions have been studied, there are other n-dimers where the ionized nitrogen is not graphitic but to facilitate the understanding of the results and not to put a complex table, the results of different ionized nitrogens (graphitic, pyrrolic, pyridinic) will be plotted separately.

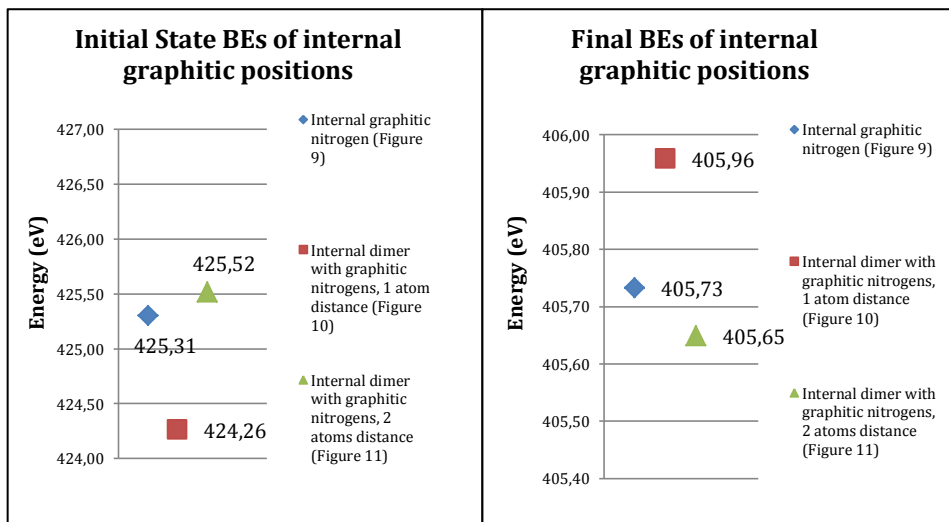


Figure 15 (left) and 16 (right). Plots of initial state BEs and final BEs where are considered all the internal graphitic possibilities.

It can be difficult to analyse the results achieved in the figures 15 and 16, as there is not any pattern or tendency, but there are some considerations that we have to know. First of all, the initial state BE of the dimer of (n,n) graphitic nitrogens is an approximation to the real theoretical initial state BE, that it is because when the ground state geometry of the molecule is calculated the 1s atomic orbitals of the two nitrogens are degenerated, it means that the contribution of the 1s atomic orbitals contribute in two different molecular orbitals, they are not localized. This fact produces that when we ionize the molecular orbital with more contribution of the 1s atomic orbital of the atom which we want to ionize, in fact, we are ionizing only a part of this contribution, the initial state BE will be also a part of the total contribution because the molecular orbital ionized has not the total contribution of the 1s atomic orbital. This accidental degeneracy of the molecular orbitals is not an isolated fact, this happens in every (n,n) dimer with the same type of nitrogen, namely; graphitic-graphitic, pyridinic-pyridinic and pyrrolic-pyrrolic. But the value achieved is not directly the result of the ionization of a degenerated molecular orbital, it is a better approximation done to solve this problem of degeneracy.

If we analyse the final molecular orbitals of the SCF calculation, so the molecular orbitals of the relaxed and ionized molecule, we see that the degeneracy problem is iteratively solved, the contribution of 1s atomic orbitals is localized in different molecular orbitals, then we can use this

final relaxed and localized molecular orbitals to achieve the initial state BE, we have to change these molecular orbitals (written as vectors) by the initial degenerated and not localized molecular orbitals, then if we restart the single point energy calculation (SCF) the first iteration will be made with those new molecular orbitals and as they are localized the result will be more nearby to the real theoretical initial state BE. But this is still an approximation, because this localized orbitals used to achieve the initial state BE comes from the final SCF calculation, so these orbitals have gone through a process of relaxation that it is the same to say that these orbitals have contribution of initial state effects and final state effects, when the ideal result would be using localized (not degenerated) and not relaxed orbitals, where we only have initial state effects. Of course this approximation is better than if we use degenerated molecular orbitals, but we cannot use it to compare with the other initial state BE. So in figure 15 only the results of the (n,n,n) dimer and the single graphitic nitrogen can be compared, and those results can be explained as a charge transfer effect, because in the dimer, the ionized nitrogen, feels a more electronegative environment due to the change of a carbon by a nitrogen atom and this produce that the nitrogen atom that we want to ionize has a more positive charge that increase the energy needed to ionizes the electron, translated to a higher initial state BE. But this argument is a simplification of the problem because the initial state effects are not only related to charge transfer effects, there is a minimum of 5 different effects<sup>5</sup> that contribute to the initial state BE and also can explain this difference.

Another interesting consideration is that the relaxation process can contribute in many different ways, a clear example of this is observed when we analyse the final BE of the single graphitic nitrogen and the (n,n,n) graphitic dimer. The initial state BE of the single nitrogen is lower than the initial state BE of the dimer, but the final BE of the single nitrogen is higher than the final BE of the dimer, the order is changed as a consequence of the relaxation process, because the relaxation energy of dimer is higher than the relaxation energy of the single graphitic nitrogen, that means that in this case the difference of final state effects is so important that can change the order of stability. This analysis cannot be done for the (n,n) dimer, because the initial state BE is an approximation so we don't know if the order of stability is changed between the initial state BE and the final BE.

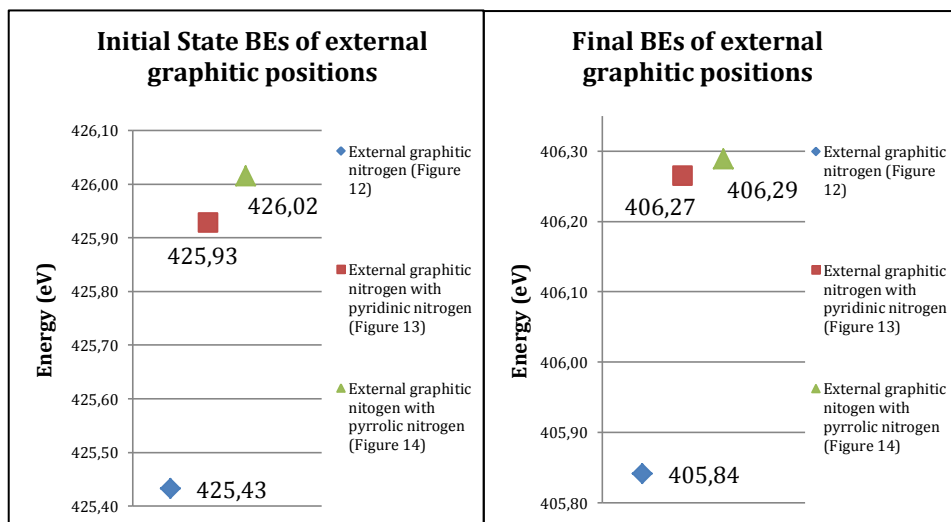
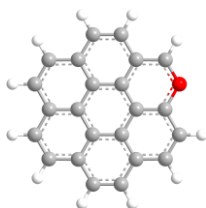


Figure 17 (left) and 18 (right). Plots of initial state BEs and final BEs where are considered all the external graphitic possibilities.

For the external graphitic options (Figure 17 and 18), the results achieved follow a different tendency, in this case the pattern seen for initial state BEs is also the same for final BEs. The single graphitic nitrogen has a final BE displaced from the other final BEs, that means that dimers really affect to the BE and in this case, as the relaxation process (appendix 1) is practically equal for the three positions, this difference between single graphitic and dimers is essentially an initial state effect. We can also determine that if the dimer is made with pyrrolic nitrogen or pyridinic nitrogen that does not really matter, as the two options have practically the same final BE, think that synchrotron<sup>10</sup>, probably the most advanced instrument used to produce monochromatic beams, has an accuracy of 0,1eV, so if the difference between two final energies is less than this threshold we will not be able to differentiated them (like in this case).

#### 6.4.2. When the pyridinic nitrogen is ionized

In this section we consider possibilities where the ionized atom is a pyridinic nitrogen. Those options only can be found in the external ring, because as it has been already explained the pyridinic nitrogen only has two bonds with two carbon atoms, as external ring atoms. Four different options have been studied, and obviously the first one is the single pyridinic nitrogen.

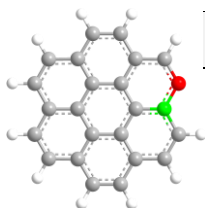


Pyridinic nitrogen	Before ionization	After ionization
<b>Total number of electrons</b>	156	155
<b>Multiplicity</b>	1	2
<b>Charge</b>	0	+1

(a) red atom is the ionized nitrogen atom.

Figure 19 and Table 13. Description of the coronene system with pyridinic nitrogen.

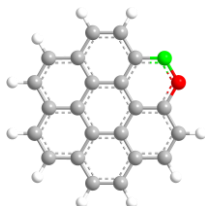
The next three positions are different dimer combinations of graphitic, pyridinic and pyrrolic nitrogens with pyridinic nitrogen ionized.



N-dimer of pyridinic and graphitic nitrogens	Before ionization	After ionization
<b>Total number of electrons</b>	157	156
<b>Multiplicity</b>	2	3
<b>Charge</b>	0	+1

(a) red atom is the ionized one (pyridinic) and green atom is a graphitic nitrogen.  
 (b) note that the red atom (pyridinic) is not bonded to an hydrogen, as in pyridine.  
 (c) note that Figure 20 is the same as Figure 13 but the ionized atom is the pyridinic nitrogen.

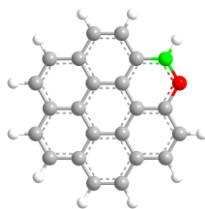
Figure 20 and Table 14. Description of the coronene system with n-dimer formed of pyridinic and graphitic nitrogens, where the ionized one is the pyridinic nitrogen.



N-dimer of pyridinic nitrogens	Before ionization	After ionization
<b>Total number of electrons</b>	156	155
<b>Multiplicity</b>	1	2
<b>Charge</b>	0	+1

(a) red atom is the ionized one (pyridinic) and green atom is another pyridinic nitrogen.  
 (b) note that the red and green atoms (pyridinic) are not bonded to an hydrogen, as in pyridine.  
 (c) in this case not matter which atom we ionize because the two positions are equivalent.

Figure 21 and Table 15. Description of the coronene system with n-dimer formed of pyridinic nitrogens, where we ionize one of them.



N-dimer of pyridinic and pyrrolic nitrogens	Before ionization	After ionization
Total number of electrons	157	156
Multiplicity	2	3
Charge	0	+1

(a) red atom is the ionized one (pyridinic) and green atom is a pyrrolic nitrogen.

(b) note that the red atom (pyridinic) is not bonded to an hydrogen, as in pyridine.

Figure 22 and Table 16. Description of the coronene system with n-dimer formed of pyridinic and pyrrolic nitrogens, where the ionized one is the pyridinic nitrogen.

Regarding the results only two of the four options described have been completed until now, because of convergence problems that will be explained below. We hope to have all results at the presentation time. The conflictive positions are the dimer of pyridinic nitrogens (Figure 21) and the dimer of pyridinic and pyrrolic nitrogens (Figure 22).

The main problem of those positions is that the SCF calculation does not converge; we have tried changing the convergence algorithm, made the calculation first with HF and then with the obtained orbitals make the DFT calculation and also change the initial geometry, but so far the problems remain. We will continue trying to have values until the last moment, but they may not be achieved.

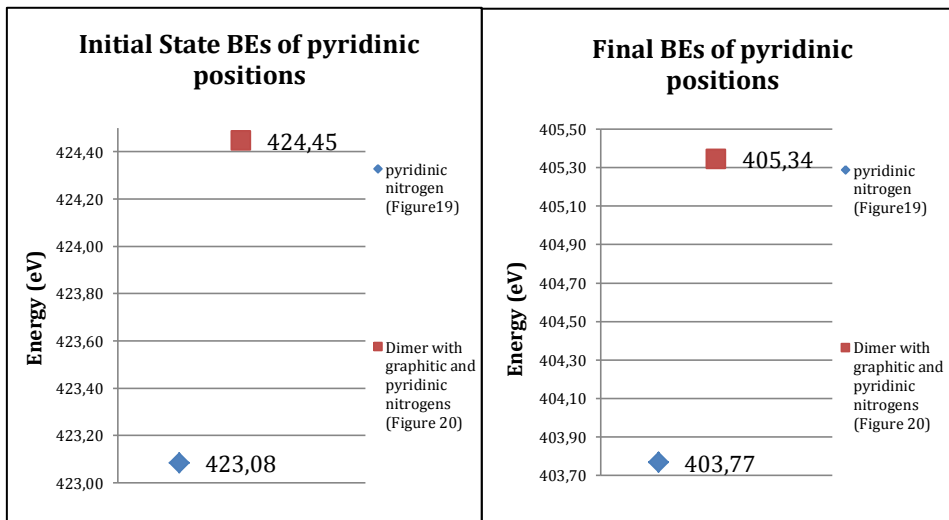
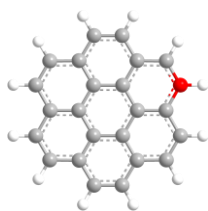


Figure 23 (left) and 24 (right). Plots of initial state BEs and final BEs where are considered pyridinic possibilities.

The results obtained so far follow the observed tendency for other cases, where binding energy of the N(1s) in the dimers is displaced from single nitrogen positions (in this case pyridinic). But as we do not know yet the energy of the other two positions it is not possible to affirm that the dimer made can be distinguished from the others. As in the case of (n,n) graphitic dimer, accidental degeneracy exists which make the calculation of the initial state BE cumbersome.

#### 6.4.3. When the pyrrolic nitrogen is ionized

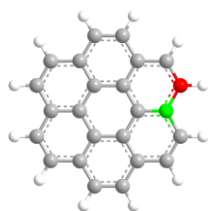
This is the last group of nitrogens pairs studied, where we will have different positions with pyrrolic nitrogen always that will be ionized. As in the section before, the different positions considered are very similar; we will have single pyrrolic nitrogen and different dimers with graphitic, pyridinic and pyrrolic nitrogens.



<b>Pyrrolic nitrogen</b>	<b>Before ionization</b>	<b>After ionization</b>
<b>Total number of electrons</b>	157	156
<b>Multiplicity</b>	2	3
<b>Charge</b>	0	+1

(a) red atom is the ionized nitrogen atom.

Figure 25 and Table 17. Description of the coronene system with pyrrolic nitrogen.



<b>N-dimer of pyrrolic and graphitic nitrogens</b>	<b>Before ionization</b>	<b>After ionization</b>
<b>Total number of electrons</b>	158	157
<b>Multiplicity</b>	1	2
<b>Charge</b>	0	+1

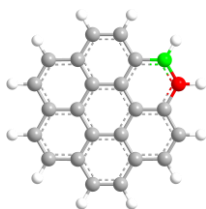
(a) red atom is the ionized one (pyrrolic) and green atom is a graphitic nitrogen.

(b) note that the red atom (pyrrolic) is bonded to an hydrogen, as in pyridine.

(c) note that Figure 26 is the same as Figure 14 but the ionized atom is the pyrrolic nitrogen.

Figure 26 and Table 18. Description of the coronene system with n-dimer formed of pyrrolic and graphitic nitrogens, where the ionized one is the pyrrolic nitrogen.





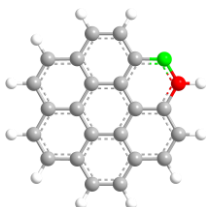
<b>N-dimer of pyrrolic nitrogens</b>	<b>Before ionization</b>	<b>After ionization</b>
<b>Total number of electrons</b>	156	155
<b>Multiplicity</b>	1	2
<b>Charge</b>	0	+1

(a) red atom is the ionized one (pyrrolic) and green atom is another pyrrolic nitrogen.

(b) note that the red and green atoms (pyrrolic) are bonded to an hydrogen, as in pyrrole.

(c) in this case not matter which atom we ionize because the two positions are equivalent.

Figure 27 and Table 19. Description of the coronene system with n-dimer formed of pyrrolic nitrogens, where we ionize one of them.



<b>N-dimer of pyrrolic and pyridinic nitrogens</b>	<b>Before ionization</b>	<b>After ionization</b>
<b>Total number of electrons</b>	157	156
<b>Multiplicity</b>	2	3
<b>Charge</b>	0	+1

(a) red atom is the ionized one (pyrrolic) and green atom is a pyridinic nitrogen.

(b) note that the red atom (pyrrolic) is bonded to an hydrogen, as in pyridine.

Figure 28 and Table 20. Description of the coronene system with n-dimer formed of pyridinic and pyrrolic nitrogens, where the ionized one is the pyrrolic nitrogen.

Pyrrolic positions have the same problem seen in pyridinic positions; there are two positions that do not converge even trying the same mechanisms used for pyridinic positions. It is possible that we have the results for the presentation.

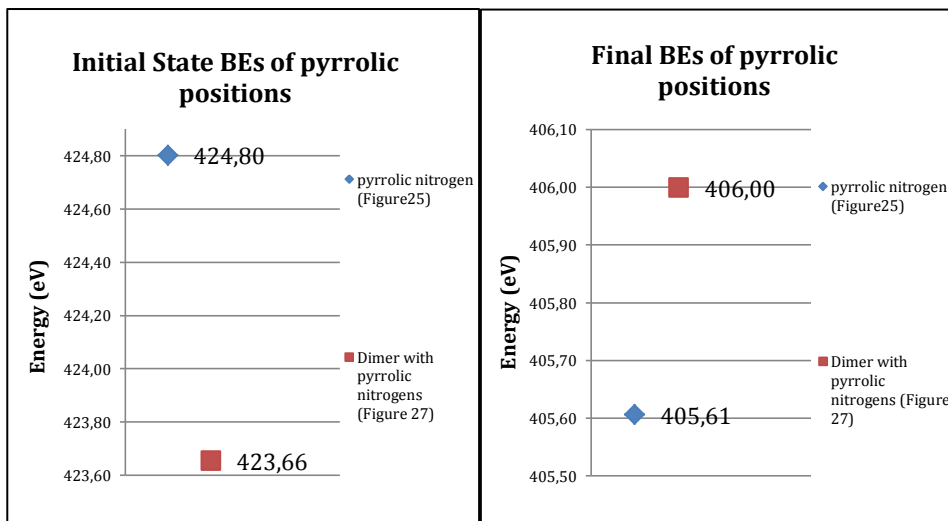
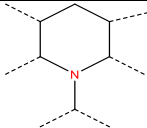
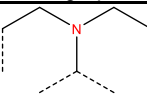
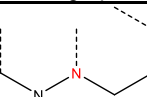
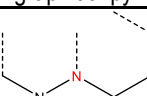
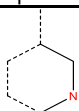
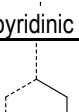


Figure 29 (left) and 30 (right). Plots of initial state BEs and final BEs where are considered pyrrolic possibilities.

Observing the results achieved for the final BE in pyrrolic possibilities we see the same tendency observed in other cases, dimer have a BE displaced from the single pyrrolic nitrogen BE that is possible to distinguish in a XPS spectra as different peaks because the difference between energies is more than 0,1 eV. It is interesting to note that for the dimer the initial state BE does not follow the tendency observed in other systems and that is because this BE is not the real theoretical result, in this dimer we have exactly the same as in dimer made of two (n,n) graphitic nitrogens, the accidental degeneracy of the orbitals, explained above.

## 7. RESULTS AND DISCUSSIONS

Until now all values were shown to have a qualitative perspective of the BE energies, but in this section will be discussed the real meaning of the results, which is none other than trying to determine if it is possible to distinguish the N-dimer basing on the final BE. To show those results in an easy way we will not look for the absolute values, we will show the shifts of the different final BE respect to a reference that in this case will be the final BE of the single internal graphitic nitrogen placed on coronene (Figure 9).

CORONENE MOLECULE VALUES	Final BE (eV)	BE shifts (eV)
 Single internal graphitic nitrogen	405,73	0,00
 Single external graphitic nitrogen	405,84	0,11
 Dimer external graphitic+pyridinic nitrogens	406,27	0,54
 Dimer external graphitic+pyrrolic nitrogens	406,29	0,56
 Single pyridinic nitrogen	403,77	-1,96
 Single pyrrolic nitrogen	405,61	-0,12

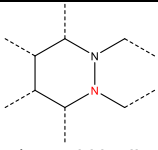
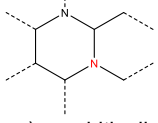
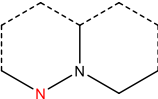

 <p>(n,n) graphitic dimer</p>	405,96	0,23
 <p>(n,n,n) graphitic dimer</p>	405,65	-0,08
 <p>Dimer pyridinic+graphitic nitrogens</p>	405,34	-0,39
 <p>Dimer pyrrolic+pyrrolic nitrogens</p>	406	0,27

Table 21. Calculated  $\Delta$ SCF final BE values and shifts in function of the single internal graphitic final BE. A red colour is used to indicate the N atom which is ionized.

The results have to be analysed, to determine whether a system can be distinguished in the spectra. To this end one needs to realize that some situations may have significant shifts from a given reference but in the same direction so that distinguishing among them may be not possible.

- Single and external graphitic nitrogens and also the (n,n,n) graphitic dimer and the single pyrrolic nitrogen cannot be distinguished because the difference between the final BEs is too small.

- It is possible to distinguish peaks related to N-dimers where the ionized atom is an external graphitic nitrogen, but it is not possible to determine if it is an N-dimer made with a pyrrolic nitrogen or a pyridinic nitrogen.

- The single pyridinic nitrogen can be distinguished because this system has a very different energy from all other.

- The N-dimer made with pyrrolic nitrogens and also the N-dimer made with a pyridinic nitrogen and graphitic nitrogen where the ionized nitrogen is pyridinic nitrogen, can be distinguished from all other possibilities because, as in sentence above, their final BE is enough different.

- Observing the result achieved for the (n,n,n) graphitic dimer is possible to determine, without more results, that the (n,n,n) dimers cannot be distinguished from the single nitrogen system, where the ionized nitrogen of the dimer is of the same type as the single nitrogen studied.

That is not the unique information that you can get from all the values achieved, for example, is possible to determine which systems are more stable observing the final energy of the optimized geometry for isomers (identical empirical formula). This, however, has not been considered here.

## 8. CONCLUSIONS

In this TFG a rather deep knowledge of XPS and its theoretical interpretation has been reached. In addition, several theoretical methods not used during my previous degree studies have been learned and properly used. Regarding the results obtained the following conclusions emerge.

- Obviously, the method (HF or DFT) used and the basis chosen (6-31G, 4-31G...) largely affects the accuracy of the results.
- Major problems encountered during this work have been successfully solved.
- The initial state and final (SCF) CLBE for different systems involving isolated or dimer N atoms have been determined.
- Analyzing the final BEs in coronene molecule we are able to suggest which systems could be distinguished in XPS spectra.

Deconvolution of experimental XPS results<sup>11</sup> of N-doped graphene in the literature show three main peaks which are often assigned to graphitic, pyrrolic and pyridinic types of N. Accurate calculations accounting for initial and final state effects show that graphitic and pyrrolic N atoms cannot be distinguished. This fact opens a question regarding the assignment of the experimental peak at higher CLBEs. The present results show that this third peak at higher binding energy is consistent with the existence of (n,n) dimers and suggest that this possibility should be considered.

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## **10. ACRONYMS**

BE: Binding Energy

CLBE: Core Level Binding Energy

HF: Hartree-Fock

DFT: Density Functional Theory

XPS: X-ray Photoelectron Spectroscopy

STO: Slater Type Orbital

GTO: Gaussian Type Orbital

CGF: Contracted Gaussian Function

SOMO: Singly Occupied Molecular Orbital

HOMO: Highest Occupied Molecular Orbital

E<sub>r</sub>: Relaxation Energy

FO: Frozen Orbital

GS: Ground State

SCF: Self-Consistent Field



# APPENDICES



## APPENDIX 1: TABLE WITH THE ACHIEVED VALUES FOR EVERY CALCULATION WITH CORONENE MOLECULE

CORONENE MOLECULE VALUES	Optimization (hartree)	FO energy (hartree)	SCF energy (hartree)	BE(FO) (eV)	BE(SCF) (eV)	ER (eV)
coronene	-921,30					
single external graphitic	-937,90	-922,27	-922,98	425,43	405,84	19,59
Single internal graphitic	-937,89	-922,27	-922,98	425,31	405,73	19,57
Dimer external graphitic+pyridinic	-953,94	-938,29	-939,01	425,93	406,27	19,66
Dimer external graphitic+pyrrolic	-954,49	-938,83	-939,56	426,02	406,29	19,73
Single pyridinic	-937,36	-921,81	-922,52	423,08	403,77	19,32
Single pyrrolic	-937,92	-922,31	-923,01	424,80	405,61	19,20
(n,n) graphitic dimer	-954,47	-938,88	-939,55	424,26	405,96	18,30
(n,n,n) graphitic dimer	-954,49	-938,85	-939,58	425,52	405,65	19,87
Dimer pyridinic+graphitic	-953,94	-938,34	-939,04	424,45	405,34	19,10
Dimer pyrrolic+graphitic	-954,49	-938,95	-	422,71	-	-
Dimer pyrrolic+pyrrolic	-954,53	-938,96	-939,61	423,66	406,00	17,66
Dimer pyrrolic+pyridinic	-953,96	-938,33	-	425,37	-	-
Dimer pyridinic+pyridinic	-953,38	-938,30	-	410,29	-	-
Dimer pyridinic+pyrrolic	-953,96	-938,33	-	425,37	-	-



## APPENDIX 2: TABLES WITH THE ACHIEVED VALUES FOR EVERY CALCULATION WITH PYRROLE AND PYRIDINE MOLECULES

PIRROL	Optimization (hartree)	FO energy (hartree)	SCF energy (hartree)	BE(FO) (eV)	BE(SCF) (eV)	ER (eV)
HF/STO3G	-206,23	-190,83	-191,27	418,95	407,01	11,93
DFT:B3LYP/STO3G	-207,41	-191,96	-192,40	420,42	408,38	12,04
HF/4-31G	-208,51	-192,94	-193,55	423,69	407,06	16,63
DFT:B3LYP/4-31G	-209,76	-194,17	-194,78	424,13	407,68	16,45
HF/6-31G**	-208,82	-193,22	-193,83	424,46	407,98	16,49
DFT:B3LYP/6-31G**	-210,04	-194,42	-195,02	424,97	408,65	16,32

PIRIDINA	Optimization (hartree)	FO energy (hartree)	SCF energy (hartree)	BE(FO) (eV)	BE(SCF) (eV)	ER (eV)
HF/STO3G	-243,64	-228,30	-228,74	417,49	405,51	11,98
DFT:B3LYP/STO3G	-245,03	-229,65	-230,08	418,52	406,77	11,74
HF/4-31G	-246,33	-230,79	-231,41	422,89	405,90	16,99
DFT:B3LYP/4-31G	-247,80	-232,25	-232,86	423,12	406,40	16,71
HF/6-31G**	-246,70	-231,14	-231,76	423,43	406,62	16,80
DFT:B3LYP/6-31G**	-248,13	-232,56	-233,17	423,80	407,25	16,55





