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Article

CHARACTERIZATION OF BENZENE AND CORONENE MOLECULES AS SUBSYSTEMS OF A GRAPHENE NANORIBBON IN DIFFERENT BONDING STATES

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ABSTRACT

Following the transdisciplinarity trend in science, this study was design to presents a way in which mathematical functions can be used in molecular characterization. Thus, the selected working system is a graphene nanoribbon consisting in 25 fused benzene rings, divided in two sub-systems i.e. unit cell and hypercell. For the two selected sub-systems, first was determined their physico-chemical parameters, than the obtained values were computed using the Heavisade based Gradient function formula, leading to a new set of parameters which can also offers new information about the working system.

Keywords: graphene nanoribbon, benzene, atomic gradient, wave equation, Heaviside (Gradient) function.

1. INTRODUCTION

Graphene has attracted a lot of attention in the last years due to the fact that exhibit extraordinary physical and mechanical properties, i.e. is considered stronger than steel, very flexible and light, having at the same time high thermal and electronic conductivities. In literature, graphene is known as a carbon allotrope with the shape of a bi-dimensional crystal with sp^2 orbital hybridization and 0.34 nm thicknesses. In graphene, each carbon atom is

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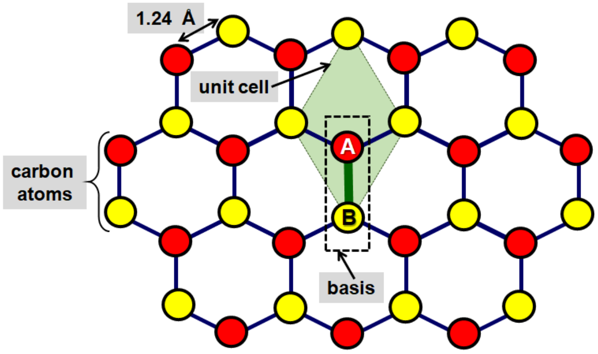
♣ Correspondent author: mihai.putz@e-uvt.ro bonded with other three carbon atoms, resulting in a very stable hexagonal lattice (in order to form a chemical bond with graphene, the sp^2 bond must be converted into a sp^3 bond). A graphene sheet can be "*cut*" into thin nanoscale ribbons, thus being created structures with a finite number of benzene rings called graphene ribbons (GNR). Besides, graphene is also the basic structure for fullerenes, carbon nanotubes and graphite [1-5].

As the sixth element in the periodic table, carbon has six protons in the nucleus and six electrons, the latter filling the lowest three orbitals in the arrangement [1s]^2[2s]^2[2p]^2; type $|s\rangle$ orbitals are spherical and symmetrical, $|p\rangle$ type orbitals are elongated along a linear axis. If the carbon atoms approach each other, the two electrons from the [1s]^2 orbitals do not participate on the bond formation (they remain close to the nucleus), the ones involved in the chemical bonds being the outermost orbitals. Thus, different form of carbon can be constructed due to the fact that there are different ways in which the four electrons in the outer orbitals [2s]^2[2p]^2 can be divided between atoms.

Figure 1: Grafene lattice with basic structural units; [4]



The sp^3 bond is tetrahedral (3D) and is formed when a carbon atom equally share its four electrons with four nearest carbon atoms (e.g. the crystal structure of the diamond). Electrons in carbon atoms can also combine with hydrogen atoms [4] and form sp^2 or sp bonds (e.g. 2D planar molecules - benzene, or long one-dimensional chains - conductive polymers).

In his work, Debdeep [4] presents the crystalline structure of graphene considering two nearest-neighbor carbon atoms as the smallest unit which can be translated over the entire 2D space of the graphene plane (Figure 1). The author states that the two carbon atoms (denoted by A and B) are not identical due to the fact that the electronic wave function associated with them can break the "mechanical" symmetry. The sp^2 bond, characteristic of graphene, is denoted by $|sp^2\rangle = a|s\rangle + b|px\rangle + c|py\rangle$ with *a*, *b*, *c* - constants, and is formed when a carbon atom shares electrons with three of its nearest neighbors, leaving one electron free for each carbon atom [4]. The electrons energies composing the sp^2 bonds constitute the so-called σ *bands*, which gives graphene its vibrational and structural properties (e.g. Young's modulus, thermal conductivity, etc.), being also responsible for its perfectly flat nature. The electrons which do not participate in the chemical bond formation come from the $|p_z\rangle$ orbitals and can move between the nearest neighboring carbon atoms with a hoop energy of $\gamma_0 \sim 3.0\,eV$, having delocalized wave functions [4]. Thus, the allowed energies of these electrons constitute the so called *π bands*. The delocalized electrons are responsible for the exceptional electrical conductivity of graphene, their allowed energies depending on their wavelength, following the rules of quantum mechanics. Moving forward, one will consider the de-Broglie relation, which states that the wavelength is inversely proportional to the momentum. Thus, the momentum is expressed by $\hbar k$, with $\hbar$ - the Planck's constant, and $k = 2\pi / \lambda$ with λ - the wavelength. If one will consider the basis of two atoms, the wavefunctions of graphene electrons can be represented as "spinors", i.e. two components matrices of the form $\frac{\exp[ik \cdot r]}{\sqrt{2}}\begin{pmatrix} 1 \\ \exp[i\theta] \end{pmatrix}$ with $k = xk_x + yk_y$ and $\tan\theta = k_y / k_x$ [4].

On the other hand, Green's function is widely used in electrodynamics and quantum field theory [6], especially for problems where the relevant differential operators are often difficult or impossible to solve exactly (but can be solved in a perturbative way using Green's functions). There are many definitions for Green’s function known in literature, depending on its representation domain and its application [7].

In his work, Rastegin [8] derive the Green’s function of the wave equation by considering that the non-homogeneous wave equation for a field described by a function of the scalar potential $\phi(r,t)$ can be written as following:

$$\nabla^2\phi - \frac{1}{c^2}\frac{\partial^2\phi}{\partial t} = Q(r,t) \tag{1}$$

with $Q(r,t)$ - the function describing the source of action, with the physical meaning determined by the considered processes nature; the model is linear (i.e. Eq. (1)), and as a result, this equation allows overlapping solutions.

Thus, for a source Q represented as the sum of two other sources, e.g. Q_1 and Q_2, with several solutions ϕ_1 and ϕ_2, known for each of them separately, a solution of the previous equation can be of the form:

$$\phi(r,t) = \phi_1(r,t) + \phi_2(r,t) \tag{2}$$

Based on these considerations, the author [8] considers the Green function as a viable method for solving inhomogeneous linear models; in this case, the given source is represented in the form of some "elementary" sources superpositions with known solutions.

More precisely, the inhomogeneous equation is considered as follow:

$$\nabla^2\psi = \rho(r) \tag{3}$$

with $\psi(r)$ - an abstract potential, and $\rho(r)$ - describes the sources distribution. Eq. (3) can be solved using the integral:

$$\psi(r) = \int G(r,R)\rho(R)dV_R \tag{4}$$

whit $G(r,R)$ as the Green’s function with standard expression $G(r,R) = -\frac{1}{4\pi|r-R|}$ which depends only on $|r-R|$.

Starting from these considerate, the author [8] proceeds in his study by deriving the Green function for the wave equation, starting from considering a material point which varies in time, located at the coordinate origin, of the form:

$$Q(r,t)=\delta(r)q(t) \tag{5}$$

as the source for the inhomogeneous wave equation Eq. (1).

Thus, Eq. (1) with the source as Eq. (5) constitutes a new system with spherical symmetry, so the solutions should be represented as $\phi(r,t)$, with $r=|r|$. At the same time, the radial part of the Laplacian can be expressed as [8]:

$$\nabla^2\phi(r,R)=\frac{1}{r}\frac{\partial^2}{\partial r^2}r\phi(r,t) \tag{6}$$

In the case of $r\neq 0$, there is an auxiliary function $f(r,t)=r\phi(r,t)$ which respects the homogeneous wave equation with a single spatial variable:

$$\frac{\partial^2 f}{\partial r^2}-\frac{1}{c^2}\frac{\partial^2 f}{\partial t^2}=0 \tag{7}$$

According to d'Alembert's formula, $f(r,t)$ represents the sum of two terms depending on $r\pm ct$, for which the solution can be written in the form $f(r,t)=u(t-r/c)+v(t+r/c)$. After several calculations, for Eq. (1) with the source as Eq. (5) one will obtain [8]:

$$\phi(r,t)=-\frac{q(t-r/c)}{4\pi r} \tag{8}$$

If the substitution $q(t)=\delta(r)$ is made, will results the function:

$$g(r,t)=-\frac{\delta(t-r/c)}{4\pi r} \tag{9}$$

The wave operator acting on the Eq. (9) gives $\delta(r)\partial(t)$, with $g(r,t)$ as its fundamental solution. Moreover, because for $t>0$ the right member of Eq. (9) is equal to zero, one can explicitly add the Heaviside function as a factor. Thus, the basic Green function in infinite space without boundary is obtained by replacing *r* with $|r-R|$ and *t* with $t-\tau$ [8].

In another approach [9], the Green function *g* is considered as a solution of the wave equation with an impulsive source function δ (i.e. the space-time impulse δ is situated in the right member):

$$\frac{\partial^2 g(r,t)}{\partial t^2}-v^2\nabla^2 g(r,t)=\delta(r,t) \tag{10}$$

where v is a positive constant.

In practice, the equation for *g* can be solved with the aid of the spatial Fourier transform, denoted by $\mathcal{F}$, defined as [9]:

$$\mathcal{F}g(r,t)\equiv G(k,t)=\int_{-\infty}^{+\infty} g(r,t)e^{ik\cdot t}dv \tag{11}$$

Starting from the fact that the spatial Fourier transform for $\partial^2 g/\partial t^2$ is of the form:

$$\mathcal{F}\frac{\partial^2 g}{\partial t^2}=\frac{\partial^2 G}{\partial t^2} \tag{12}$$

and considering the spatial Fourier transform for $\nabla^2 g$ as $\mathcal{F}\left(\nabla^2 g\right)=k^2 g$ and for $\delta(r,t)$ as $\mathcal{F}\left(\nabla^2 g\right)=F[\delta(x)\delta(y)\delta(z)\delta(t)]=\delta(t)$, one will obtain the spatial Fourier transform for Eq. (12) as [9]:

$$\frac{\partial^2 G}{\partial t^2}=v^2\left(k^2 G\right)=\delta(t) \tag{13}$$

Due to the fact that in Eq. (12) there are no spatial variable, the partial derivative can be replaced by the total derivative, leading to the following ordinary differential equation:

$$\frac{d^2 G}{dt^2}=v^2\left(k^2 G\right)=\delta(t) \tag{14}$$

Since the right member of the Eq. (14) is represented by delta function, *G* is considered the Green's function for the ordinary differential equation, whose solutions can be determined by the Laplace transform method [9].

Thus, for $G_L(k,s)$as the Laplace transform of $G(k,t)$, i.e.

$$G_L(k,s)=\int_0^\infty G(k,t)e^{-st}dt \tag{15}$$

for the ordinary differential equation, its Laplace transform will be the algebraic equation

$$s^2 G_L+v^2 k^2 G_L=1 \tag{16}$$

with $G_L(k,s)=\dfrac{1}{s^2+v^2 k}$ as the solution [9].

At the same time, according to the table of the Laplace transform, $G(k,t)=\dfrac{\sin vkt}{vk}$, from which results that the Green's function for the Eq. (14) is the sinc (Cardinal sine) function.

Based on these considerations, the author [9] states that the inverse Fourier spatial transform of $G(k,t)$ gives the Green function *g* for the 1D wave equation, of the form:

$$g(k,t)=\frac{\theta(vt-r)}{2v} \tag{17}$$

for $r\geq 0$ and $t\geq 0$, with θas the Heaviside function [9].

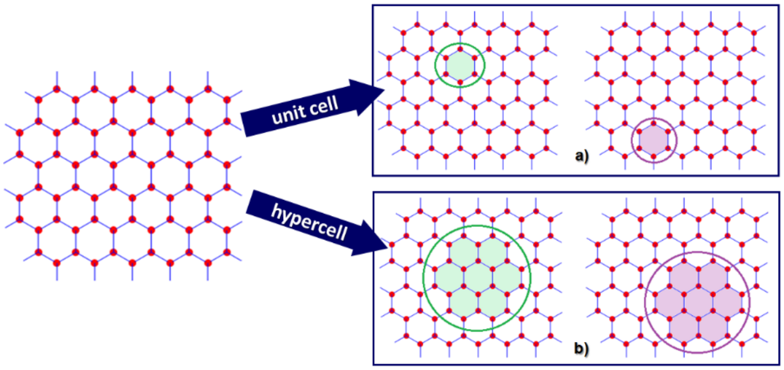
Nevertheless, there are many fields where the Green's function formalism was successfully used, such as statistical, nuclear, solid-state physics, and also in atomic and molecular physics [10]. Green's function can be also used in transport calculation, by solving the problems of single-particle electronic transport, when the density functional Hamiltonian from the Schrodinger equation is used in order to describe the particle energetic [11].

2. METHOD

2.1. Atomic Cumulative Gradients Model

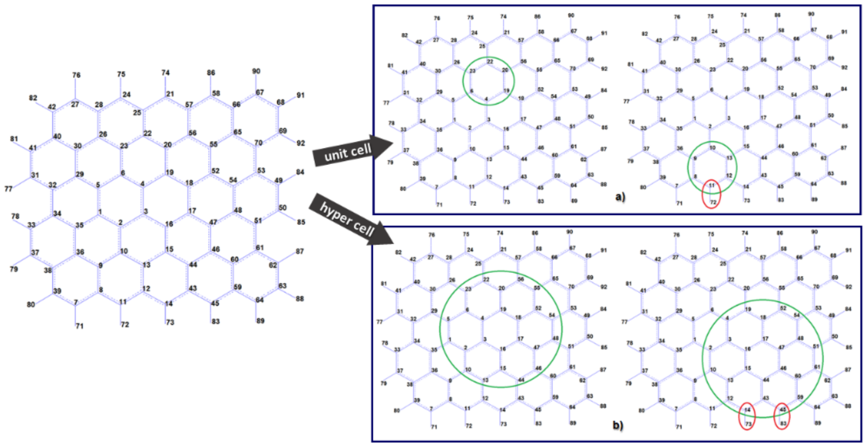
For the present study, the working system consists in a graphene nanoribbon with 25 benzene molecules ($C_{70}H_{22}$) in which one can notice two types of structures – subsystems which can be translated – the smallest, i.e. benzene, generically named unit cell, and a cluster of unit cells, i.e. coronene, generically named hypercell (Figure 2).

Figure 2: Graphical representation of the studied system and its corresponding subssistems in monobond and heterobond state. **(a)** Benzene. **(b)** Coronene



The two subsystems form two types of chemical bonds **-** only with carbon atoms i.e. monobond, and with 1 and 2 hydrogen atoms respectively i.e. heterobond. The aim is to determine how sub-systems energy inside the global system is influenced by the type of bonds created between carbon atoms and hydrogen atoms.

Figure 3: Optimized unit cell and hypercell (representation using Hyperchem). **(a)** Benzene. **(b)** Coronene



In order to accurately describe the electronic configuration and the bonds between atoms for the $C_{70}H_{22}$ molecule it was used the Hyperchem 8.1 program, and geometry optimization calculations were performed in order to determine its most stable configuration (i.e. in which net forces on each atom are reduced to zero); these calculations are made by adjusting atomic coordinates in steps. As a method of optimization, PM3 semi-empirical method was selected, which describes the electron properties of atoms and molecules by solving the Schrödinger equation with certain approximations. In Hyperchem program, the molecule in study reaches a stable conformation due to the fact that the molecular geometry is altered by energy minimization, leading to lowering the system energy. The minimization progresses by searching the molecular structure in which the energy is not affected by infinitesimal changes in geometry, in other words, the derivative of the energy with respect to all Cartesian coordinates (i.e. the *gradient*) has a value near zero.

2.2. Benzene and Coronene Atoms-in-Bonding Gradients

Single point calculations were performed on the optimized system, in order to determine the gradient and the total energy for the working system; for this type of calculations, the input molecular structure will show which are the coordinates for a stationary point on the surface of the potential energy. In HyperChem program, the gradient represents the energy rate of change (first derivative) for a molecular system, defined as a function of atomic positions; if its value is very close to zero than the system configuration has minimum energy.

- ***Benzene characterization***

From the results obtained with single point, the values representing the atomic gradients for both *x* and *y* coordinates were selected (see Table 1), for the specific carbon atoms form the unit cell in monobond state (i.e. **C_{22}, C_{20}, C_{19}, C_4 C_6, C_{23}**) and heterobond state respectively (i.e. **C_{10}, C_{13}, C_{12}, C_{11}, C_8, C_9**).

Table 1: Atomic gradients for the unit cell obtianed with Hyperchem

BENZENE					
Monobond state			Heterobond state		
Carbon atom	Atomic gradients (kcal/mol/Anstrom)		Carbon atom	Atomic gradients (kcal/mol/Anstrom)	
	x	**y**		**x**	**y**
C_{22}	*0.03867*	*-0.01046*	**C_{10}**	*-0.02062*	*0.02395*
C_{20}	*-0.03495*	*0.01800*	**C_{13}**	*0.03867*	*0.01046*
C_{19}	*-0.04216*	*-0.01900*	**C_{12}**	*0.04206*	*-0.00817*
C_4	*0.04519*	*0.01768*	**C_{11}**	*-0.04225*	*0.00070*
C_6	*-0.02502*	*0.02361*	**C_8**	*0.03036*	*-0.02978*
C_{23}	*-0.02062*	*-0.02395*	**C_9**	*-0.01040*	*0.03250*

- ***Coronene characterization***

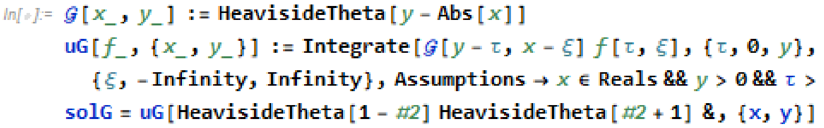
The molecular characterization of the hypercell (in monobond and heterobond states) was made in the same way as for unit cells, the atomic gradients for both *x* and *y* for the specific carbon atoms being presented in Table 2.

Table 2: Atomic gradients for the hypercel obtianed with Hyperchem

CORONENE					
Monobond state			Heterobond state		
Carbon atom	Atomic gradients (kcal/mol/Anstrom)		Carbon atom	Atomic gradients (kcal/mol/Anstrom)	
	x	**y**		**x**	**y**
C_{22}	*0.03867*	*-0.01046*	**C_{19}**	*-0.04216*	*-0.01900*
C_{20}	*-0.03495*	*0.01800*	**C_{18}**	*0.01637*	*-0.02733*
C_{19}	*-0.04216*	*-0.01900*	**C_{17}**	*0.01637*	*0.02733*
C_{4}	*0.04519*	*0.01768*	**C_{16}**	*-0.04216*	*0.01900*
C_{6}	*-0.02502*	*0.02361*	**C_{3}**	*0.04519*	*-0.01768*
C_{23}	*-0.02062*	*-0.02395*	**C_{4}**	*0.04519*	*0.01768*
C_{56}	*0.01424*	*0.02172*	**C_{52}**	*0.01455*	*-0.02717*
C_{55}	*0.01024*	*0.02590*	**C_{54}**	*-0.03320*	*-0.00554*
C_{52}	*0.01455*	*-0.02717*	**C_{48}**	*-0.03320*	*0.00554*
C_{18}	*0.01637*	*-0.02733*	**C_{47}**	*0.01455*	*0.02717*
C_{54}	*-0.03320*	*-0.00554*	**C_{51}**	*0.03908*	*0.00686*
C_{48}	*-0.03320*	*0.00554*	**C_{61}**	*0.02427*	*-0.00592*
C_{47}	*0.01455*	*0.02717*	**C_{60}**	*-0.02350*	*-0.00166*
C_{17}	*0.01637*	*0.02733*	**C_{46}**	*0.01024*	*-0.02590*
C_{46}	*0.01024*	*-0.02590*	**C_{59}**	*-0.01654*	*0.00363*
C_{44}	*0.01424*	*-0.02172*	**C_{45}**	*0.00631*	*0.00374*
C_{15}	*-0.03495*	*-0.01800*	**C_{43}**	*0.01519*	*0.02315*
C_{16}	*-0.04216*	*0.01900*	**C_{44}**	*0.01424*	*-0.02172*
C_{13}	*0.03867*	*0.01046*	**C_{14}**	*-0.03637*	*0.00379*
C_{10}	*-0.02062*	*0.02395*	**C_{12}**	*0.04206*	*-0.00817*
C_{2}	*-0.02502*	*-0.02361*	**C_{13}**	*0.03867*	*0.01046*
C_{3}	*0.04519*	*-0.01768*	**C_{15}**	*-0.03495*	*-0.01800*
C_{1}	*-0.00955*	*-0.04224*	**C_{10}**	*-0.02062*	*0.02395*
C_{5}	*-0.00955*	*0.04224*	**C_{2}**	*-0.02502*	*-0.02361*

The atomic gradient values obtained for the selected carbon atoms of unit cell and hypercell (in mono/hetero-bond) were used as input values for calculating the Gradient function, using its algorithm for 1D wave equation from Wolfram Mathematica 11.3 program (see Figure 4).

Figure 4: Algorithm for Gradient function for 1D form Wolfram Mathematica 11.3



```
In[•]:= G[x_, y_] := HeavisideTheta[y - Abs[x]]
        uG[f_, {x_, y_}] := Integrate[G[y - τ, x - ξ] f[τ, ξ], {τ, 0, y},
          {ξ, -Infinity, Infinity}, Assumptions → x ∈ Reals && y > 0 && τ > 0]
        solG = uG[HeavisideTheta[1 - #2] HeavisideTheta[#2 + 1] &, {x, y}]
```

3. RESULTS AND DISCUSSIONS

The Heaviside based Gradient function values obtained with Mathematica algorithm for each carbon atom from the unit cell and hypercell are presented in Table 3 and Table 4, and their distribution over the origin is presented in Figure 5 (for benzene) and Figure 6 (for coronene). The total Gradient function was calculated as a sum of the individual values for both cases in each type of bonding.

- ***Case 1 - Benzene***

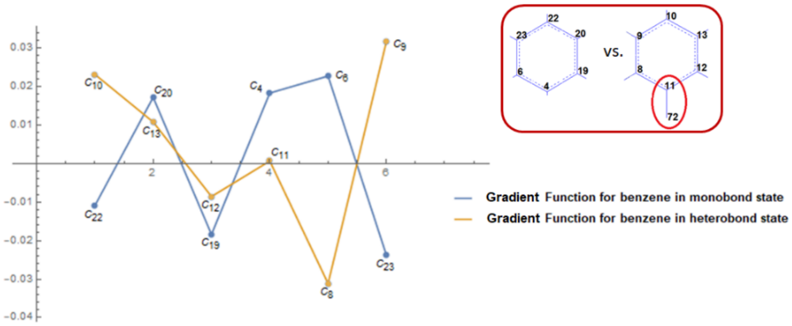
For the unit cell, the results show a difference in the number of positive and negative values between the two bonding states. In monobond state, the negative and positive results are equally distributed over the origin, i.e. the Gradient function values obtained for $\mathbf{C_{22}}$, $\mathbf{C_{19}}$, and $\mathbf{C_{23}}$ has negative sign, while the ones for the other three carbon atoms has positive values. However, the positive values are slighty higher than the negative ones; as a result, the total Gradient funtion value has positive sign and is more close to *0*.

On the other hand, in heterobond, only two negative values were obtained, i.e. for $\mathbf{C_{12}}$ and $\mathbf{C_8}$, the ones for the other four carbon atoms being with positive sign. For this case, the positive values are even higher than in the previous case, compared to the negative ones; as a result, the total Gradient funtion value is also positive but more close to *0.1*.

Table 3: Calculated values of Gradient function for benzen

BENZEN					
Monobond state			Heterobond state		
Carbon atom		Gradient function	*Carbon atom*		Gradient function
	$\mathbf{C_{22}}$	-0.0109192		$\mathbf{C_{10}}$	0.0231693
	$\mathbf{C_{20}}$	0.0172089		$\mathbf{C_{13}}$	0.0108098
	$\mathbf{C_{19}}$	-0.0183795		$\mathbf{C_{12}}$	-0.008547
	$\mathbf{C_4}$	0.0183227		$\mathbf{C_{11}}$	0.00067018
	$\mathbf{C_6}$	0.0227406		$\mathbf{C_8}$	-0.0311275
	$\mathbf{C_{23}}$	-0.023743		$\mathbf{C_9}$	0.0316339
Total Gradient **function**					
0.0052305			**0.02660868**		

Figure 5: Gradient function distribution for benzen in monobond vs. heterobond state



- ***Case 2 - Coronene***

For the hypercell (i.e. coronene) there is also a difference in the number of positive and negative values between the two bonding states. In monobond, the equal distribution between the negative and the positive results is maintained, same as in benzene monobond i.e. the Gradient function values obtained for **C_{22}**, **C_{19}**, **C_{23}**, **C_{52}**, **C_{18}**, **C_{54}**, **C_{46}**, **C_{44}**, **C_{15}**, **C_{2}**, **C_{3}** and **C_{1}** has negative sign, while the ones for the other twelve carbon atoms has positive value. In this case, the positive values are slighty smaller than the negative ones; as a result, even if the total Gradient funtion value has negative sign, is still more close to *0*.

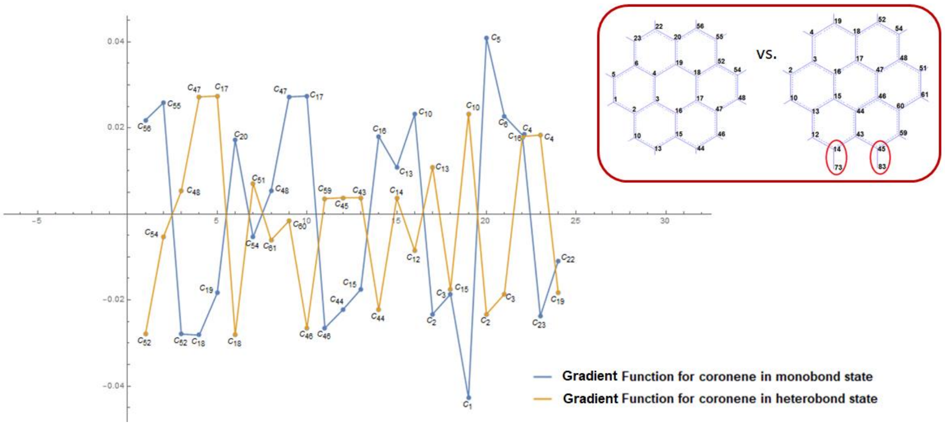
Table 4: Calculated values of Gradient function for coronene

CORONENE					
Monobond state			Heterobond state		
		Gradient function			Gradient function
Carbon atom	**C_{22}**	-0.0109192	*Carbon atom*	**C_{19}**	-0.0183795
	C_{20}	0.0172089		**C_{18}**	-0.0281509
	C_{19}	-0.0183795		**C_{17}**	0.0274039
	C_{4}	0.0183227		**C_{16}**	0.0180185
	C_{6}	0.0227406		**C_{3}**	-0.0186353
	C_{23}	-0.023743		**C_{4}**	0.0183227
	C_{56}	0.0217934		**C_{52}**	-0.0279344
	C_{55}	0.0258298		**C_{54}**	-0.00537142
	C_{52}	-0.0279344		**C_{48}**	0.00534073
	C_{18}	-0.0281509		**C_{47}**	0.0271962
	C_{54}	-0.00537142		**C_{51}**	0.00710456
	C_{48}	0.00534073		**C_{61}**	-0.0060812
	C_{47}	0.0271962		**C_{60}**	-0.00162237
	C_{17}	0.0274039		**C_{46}**	-0.0265006
	C_{46}	-0.0265006		**C_{59}**	0.00356337
	C_{44}	-0.0222652		**C_{45}**	0.00375661
	C_{15}	-0.0175329		**C_{43}**	0.00375661
	C_{16}	0.0180185		**C_{44}**	-0.0222652
	C_{13}	0.0108098		**C_{14}**	0.00364498
	C_{10}	0.0231693		**C_{12}**	-0.008547
	C_{2}	-0.023298		**C_{13}**	0.0108098
	C_{3}	-0.0186353		**C_{15}**	-0.0175329
	C_{1}	-0.0427287		**C_{10}**	0.0231693
	C_{5}	0.0409445		**C_{2}**	-0.023298
Global Gradient **function**					
-0.00668079			**-0.05223153**		

For the second case, in heterobond, the equality between the number of positive and negative values is also maintained, i.e. the Gradient function values obtained for **C_{19}**, **C_{18}**,

C_3, **C_{52}**, **C_{54}**, **C_{61}**, **C_{60}**, **C_{46}**, **C_{44}**, **C_{12}**, **C_{15}** and **C_2** has negative sign, the ones for the other twelve carbon atoms being with positive sign. However, the positive values are even smaller than the negative ones, compaerd to the ones from monobond, this time, the total Gradient function value being with negative sign and more close to *-0.1*.

Figure 6: Gradient function distribution for coronen in monobond vs. heterobond state



A possible explanation for the difference between the total Gradient function of the benzene bonding states can be the fact that the bond between hydrogen and carbon is stronger than the bond between carbon and carbon. At the same time, the positive value of the total Gradient function can indicate that is more probable for the benzene ring (as a subsystem in the carbon nanoribbon) to became involved in bonds formation with other molecules.

There is also a difference between the two states of coronene, i.e. the global Gradient function for coronene in monobond state is higher than the global Gradient function for coronene in heterobond state, which can be explained by the fact that systems with multiple benzene rings are more stable when bond with other carbon atoms than in the case when bond with hydrogen. At the same time, the negative value of the total Gradient function (different form the positive one obtained for benzene) can also be regarded as a marker of a more stable configuration for coronene as a sub-system of the nanoribbon.

4. CONCLUSION

Nowadays, there is still an increased interest in studding graphene due to its applicability in many domains of interest. Recent studies presents graphene as an active material [12] when is used in energy storage mechanisms: it can capture ions (e.g. Na^+ or Li^+ ions in ion-metal batteries), can store electrostatic charge (e.g. in double-layer electrochemical capacitors) or it can act as a catalyst (e.g. in metal-air batteries). At the same time, graphene is considered a suitable alternative as an anodic material [13] because it is chemically stable, can exchange electrons easily and has high electrical conductivity, which causes a lower resistive heat inside the electrode (batteries can operate at lower temperatures, being safer). In this context, it is well known in the scientific community that the computational methods are seen as good alternatives to the classical experimental methods, being faster, less expensive and more environmentally friendly, especially when combined with mathematical formalisms. Starting from these considerations, Gradient function formalism can be seen as a very useful mathematical model in studies of chemistry and physics due to the fact that depends only on the differential operator and the boundary conditions, meaning that it can be easily solved once these conditions are fulfilled. Further connections between the actual Gradient function assessment and the atoms-in-nanostructures Green's functions distribution are to be next studied.

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