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Theoretical Study of the Chemisorption of Hydrogen Atom on Perfect Graphene

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Abstract

We use the Newns-Anderson model to study the chemisorption process for hydrogen atom on perfect graphene. The self-consistent solutions for hydrogen atom occupation levels show that the physical solution is magnetic for all normal distance values from the graphene sheet. And the metallic part of the chemisorption energy is the dominant one for all distance values, which gives the obvious description to the type of hydrogen bonding formed with the graphene.

Key wards: Graphene, Chemisorption, Newns-Anderson Model, Nanotechnology.

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1. Introduction

The graphene, a type of carbon based material, has attracted great attention from both experimentalists and theoretists since its experimental discovery in 2004[1]. Structurally, graphene consists of a single-layer graphite sheet(SLG), thus the electrons are restricted to the atomic thin sheet, forming two dimensional electron gas (2DEG)[2]. It is the basic material to form nanotube, fullerene and graphite. Graphene is a substance that attracts attention not only as parts of the nano carbons but also for its own interesting electronical and mechanical properties.

The Chemisorption of species on solid surface can be defined as the bonding of atoms or molecules to a solid surface and refers to bonds of chemical strength, as opposed to physisorption which refers to weaker bonds that can only be stabilized on the surface at low temperatures. Because chemisorption involves energies that are sizable on chemical scale the chemisorption process is often associated with the breaking of bonds. The description of the chemisorption bond on solid requires a detailed understanding of the electronic structure of atoms and molecules outside solid surface. The determination of the geometrical structure of solid surface with chemisorbed species is developing into an enormous industry related to surface crystallography.

Theoretically, two different approaches are taken into consideration. **The first one** is to include everything in the electronic structure calculations of the electronic structure. All of the calculations make approximations in their treatment of the electron – electron interactions [3]. **The second** is to devise simple models that can capture only the essential physics.

In our study, we shall use one of the second type models to study the time – independent chemisorption process on graphene incorporating the spin on the adsorbed atom, this model is Newns – Anderson one [4,5].

Our model calculations takes the following (adatom/graphene) system physical features into consideration,

1. All the parameters that concerned to the type of atom which adsorbed on graphene sheet,

2.The system electronic structure and then the quantum coupling effects which are expressed by the broadening chemisorption function and the quantum shift.

Our study comprises three main lines of investigation. The first is the calculation of the broadening and the quantum shift as a function of energy and the normal distance between the atom and the graphene sheet, then we calculate the adsorbate density of states on the graphene sheet. The second is the calculation of the net charge and the magnetization on the adsorbed atom. While the third is to calculate the ionic and the metallic parts of the chemisorption energy.

2. The Theoretical Treatment

In the second quantization form, the model Hamiltonian of the combined system(adsorption of atom on perfect graphene) is[4,5,6],

$$H = \sum_{k\sigma} E_k^{\sigma} n_k^{\sigma} + \sum_{\sigma} E_a^{\sigma} n_a^{\sigma} + U\, n_a^{\sigma} n_a^{-\sigma} + \sum_{k\sigma} (V_{ak}^{\sigma} C_a^{\sigma +} C_k^{\sigma} + V_{ka}^{\sigma} C_k^{\sigma +} C_a^{\sigma}) \quad \text{... (1)}$$

Where, E_k^{σ} and n_k^{σ} are the energy levels with set of quantum numbers k and the corresponding occupation numbers in the graphene energy band for spin σ respectively. E_a^{σ} is the spin dependent effective energy level of the adsorbed atom and n_a^{σ} is the corresponding occupation number.

It is well known that there is a difference in energy between the atom`s ionization V_i and the affinity V_A energy levels (far away from the graphene sheet) due to electron-electron interaction. This difference is given by [3],

$$U = V_i - V_A \quad \text{...... (2)}$$

As the atom approaches to the graphene sheet, the ionization and affinity energy levels are shifted towards each other, which means that the value of U (*i.e.* its effective value of U, which will be denoted as U_{eff}) decreases as the atom moves towards the graphene sheet due to the electron-electron correlation interaction [7].

And as our study is concerned to the chemisorption of atom on graphene sheet, the intra-atomic correlation interaction will be taken into consideration in our model calculation.

The correlation energy can be calculated as a function of the vertical distance (Z) between the adatom and the surface by using the following relation [8],

$$U_{eff}(Z) = V_i - V_A - 2\Delta E(Z) \qquad \text{...... (3)}$$

With, $\Delta E(Z)$ is the image shift which takes the image effect into consideration. U_{eff} is Z-dependent through out the image shift $\Delta E(Z)$.

The image interaction between the electrons in the adatom and the graphene sheet (at certain separation, i.e. normal distance which represents by Z) is given by [9] ,

$$\Delta E(Z) = \frac{e^2}{4(Z + Z_0)} \qquad \text{...... (4)}$$

Then by taking image effect and the correlation effect, the atomic energy level E_a^{σ} $(E_a^{-\sigma})$ with spin up (spin down) is written as [10,11],

$$E_a^{\pm\sigma}(Z) = E_a^0 + \Delta E(Z) + U_{eff}\, n_a^{\mp\sigma} \qquad \text{...... (5)}$$

E_a^0 is equal to $(\emptyset_0 - V_i)$, $\emptyset_0$ is the surface work function, n_a^{σ} is the occupation number of the atomic energy level of spin up $(i.e. E_a^{\sigma})$,

$$n_a^{\sigma} = \int_{u_\circ}^{\phi_\circ} f(E,T)\rho_{ad}^{\sigma}(E)\, dE \qquad \text{...... (6)}$$

With $u_\circ$ is the energy of the band bottom. ρ_{ad}^{σ} is the local density of states on the adatom (which will be highlighted extendedly) and $f(E,T)$ is the Fermi distribution function for the graphene sheet,

$$f(E,T) = \frac{1}{1 + e^{(E/k_B T)}} \qquad \text{...... (7)}$$

k_B is the Boltizman constant and T is the temperature.

The adsorbate density of states associated with each atomic level of spin σ $(-\sigma)$ is a Lorentzian distribution centered at $E_a^{\sigma}(E_a^{-\sigma})$ as,

$$\rho_{ad}^{\sigma}(E) = \frac{1}{\pi}\frac{\Delta^{\sigma}(E)}{[E - E_a^{\sigma} - \Lambda^{\sigma}(E)]^2 + [\Delta^{\sigma}(E)]^2} \qquad \text{......(8)}$$

Where E_a^{σ} is the effective energy level of the adsorbate atom with spin σ. $\Delta^{\sigma}(E)$ and $\Lambda^{\sigma}(E)$ are the energy dependent chemisorption functions (the adatom energy level broadening and the quantum shift due to coupling interaction between the adsorbate atom and the surface respectively),

$$\Delta^{\sigma}(E) = \pi \sum_k \left|V_{ak}^{\sigma}\right|^2 \delta(E - E_k) \qquad \text{...... (9)}$$

where [12],

$$V_{ak}^{\sigma} = v_k V_0^{\sigma} \qquad \text{...... (10)}$$

v_k is the energy phase of the interaction and V_0^σ is the strength of the coupling interaction,

$$\rho_G(E)=\sum_k |v_k|^2\,\delta(E-E_k) \qquad \ldots (11)$$

$\rho_G(E)$ is the graphene sheet density of states.

Then equation (9) can be rewritten as,

$$\Delta^\sigma(E)=\pi|V_0^\sigma|^2\rho_G(E) \qquad \ldots\ldots(12)$$

$V_\circ^\sigma$ is the strength of interaction between the adatom and the graphene sheet. The quantum shift can be rewritten as,

$$\Lambda^\sigma(E)=\frac{1}{\pi}\,P\int d\acute{E}\,\frac{\Delta^\sigma(\acute{E})}{E-\acute{E}} \qquad \ldots\ldots(13)$$

We get use of the density of states for the perfect graphene [13] (see fig.(1)) to study and investigate the chemisorption process of atoms on graphene sheet. According to the best fitting, we get the following formula,

$$\rho_G(E)=\sum_{n=1}^{13}[a_n+b_n(E-E_{p_n})^2] \qquad \ldots (14)$$

n refers to the best fitted regions. The best fitted graphene density of states is presented in Fig. (2), with ,

$$b_n=\frac{C_n}{(E_{f_n}-E_{p_n})^2} \qquad \ldots\ldots (15)$$

The coefficients $a_n, C_n, E_{p_n}, E_{f_n}$ are all presented in Table. (1).

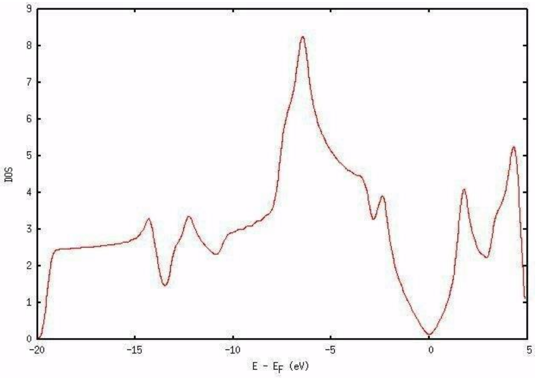


Fig.(1): The DFT graphene density of states[13]

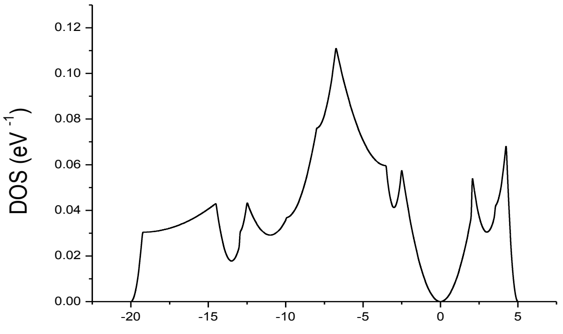


Fig.(2): The fitted graphene density of states

Table (1) : The fitting parameters for graphene density of states shown in Fig.(2)

n	$a_n\,(\frac{1}{eV})$	$E_{i_n}\,(eV)$	$E_{p_n}\,(eV)$	$E_{f_n}\,(eV)$	$c_n\,(\frac{1}{eV})$
1	0.0	-20.0	-20.0	-19.25	0.24
2	0.24	-19.25	-19.25	-14.5	0.1
3	0.14	-14.5	-13.5	-13.0	0.2
4	0.24	-13.0	-13.0	-12.5	0.105
5	0.23	-12.5	-11.0	-10.0	0.115
6	0.29	-10.0	-10.0	-8.0	0.31
7	0.6	-8.0	-8.0	-6.75	0.28
8	0.47	-8.0	-3.5	-3.5	0.41
9	0.325	-3.5	-3.0	-2.5	0.135
10	0.0	-2.5	0.0	2.0	0.46
11	0.24	2.0	3.0	3.5	0.22
12	0.33	3.5	3.5	4.25	0.22
13	0.0	4.25	5.0	5.0	0.55

The self-energy due to the coupling interaction between (perfect) graphene sheet and an adatom can be written as[14],

$$\sum{}^\sigma(E)=|V_0^\sigma|^2\,P\int\frac{\rho_G(E')}{E-E'}\,dE' \qquad \ldots\ldots (16)$$

By substituting eq.(14) in eq.(16) one can solve the integration analytically to get,

$$\sum{}^\sigma(E)=i\,\Delta^\sigma(E)+\Lambda^\sigma(E) \qquad \ldots\ldots (17)$$

$\Delta^\sigma(E)$ and $\Lambda^\sigma(E)$ represent the chemisorption functions , i.e. the adatom energy level broadening and its quantum shift (due to coupling interaction) respectively.

Now, we write,

$$\Delta^{\sigma}(E)=\pi\left|V_0^{\sigma}\right|^2\sum_{n=1}^{13}[a_n+b_n(E-E_{p_n})^2] \quad \ldots(18)$$

and ,

$$\Lambda^{\sigma}(E)=\left|V_0^{\sigma}\right|^2\sum_{n=1}^{13}\int_{E_{in}}^{E_{fn}}\frac{\left(a_n+b_nE_{pn}\right)-2b_nE_{pn}E'+b_nE'^2}{E-E'}dE' \quad \ldots(19)$$

Which is solved analytically to get ,

$$\Lambda^{\sigma}(E)=\left|V_0^{\sigma}\right|^2\sum_{n=1}^{13}\Bigg(\ [b_n(2E_{pn}-E)E-(a_n+b_nE_{pn}{}^2)]\ln\left(\frac{E-E_{fn}}{E-E_{in}}\right)-2b_n(E-E_{pn})(E_{fn}-E_{in})-\frac{b_n}{2}\left(E_{pn}{}^2-E_{in}{}^2\right)\Bigg) \quad \ldots(20)$$

All the coefficients included in eq.(20) are presented in table (1).

3.The Chemisorption Energy

The chemisorption energy can be defined as the change in the ground state energy on switching the coupling between the graphene sheet and the adatom. It is well-known that the bond formed between the adatom and the metal surface can be divided into an ionic part and metallic part.

The types of bonds that may be formed between the adatom and the graphene sheet are presented in fig (3).

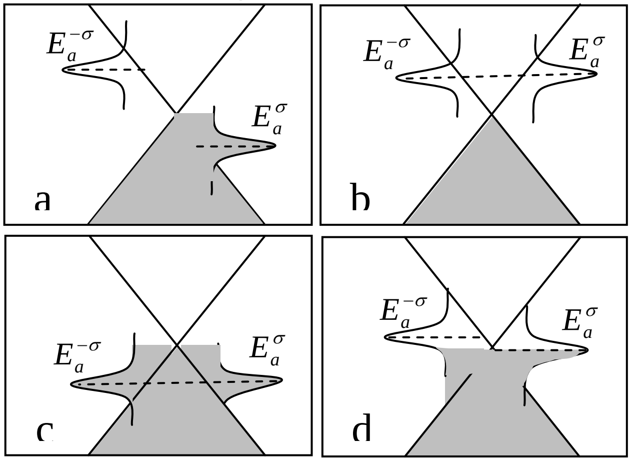


Fig. (3): The bond types (a) adsorbed atom, (b) ionic bond, (c) metallic bond and (d) mixed bonds.

This bond energy might be called a delocalization energy, resulting from allowing the valence electron of the adatom to spread throughout the graphene and the graphene electrons to spread into the region of the atom. In this way the kinetic energies of all electrons are reduced by relaxing slightly the geometrical confinement of both the graphene sheet and atomic electrons. The bond formed between the atom and the graphene sheet can be divided into metallic and ionic parts.

The expression for the metallic chemisorption energy is given by [10],

$$E_m(Z)=\sum_{\sigma}\int_{u_{\circ}}^{\phi}E\ f(E,T)\rho_{ad}^{\sigma}(E)dE-U_{eff}n_a^{\sigma}n_a^{-\sigma} \quad .(21)$$

The initial state (at $Z=\infty$) is an atom and a graphene sheet separated by "infinite" distance,

$$E_m(\infty)=\sum_{\sigma}\int_{u_0}^{\phi}E\ f(E,T)\delta(E-E_a^0)dE \quad \ldots(22)$$

$$E_m(\infty)=E_a^0f(E_a^0,T)$$
$$=(\phi-V_i)\Theta(V_i-\phi) \quad \ldots(23)$$

With Θ is unit step function.

$$\Theta(X)=\begin{cases}1 & X\geq 0\\ 0 & X<0\end{cases} \quad \ldots\ldots(24)$$

While the final state is an interacting adatom and graphene sheet separated by an equilibrium distance Z .

As the atom is brought to the graphene sheet , the sharp state broadens and overlaps with the graphene band energy levels such that the effective charge number of the atom is a function of distance and temperature[10],

$$Z_{eff}(Z) = 1 - n_a^{\sigma}(Z) - n_a^{-\sigma}(Z) \quad \ldots(25)$$

The attractive force between the effective charge $eZ_{eff}(Z)$ and its image is $-\dfrac{e^2 Z_{eff}^2(Z)}{4(Z+Z_\circ)^2}$ with $Z_\circ$ is an adjustable parameter which determines the position of the image plane. The work to bring the effective charge from $Z'=\infty$ to $Z'=Z$ is

$$W(Z) = -e^2 \int_Z^{\infty} \frac{Z_{eff}^2(Z')}{4(Z+Z_\circ)^2} dZ' \quad \ldots (26)$$

This integration must be solved numerically.

Now, the chemisorption energy can be calculated by using the following relation,

$$E_{ch}(Z) = E_m(Z) + W(Z) \quad \ldots (27)$$

and the bonding energy ,

$$E_{bond} = E_{ch}(Z_\circ) - E_{ch}(\infty) \quad \ldots\ldots (28)$$

Since, $W(\infty)=0$ and $E_m(\infty)$ is given by eq. (23), then,

$$E_{bond} = E_{ch}(Z_\circ) - (\phi - V_i)\Theta(V_i - \phi) \quad \ldots (29)$$

4. The Calculations and the Results

In order to achieve all the calculations, eq. (5) and (6) are solved self-consistently. The work function is given by the energy difference between the Fermi level E_F and the vacuum level. The work function of graphene sheet used in our calculation can be approximately given by 5.0 eV[13]. The electronic levels are filled using Fermi-Dirac statistics with a value of temperature T= 300 K. All the parameters used in our calculations are presented in table(2).

Table (2): The adatom/graphene system parameters.

Atom	V_i (eV)	Ø-V_i (eV)	V_A (eV)	R_i (A°)	V_0 (eV)	Z_0 (A°)
H	13.595	-8.595	0.7542	2.08	6.93	3.57

R_i represents the atom radius and Z_0 is the closest approach and V_0 is the strength of hybridization. The values of V_0 and Z_0 are considered as adjustable parameters.

By using the impurity Anderson model, all the functions that describe the chemisorption process for any atom on the graphene sheet are included in the self-consistent solution. The hybridization function and the quantum shift are calculated as a function of the energy system at each Z. Fig. (4) shows the hybirdyzation function and the quantum shift as a function of energy for $Z=Z_0$. As we know that the H atom attaches to the carbon atom directly, normal to the graphene plane, in an on top site, and pulls the underlying carbon atom out of the plane somewhat, i.e. the H atom is placed at Z_0 (=3.57 A°) directly above the graphene sheet.

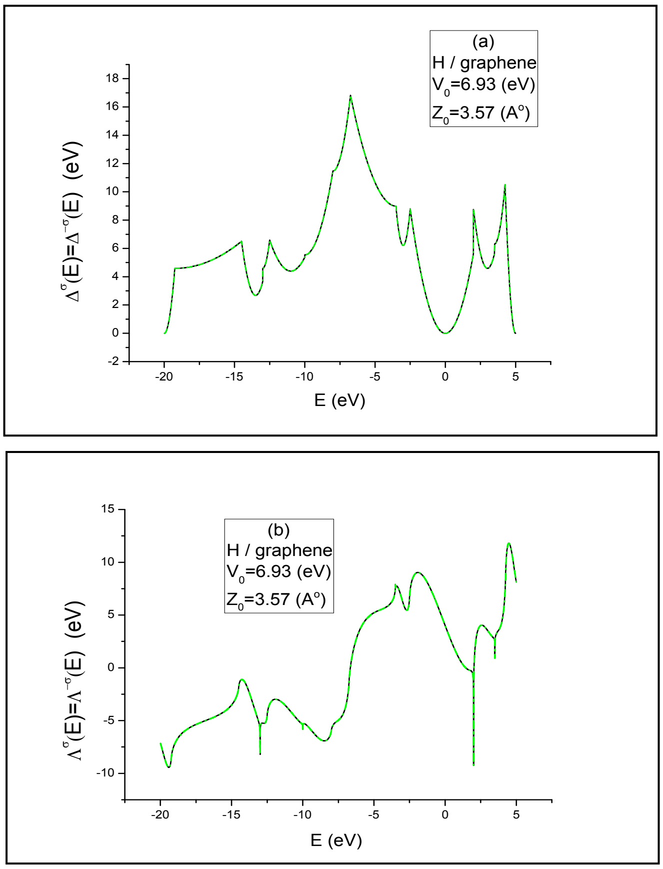


Fig. (4): The broadening and quantum shift as a function of energy for H/graphene system at Z=Z$_0$.

The adsorbate density of states $\rho^{\sigma}_{ad}(E)$, which incorporates the broadening in the adatom level due the hybridization with the sea of electrons in graphene is shown in fig.(5) at Z$_0$. This figure shows that $\rho^{\sigma}_{ad}(E) \neq \rho^{-\sigma}_{ad}(E)$, i.e. they are not identical, which means that the self-consistent solution is a magnetic one (i.e. $n^{\sigma}_{a} \neq n^{-\sigma}_{a}$).

The variation of the occupation numbers $n^{\pm\sigma}_{a}$ as a function of distance is shown in fig. (6). It shows that the physical solution, which minimizes the system's energy, is always the one for which n^{σ}_{a} is larger than $n^{-\sigma}_{a}$. This situation is consistent with the results presented in fig. (7), since E^{σ}_{a} is lying lower than $E^{-\sigma}_{a}$. The total number of electrons on the hydrogen energy levels, $N = n^{\sigma}_{a} + n^{-\sigma}_{a}$ is also shown in fig. (8), which shows that 0< $N \leq 1$.

In order to investigate the magnetic behavior on the hydrogen/graphene system, it is useful to calculate the magnetization which is given by $M = n^{\sigma}_{a} - n^{-\sigma}_{a}$ (see fig. (8)). As the self-consistent solution is magnetic for all Z values, the magnetization will be dominant for all distances.

The hydrogen effective charge number, Z$_{eff}$ (z), which is related to the ionic part of the chemisorption energy, is shown as a function of the normal distance in fig. (9). At the graphene sheet, Z$_{eff}$ is nearly zero which gives important physical information about the type of bonding on the graphene sheet. This confirms that the ionic chemisorption energy is vanished.

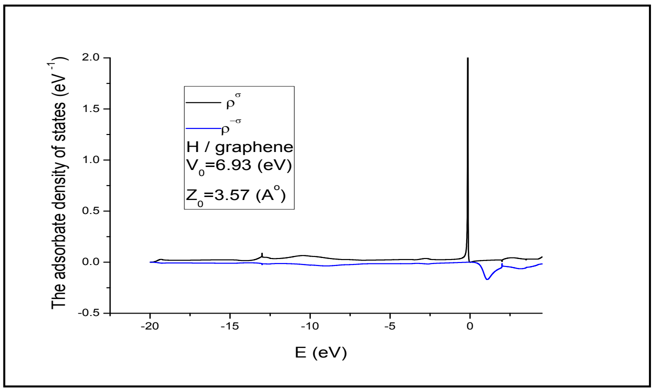


Fig. (5): The spin dependence adsorbate density of states $\rho^{\sigma}_{ad}(E)$ and $\rho^{-\sigma}_{ad}(E)$ for the H/graphene system at Z=Z$_0$.

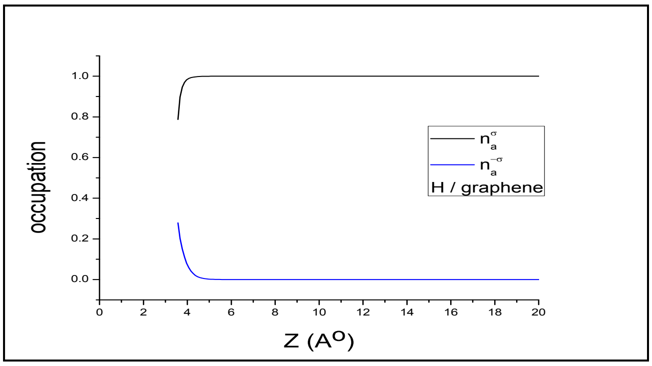


Fig. (6): The spin dependence occupation numbers $n_a^{\pm\sigma}$ as a function distance for the H/graphene system.

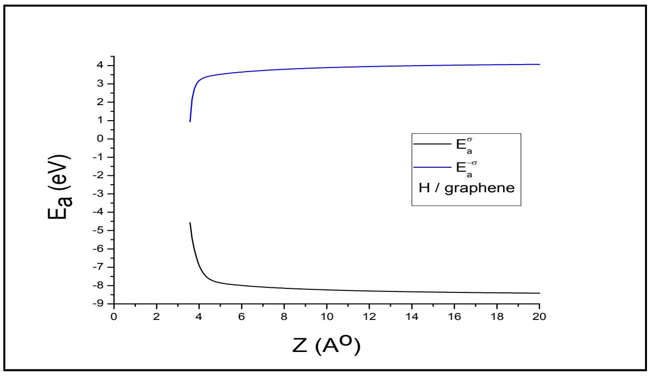


Fig. (7): The adatom energy levels $E_a^{\pm\sigma}$ as a function distance for the H/graphene.

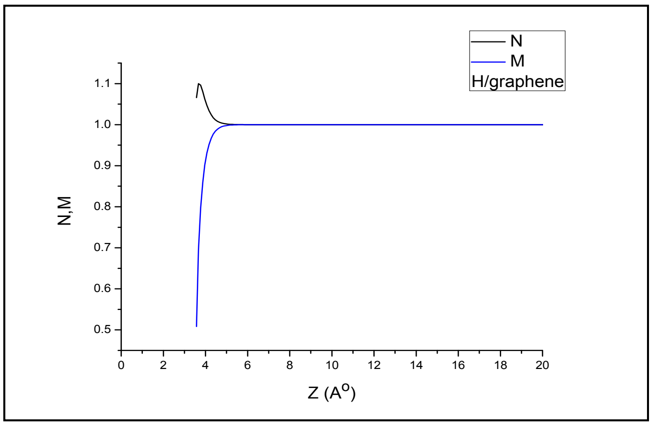


Fig. (8): The total charge number and the magnetization on the adatom for the H/graphene system.

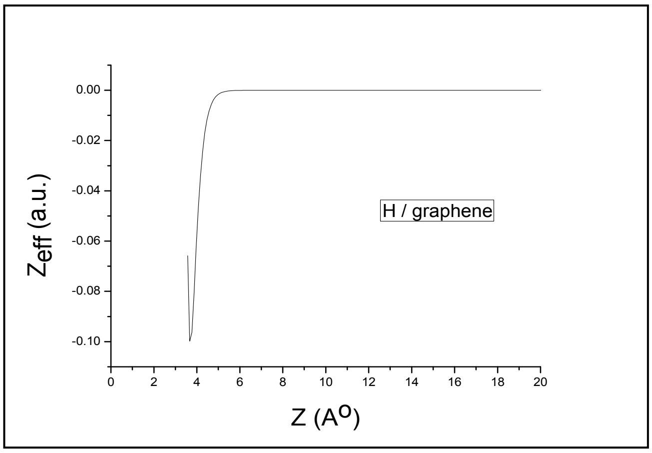
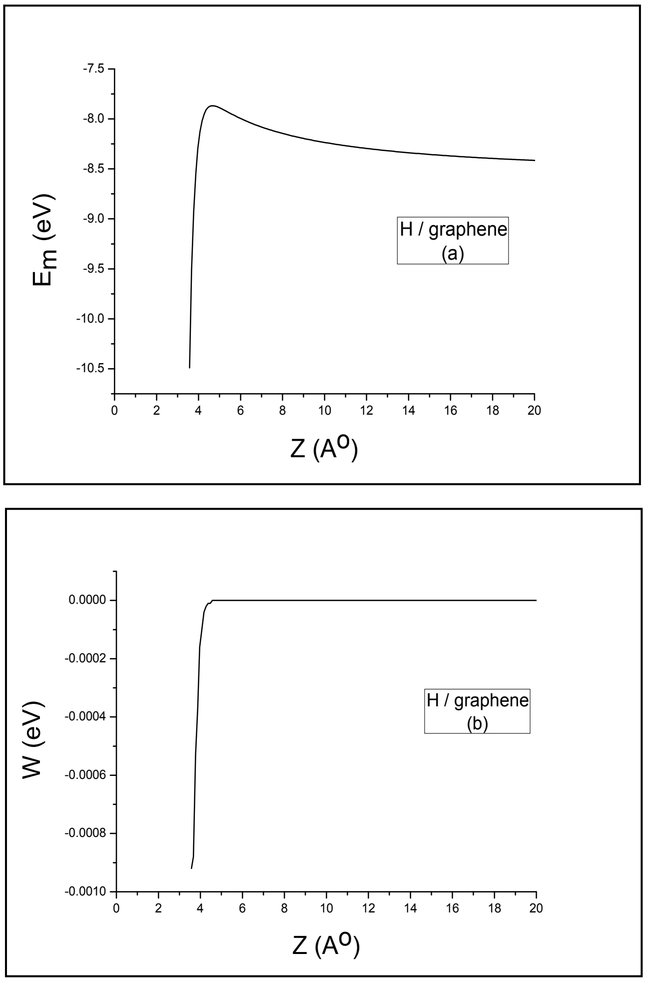


Fig. (9): The effective charge Z_{eff} on the adatom as a function of distance for the H/graphene system.

The chemisorption energy (and its contributions) for hydrogen on graphene is plotted in fig. (10) as a function of the normal distance. The metallic energy is the dominant one for all Z values, which gives the obvious description to the type of bonding formed with the graphene.



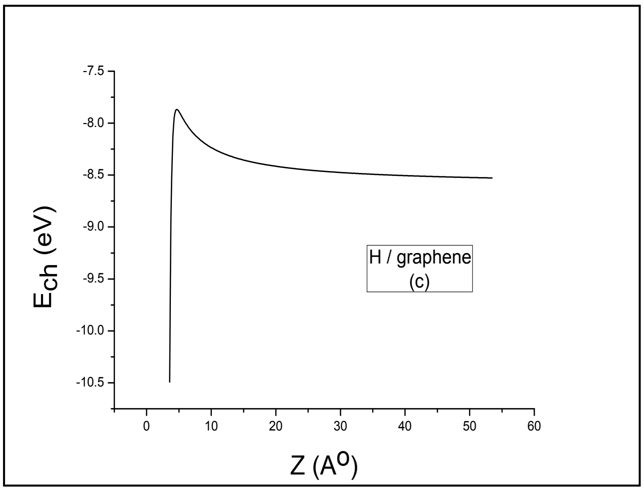


Fig. (10): The metallic, ionic and total chemisorption energy as a function of distance for the H/graphene system.

Finally, the density of states of the imperfect graphene can be easily calculated for the hydrogen/graphene system by using the following equation :

$$\rho_{im}(E)=\rho_{ad}^{\sigma}(E)+\rho_{ad}^{-\sigma}(E)+\rho_{G}(E) \qquad \text{......} (30)$$

The density of states of the imperfect graphene is calculated for H/graphene (see fig. (11)) at $Z=Z_0$. These figures insure the existence of the magnetization on the H/graphene.

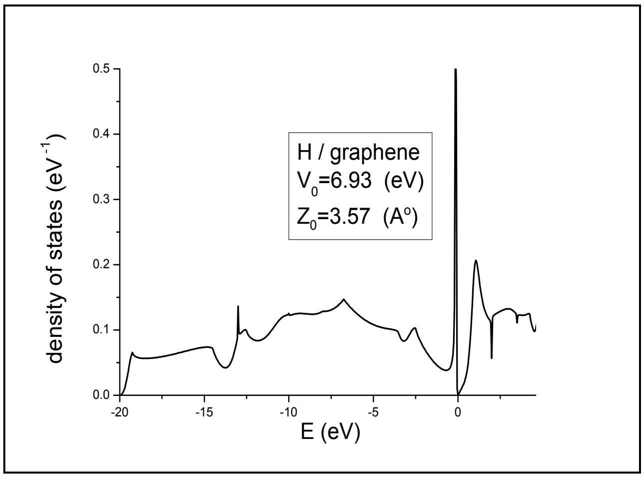


Fig. (11): The density of states of the imperfect graphene for the H/graphene system.

5.The Conclusions

The Magnetic and Nonmagnetic Solutions: The self-consistent solution for Hydrogen atom shows that the physical solution of the occupation numbers $n_a^{\pm\sigma}$ as a function of distance, which minimizes the system's energy, is always the one for which n_a^{σ} is larger than $n_a^{-\sigma}$. As the self-consistent solution is magnetic for all Z values, the magnetization will be dominant for all distances.

The Chemisorption Energy: Since the hydrogen effective charge number, Z_{eff} (z), which is related to the ionic part of the chemisorption energy, is nearly zero at surface which gives important physical information about the type of bonding on the graphene sheet. This confirms that the ionic chemisorption energy is vanished. The metallic energy is the dominant one for all Z values, which gives the obvious description to the type of bonding formed with the graphene.

The Imperfect Graphene Density of States: Finally, we must state that our simplified and extended calculations, which give obvious features about the chemisorption process of hydrogen on graphene, led to the estimation of the imperfect density of states that reflects the decorated graphene sheet electronic properties which can be considered as an entrance to study different scientific techniques.

Notably, we use the perfect density of states in our calculation. However, another formulism, will be presented in the next future work for the deformed graphene sheet that is useful for investigating the mechanical properties of the system under consideration.

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