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Tunning the Magnetic Moment of Hydrogen Atom Chemisorbed on Perfect Graphene by Magnetic Field

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Abstract

The Anderson-Newns model is used to study the chemisorption process for hydrogen atom on perfect graphene with tunning the adatom magnetic moment. The perfect graphene density of states is utilized to determine the (adatom/graphene) system electronic structure and the quantum coupling effects which are expressed by the broadening chemisorption function and the quantum shift. The self-consistent solutions for the hydrogen atom occupation numbers show that the physical solution is magnetic for all normal distances from the graphene sheet. Also, the metallic part of the chemisorption energy is the dominant one for all distance values, which gives the obvious description to the type of bonding formed with the graphene. The existence of the magnetization on H/graphene is insured by calculating the density of states of the imperfect graphene.

Keywords: *Graphene, Chemisorption, Anderson-Newns Model, Magnetic field.*

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 a part of the nano carbons but also for its own interesting electronical and mechanical properties[3].

The fast development of graphene research leaves no doubt that this material will revolutionize several markets such as electronics, medicine sensors, biodevices, catalysis [4], and energy storing [5,6,7]. For the utilization of these systems a deeper understanding of their stability and electronic properties is needed. The interest in hydrogen sensors has been increased in diverse applications related to hydrogen technologies including hydrogen purification, storage and fuel cell. One of most interesting graphene applications is the hydrogen storage, the common way of storage hydrogen in solids is the chemisorption of dissociated hydrogen in noble metals and alloys.

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 [8]. The second is to devise simple models that can capture only the essential physics.

In our work, we will 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 [9,10].

Our model calculation takes the following into consideration,

1. All the parameters that concerned to the type of atom which adsorbed on graphene sheet.
 - 2.The (adatom/graphene) system electronic structure and the quantum coupling effects which are expressed by the broadening chemisorption function and the quantum shift.
- Our work comprises three main lines of investigation. The first is the calculation of the local density of states on the graphene sheet. Since the broadening and the quantum shift are calculated as a function of system energy and the normal distance between the atom and the graphene sheet. The second is the calculation of the magnetization on the

adsorbed atom, while the third is to calculate the metallic part of the chemisorption energy in the presence of magnetic field.

2. The Theoretical Treatment

In the second quantization form, the model Hamiltonian of the combined system (adatom/ perfect graphene) is given by :[9-11],

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

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

It is well known that there is energy spacing 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 energy spacing is given by [8],

$$U = V_i - V_A \quad \dots\dots (2)$$

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 decreases as the atom moves towards the graphene sheet due to the electron-electron correlation interaction [12]. This effective value will be denoted as U_{eff} , 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 normal distance (Z) between the adatom and the surface by using the following relation [13],

$$U_{eff}(Z) = V_i - V_A - 2\Delta E(Z) \quad \dots\dots (3)$$

With, $\Delta E(Z)$ is the image shift which takes the image effect into consideration.

The image shift due to the 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 [14],

$$\Delta E(Z) = \frac{e^2}{4(Z + Z_0)} \quad \dots\dots (4)$$

Where, Z_0 represents the closest approach. Then by taking the image effect, correlation and magnetic field effect into consideration, the atomic energy level E_a^σ ($E_a^{-\sigma}$) with spin up (spin down) is written as [15,16],

$$E_a^{\pm\sigma}(Z) = E_a^o + \Delta E(Z) + U_{eff} n_a^{\mp\sigma} \mp \Delta E_H \quad (5)$$

E_a^o equals to $(\phi_0 - V_i)$, ϕ_0 is the surface work function, and ΔE_H is Zeeman splitting due the magnetic field effect on the adatom. The occupation number of the atomic energy level of spin σ (i.e. E_a^σ) is given by :

$$n_a^\sigma = \int_{u_0}^{\phi_0} f(E,T) \rho_{ad}^\sigma(E) dE \quad \dots\dots (6)$$

With U_o is the band bottom energy. 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,

$$f(E, T) = \frac{1}{1 + e^{(E/k_B T)}} \quad \dots (7)$$

k_B is Boltzman constant and T is the temperature.

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

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

where $\Delta(E)$ and $\Lambda(E)$ are the energy dependent broadening and quantum shift in the adatom energy level due to coupling interaction between the adsorbate and the graphene sheet;

$$\Delta(E) = \pi \sum_k |V_{ak}|^2 \delta(E - E_k) \quad \dots (9)$$

$$\Lambda(E) = \frac{1}{\pi} P \int d\hat{E} \frac{\Delta(\hat{E})}{E - \hat{E}} \quad \dots (10)$$

where [17],

$$V_{ak} = v_k V_o \quad \dots (11)$$

v_k is the energy phase of the interaction and V_o is the strength of the coupling interaction.

Then equation (9) can be rewritten as,

$$\Delta(E) = \pi |V_o|^2 \rho_G(E) \quad \dots (12)$$

$\rho_G(E)$ is the graphene sheet density of states. The density of states for the perfect graphene was formulated in ref.[18] as,

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

n refers to the best fitted regions. with ,

$$b_n = \frac{C_n}{(E_{f_n} - E_{p_n})^2} \quad \dots (14)$$

All the coefficients $a_n, C_n, E_{in}, E_{pn}, E_{fn}$ are presented in Table. (1).

The self-energy due to the coupling interaction between graphene sheet and an adatom can be written as[19],

$$\Sigma(E) = |V_o|^2 P \int \frac{\rho_G(E')}{E - E'} dE' \quad \dots (15)$$

By substituting eq.(13) in eq.(15) one can solve the integration analytically to get,

$$\Sigma(E) = i \Delta(E) + \Lambda(E) \quad \dots (16)$$

Now, we can write,

$$\Delta(E) = \pi |V_o|^2 \sum_{n=1}^{13} [a_n + b_n (E - E_{p_n})^2] \quad \dots (17)$$

and ,

$$\Lambda(E) = |V_o|^2 \sum_{n=1}^{13} \int_{E_{in}}^{E_{fn}} \frac{(a_n + b_n E_{pn}) - 2b_n E_{pn} E' + b_n E'^2}{E - E'} dE' \quad \dots (18)$$

Which is solved analytically to get ,

$$\Lambda(E) = |V_o|^2 \sum_{n=1}^{13} \left([b_n (2E_{pn} - E)E - (a_n + b_n E_{pn}^2)] \ln \left(\frac{E - E_{fn}}{E - E_{in}} \right) - \frac{2b_n (E - E_{pn})(E_{fn} - E_{in}) - \frac{b_n}{2} (E_{pn}^2 - E_{in}^2)}{2} \right) \quad \dots (19)$$

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 expression for the metallic part of the chemisorption energy is given by [15],

$$E_m(Z) = \sum_{\sigma} \int_{u_0}^{\phi} E f(E, T) \rho_{ad}^{\sigma}(E) dE - U_{eff} n_a^{\sigma} n_a^{-\sigma} \dots(20)$$

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

$$E_m(\infty) = \sum_{\sigma} \int_{u_0}^{\phi} E f(E, T) \delta(E - E_a^{\sigma}) dE \dots (21)$$

$$E_m(\infty) = E_a^{\sigma} f(E_a^{\sigma}, T) = (\phi - V_i) \Theta(V_i - \phi) \dots (22)$$

With Θ is unit step function.

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

$$E_{ch}(Z) = E_m(Z) + W(Z) \dots (23)$$

Notably, the final state is an interacting adatom and graphene sheet separated by the equilibrium distance Z_0 , so the bonding energy is written as [18],

$$E_{bond} = E_{ch}(Z_0) - (\phi - V_i) \Theta(V_i - \phi) \dots (24)$$

4. The Calculations and Results

In order to achieve all the calculations, equations (5) and (6) are solved self-consistently. By using the impurity Anderson model, all the functions that describe the chemisorption process for any atom on the graphene sheet can be included in the self-consistent solution. The work function of graphene sheet used in our calculations can be approximately equal to 5.0 eV[20] and firstly

ΔE_H is fixed at 0.05 eV. The electronic levels are filled using Fermi-Dirac statistics with a value of temperature $T = 300$ K. All the parameters concerned to the electronic properties of the system that used in our calculations are presented in table(2). R_i represents the hydrogen atom radius.

The H atom attaches to the carbon atom directly, normal to the graphene plane, in an on top site, i.e. the H atom is placed at $Z_0 (=3.57 \text{ \AA})$ directly above the graphene sheet. Z_0 is considered as the closest approach distance.

The adsorbate (i.e. local) density of states $\rho_{ad}^{\sigma}(E)$, which incorporates the broadening in the adatom level due the hybridization with the sea of electrons in graphene, is shown in fig.(1) at the distance of equilibrium. This figure shows that $\rho_{ad}^{\sigma}(E) \neq \rho_{ad}^{-\sigma}(E)$, i.e. they are not identical, which means that the self-consistent solution is a magnetic one (i.e. $n_a^{\sigma} \neq n_a^{-\sigma}$).

In order to investigate the magnetic behavior on the hydrogen/graphene system, the magnetization ($M = n_a^{\sigma} - n_a^{-\sigma}$) must be calculated (see fig. (2)). As the self-consistent solution is magnetic for all Z values, the magnetization will be dominant for all distances.

The hydrogen effective charge number, which is related to the ionic part of the chemisorption energy, is also calculated as a function of the normal distance. At the

graphene sheet, the effective charge number 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.

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 (see fig (3)).

Finally, the density of states of the imperfect graphene can be easily calculated for the hydrogen/graphene system by using the following equation [18] :

$$\rho_{im}(E) = \rho_{ad}^{\sigma}(E) + \rho_{ad}^{-\sigma}(E) + \rho_G(E) \quad \dots\dots (25)$$

The density of states of the imperfect graphene for H/graphene at $Z=Z_0$ is presented in fig (4).

In order to investigate the role of magnetic field effect, the energy ΔE_H is varied and the above-mentioned calculations are achieved for each value of ΔE_H at the closest approach.

The results that reflect the most important physical features are summarized in table (3).

Table (3) insures that increasing the magnetic field enhances the self – consistent magnetic solution, since all values of E_a^{σ} ($E_a^{-\sigma}$) are lying below (above) Fermi level. So the magnetization is increasing with ΔE_H

As the splitting energy due to magnetic field increases the metallic energy contribution increases, i.e. the bonding energy increases. The most important physical feature in our results can be concluded by getting use of the calculated density of states. Since, the energy corresponding to the maximum (minimum) value of the density of states for spin up (spin

down) $E_{\rho m, \sigma}$ ($E_{\rho m, -\sigma}$) is shifted up (down). These results can be utilized experimentally to guess the splitting energy and then the magnetic field strength.

5.The Conclusions

The self-consistent solution for Hydrogen/graphene system shows that the physical solution of the occupation numbers $n_a^{\pm\sigma}$ as a function of distance, that 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.

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.

Notably, 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 imperfect graphene sheet electronic properties which can be considered as an entrance to study different scientific techniques.

Finally, the perfect graphene density of states was included in our calculation. However, another formulism, will be presented in the next future work for the deformed graphene sheet which is useful for investigating the mechanical properties of the system under consideration.

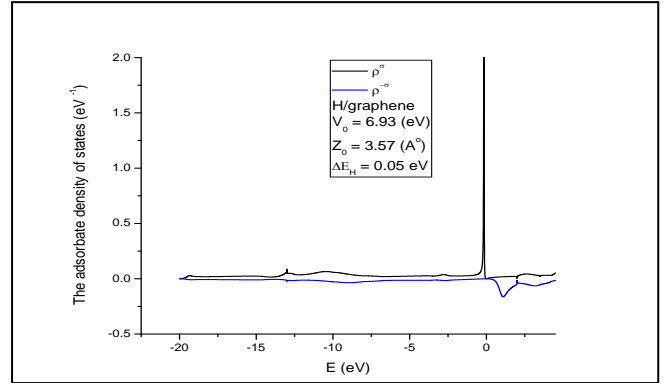


Fig. (1): The spin dependence adsorbate density of states $\rho_{ad}^{\sigma}(E)$ and $\rho_{ad}^{-\sigma}(E)$ for the H/graphene system at $Z=Z_0$.

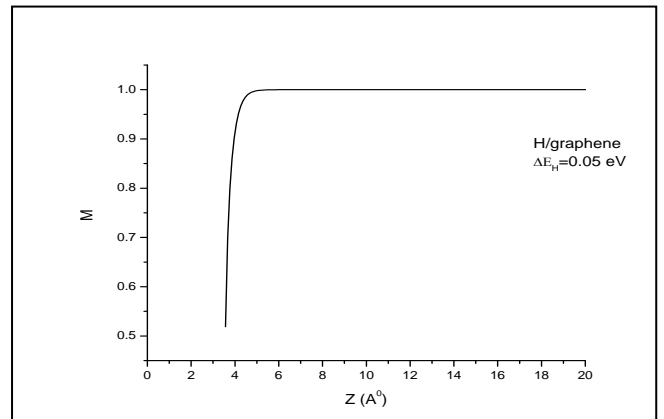


Fig. (2): The magnetization on the adatom for the H/graphene system.

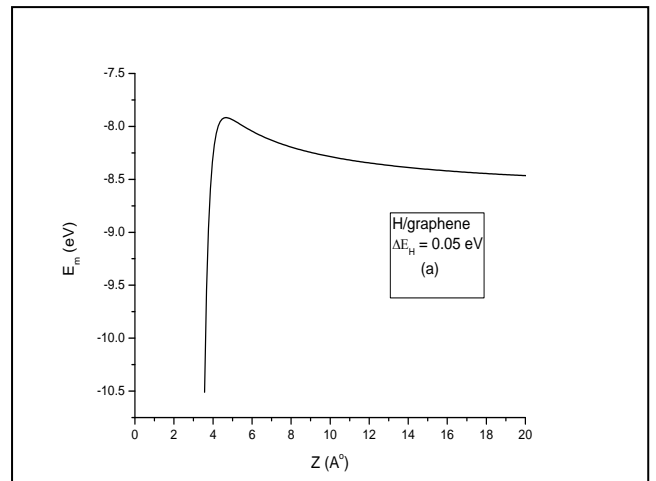


Fig. (3): The metallic chemisorption energy as a function of distance for the H/graphene system.

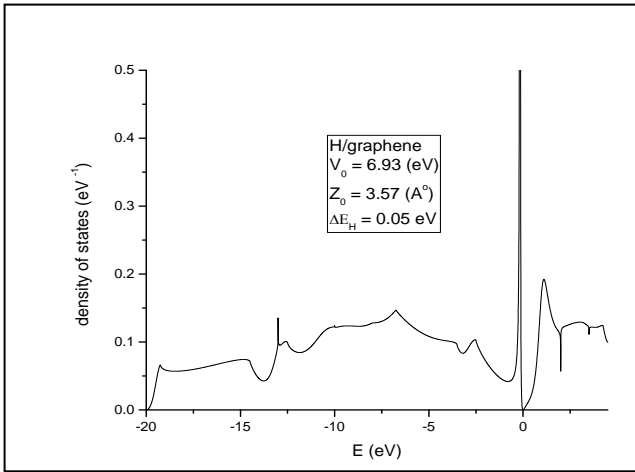


Fig. (4): The density of states of the imperfect graphene for the H/graphene system.

Table (1) : The best fitting parameters for graphene density of states.

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

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

Atom	V_i (eV)	V_A (eV)	R_i (Å°)	$\emptyset-V_i$ (eV)	V_o (eV)	Z_o (Å°)
H	13.595	0.7542	2.08	-8.595	6.93	3.57

Table (3): The adatom energy levels, the magnetic moment, the metallic energy, the bonding energy and $E_{\rho m, \sigma}$ and

$E_{\rho m, -\sigma}$ as a function of ΔE_H .

ΔE_H	E_a^σ (eV)	$E_a^{-\sigma}$ (eV)	M	E_m (eV)	E_{bond} (eV)	$E_{\rho m, \sigma}$ (eV)	$E_{\rho m, -\sigma}$ (eV)
0	-4.5699	0.9328	0.5083	-10.4912	-1.8962	-0.140	1.075
0.03	-4.6270	1.0093	0.5149	-10.5025	-1.9075	-0.150	1.085
0.05	-4.6637	1.0522	0.5188	-10.5104	-1.9154	-0.160	1.095
0.1	-4.7528	1.1603	0.5278	-10.5308	-1.9358	-0.175	1.110
0.15	-4.8391	1.2624	0.5359	-10.5523	-1.9573	-0.195	1.130
0.2	-4.9235	1.3607	0.5436	-10.5746	-1.9796	-0.210	1.145
0.25	-5.0065	1.4561	0.5508	-10.5976	-2.0026	-0.215	1.165
0.3	-5.0883	1.5493	0.5578	-10.6214	-2.0264	-0.245	1.180
0.5	-5.4055	1.9047	0.5829	-10.7224	-2.1274	-0.310	1.240

REFERENCES

- [1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, "Electric Field Effect in Atomically Thin Carbon Films", *Science*, 306, 666 (2004).
- [2] Jonathan Guillemette, "Electronic Transport in Hydrogenated Graphene", Ph. D. Thesis, McGill University, Canada, (2014).
- [3] C Backes et al., "Production and processing of graphene and related materials", *2D Mater.* 7 (2020) 022001
- [4] Y. Shao, J. Wang, H. Wu, J. Liu, I. A. Aksay and Y. Lin, "Graphene based electrochemical sensors and biosensors", A review, *Electroanalysis*, 22, No.10, 1027–1036(2010).
- [5] Y. G. Zhou, X. T. Zu, F. Gao, H. F. Lv. and H. Y. Xiao, "Adsorption-induced magnetic properties and metallic behavior of graphene", *Applied Physics Letters* 95, 123119 (2009).
- [6] D. C. Elias, R. R. Nair, T. M. G. Mohiuddin, S. V. Morozov, P. Blake, M. P. Halsall, A. C. Ferrari, D. W. Boukhvalov, M. I. Katsnelson, A. K. Geim and K. S. Novoselov, "Control of graphene's properties by reversible hydrogenation", Evidence for Graphane, *Science* 323, 610 (2009).
- [7] X. Liu, C. Z. Wang, Y. X. Yao, W. C. Lu, M. Hupalo, M. C. Tringides and K. M. Ho, "Bonding and charge transfer by metal

adatom adsorption on graphene", *Physical Review B* 83, 235411(2011).

[8] A. W. Weiss, "Theoretical Electron Affinities for Some of the Alkali and Alkaline-Earth Elements", *Phys. Rev.* 166, 70 (1968).

[9] P. W. Anderson, "Localized Magnetic States in Metals", *Phys. Rev.* 124, 41 (1961).

[10] D. M. Newns, "Self-Consistent Model of Hydrogen Chemisorption", *Phys. Rev.* 178, 1123(1969).

[11] T. B. Grimley, "The indirect interaction between atoms or molecules adsorbed on metals", *Proceedings of the Physical Society*, Vol. 90, No.3(1967).

[12] B. Kjällström, D. J. Scalapino, and J. R. Schrieffer, "Energy and Specific Heat Due to an Impurity Atom in a Dilute Alloy", *Phys. Rev.* Vol.148, No.665(1966).

[13] J. M. Al-Mukh and S. I. Easa, "The Chemisorption Energy of Impurity (Na-adatom) and its contribution to the specific heat as a function of a Ni-Surface Crystallography", *Basrah J. Science*, 19, 1(2000).

[14] A. J. Dekker, in "Solid State Physics", edited by The Macmillan Press LTD, P.228-230(1971).

[15] J. W. Gadzuk, J. K. Hartman, and T. N. Rhodin, "Approach to Alkali-Metal Chemisorption within the Anderson Model", *Phys. Rev. B*, Vol.4, No.241(1971).

[16] J. M. Al-Mukh and S. I. Easa, "Study in the Chemisorption Theory: Adatom's

Parameters Model Calculation", *Basrah J. Science*, 18,145(2000).

[17] Thikra S. Dh. Al-Naser, "Charge Exchange Process in the Scattering of Ions off Adsorbate-Covered Surface", MSc. Thesis, Department of physics, University of Basrah, Basrah, Iraq (2003).

[18] Abadhar Rahman Ahmed, "The Chemisorption of Hydrogen and Alkali Atoms on Graphene with and without Decoration", Ph.D. Thesis, Department of physics, college of Education for Pure science, University of Basrah, Basrah, Iraq (2017).

[19] Lafy Faraj Al-Badry, "Theoretical Study of the Thermoelectric Properties and Performance Efficiency for Some Nanostructured Systems", Ph.D. Thesis, Department of physics, college of Education for Pure science, University of Basrah, Basrah, Iraq (2013).

[20] Elizabeth J. Duplock, Matthias Scheffler, and Philip J. D. Lindan, "Hallmark of Perfect Graphene", *Physical Review Letters*, Vol. 92, N.22(2004).

ضبط العزم المغناطيسي لذرة الهيدروجين الملتصقة كيميائياً على الكرافين التام باستخدام مجال مغناطيسي

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الخلاصة:

تم استخدام نموذج اندرسون- نيونز لدراسة عملية الالتصاق الكيميائي لذرة الهيدروجين على الكرافين التام مع ضبط العزم المغناطيسي للذرة الملتصقة. وظفت كثافة الحالات للكرافين التام لتعيين التركيب الالكتروني للنظام ذرة ملتصقة/كرافين وتأثيرات الاقتران الكمي والتي وصفت بدالة التعريض والازاحة الكمية. أظهرت الحلول التوافقية الذاتية لأعداد اشغال ذرة الهيدروجين أن الحل الفيزيائي يكون مغناطيسياً لكل المسافات العمودية من شريحة الكرافين. كذلك، يكون الجزء المعدني من طاقة الالتصاق الكيميائي سائداً لكل قيم المسافة، والذي يعطي وصفاً واضحاً لنوع الاصرة المتكونة مع الكرافين. إن وجود التمعنط على (هيدروجين/كرافين) تم تأكيده بحساب كثافة الحالات للكرافين غير التام.

الكلمات المفتاحية: كرافين، التصاق كيميائي، نموذج اندرسون- نيونز، مجال مغناطيسي.