ELECTRON STRUCTURE OF GRAPHENE BASED MATERIAL

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In the paper, the theoretical models of shockproof material based on double layers graphenes have been constructed, and the electronic structure has been investigated by using semi empirical Extended Hukkel method, which is one of the variant of molecular orbital method. Based on the theoretical models the orbital energies, ionization potentials, full electron's energies etc. of graphene-based materials have been calculated. These materials can be used in military area, for example, for bulletproof vest making.

Keywords: Mathematical modeling, graphene, quantum mechanical methods, shockproof material, electronic structure.
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INTRODUCTION

Consuited by carbon atoms a graphene is presented as one atom thickness layer in hybrided sp^2 state and 2D-crystal lattice connected by σ and π bands [1]. In the graphene level carbon atoms are connected each of other by strong covalent band. Three carbon's valent electrons of four are taken part in formation of σ-band, and one of them is taken part in formation of π-band. The overlap of electron's cloud in π-band state is less than in σ–band. Therefor, the π-bands are broken easily and π-electrons move in lattice around all atoms' nucleuses. And it provides a conductivity of graphene.

Graphene has a very interesting band structure. Its conduction band crosses a valent band in 6 points. It provides graphene possession of many electron properties. Graphene is a semiconductor without pores. In the same time, the finite energy pore is formed in crossed points of conductivity and valent bands, that is, graphene has a property of little pore semiconductor. And this, like a quantum well, is connected with graphene possession of planar heterostructure and at low temperature it creates a possibility to use this energy pore as energy barrier.

Graphene has a high hardness [2, 3, 4]. These properties provide to use graphene in wide areas, and now it is very interesting to investigate of graphene based shockproof material. At this point of view, an investigation of graphene based materials by theoretical methods is very interesting and necessary.

In the presented paper, the theoretical models of two layers graphene based material have been constructed and its electron structure has been investigated by semiempiric extended Hückel method (EHM).

THEORETICAL METHODOLOGY

The mathematical modelling and quantum-mechanical investigation of graphene based shockproof materials are carried out usually by molecular orbitals (MO) method [5-11]. It is known, that semiempiric EHM is one of the simple semiempiric variant of the MO method. In MO the state of the electron is described with one electron wave function so-called molecular orbital. In according of MO method each electron in molecule moves in certaine effective field created by atoms and electrons of molecules not depended on other electrons. The electron's state in molecula is described by one electron wave function (molecule orbital) [8, 9, 12]. These functions are multicentered ones. That is, its expressions include a distance of electrons from nucleuse of various atoms.

There are various variants of seaching of the molecule's orbites. The MO LCAO method of the seaching of U_i molecule orbits as the atoms' orbits linear combination is one of them [11]:

$$U_i = \sum_{q=1}^{m} c_{qi}\chi_q \qquad (1)$$

Here: c_{qi} are unknown factors, χ_q are atoms' orbits as basis functions. In (1) equation Gauss functions were used as χ_q atoms' orbits [13]. c_{qi}- factors are determined from solution of below equations system:

$$\sum_q (H_{pq} - \varepsilon_i S_{pq})c_{qi} = 0 \qquad (2)$$

Here:

$$H_{pq} = \int \chi_p^* \hat{H}_{ef}\, \chi_q dV \qquad (3)$$

$$S_{pq} = \int \chi_p^* \chi_q dV \qquad (4)$$

S_{pq} are overlap integrals between χ_p and χ_q atom orbits. $\hat{H}_{ef}$ is effective Hamiltonian for one electron moved irrespective of other electrons in effective field created by molecule:

$$\hat{H}_{ef} = -\frac{1}{2}\nabla^2 + U(r). \qquad (5)$$

The full formule of $U(r)$ is unknown, therefore, it is impossible to cakculate H_{pq}. These values are evaluated by use some experimental parameters. In EHM H_{pq} matrix diagonal elements are taken equal to ionization potential of atom valent state with opposite sign [13].

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$$(1s \mid H \mid 1s) = -0.499786 \quad \text{amu}$$
$$(2s \mid C \mid 2s) = -0.772096 \quad \text{amu} \qquad (7)$$
$$(2p \mid C \mid 2p) = -0.419161 \quad \text{amu}$$

The nondiagonal elements of H_{pq} are calculated by Wolfsberg – Helmholz method [7,11]:

$$H_{pq} = 0.5 \cdot K \cdot S_{pq}(H_{pp} + H_{qq}) \qquad (8)$$

k is detemined by comparision of experimental facts or by condition of energy minimum. In given work it was taken k = 1.75. The equation (2) is linear homogeneous equations' system. Bu tənliklər məlum qaydalara əsasən həll olunaraq The values of ε_i and C_{qi} are determined by solution of equations' system (2). By using of ε_i values for graphen based materials we can calculate the full electron energy, ionization potentials, and investigate mechanical, electrical, magnit properties.

RESULTS AND DISSCUSIONS

In given paper we have calculated orbital energy, ionization potentials, full electron energies of hraphene $C_{62}H_{20}$ and two layers graphene $C_{124}H_{40}$ [14] by semiempiric EHM. The dependence of orbital energies ε on atom mass for two layers graphene $C_{124}H_{40}$, when the distance between layers is taken as D=0.142 nm, is shown in figure 1.

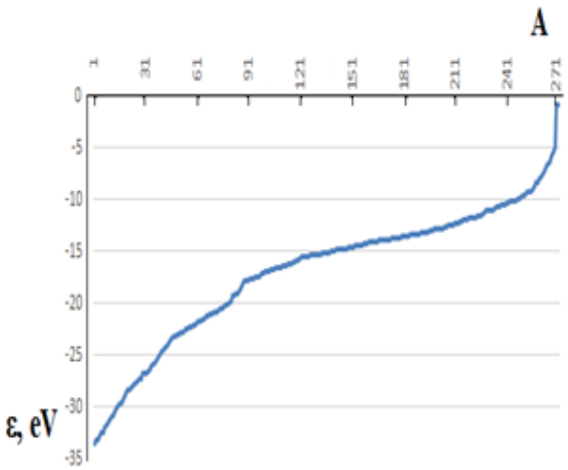


Fig. 1. The dependence of orbital energies ε on atom mass for two layers graphene $C_{124}H_{40}$.

As we can see from figure 1, the dependence till A=257 is expressed by formule

$$\varepsilon = -b_1 \exp(-b_2 A) \qquad (9)$$

here: b_1 and b_2 are some factors.

Bu, when beginning from A=257 (it is Fermiy element and its electron structure of $5f^{12}6d^{0}7s^{2}$) the curve is sharply down, that is, the law (9) is broken.

In presented paper, there is a graphene fragment consisted of 62 carbon atoms in each layer. The edges of fragment are locked by 20 hydrogen atoms.

For each object, electrons are located two by two on energies levels beginning of lowest level. It was determined trapped by electrons the highest molecular orbital energy ε_{HOMO} and the lowest empty molecular orbital energy ε_{LUMO}. There is an ionization potential formule $I_p = -\varepsilon_{HOMO}$, a band gap formule $E_g = \varepsilon_{LUMO} - \varepsilon_{HOMO}$ and a strength parameter formule $\eta = \frac{1}{2} E_g$ [5-11].

The wavelength of radiated photon of this material is calculated by formula $\lambda = \frac{c \cdot h}{1.6 \cdot E_g} \cdot 10^{28}\ nm$. Here: h is the Planck constant, c is the speed of light in vacuum. When λ is calculated then the values of E_g in eV are used. It is considered that when η < 1 eV the material is soft and when η > 1 eV one is solid.

The stability of material is calculated by formula $\Delta E = E - \sum_A E_A$ [11-14]. Here: E is total energy of system, E_A is total energy of A atom in system and ΔE is a parameter characterizing the stability of system. It is considered that when ΔE > 0 the material is unstable and when $\Delta E < 0$ one is stable. The results are presented in table 2.

The theoretical models of graphene fragment of $C_{62}H_{20}$ are shown in figure 2: a-by lines, b-by lines and spheres, c-by spheres. The theoretical models of two layers graphene fragment of $C_{124}H_{40}$ are shown in figure 3: a-by lines, b-by lines and spheres, c-by spheres. From comparision of figures 2 and 3 we can conclude that two layers graphene is more hard than one layer one.

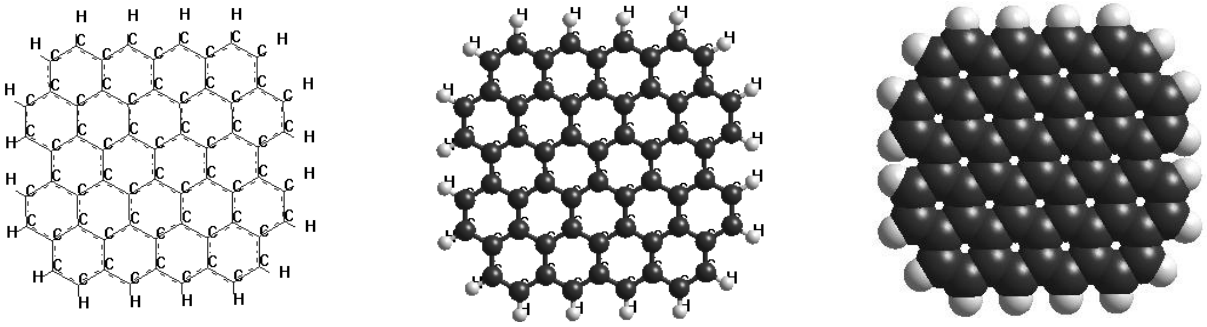
From analysing of table 2 data we can conclude that when the distance between two layers' graphene of D=1.42 nm then a band gap of E_g=4.1 eV and a strength parameter of η=4.05 eV are maximal, but a wavelength of radiated photon of λ=303 nm is minimal. The strength of two layers' graphene is much than one layer one in 5 times. Therefore, the distance between two layers' graphene we must take D=1.4 nm that we get very strength material (for example, for making bullet-proof vest).

In the paper, the theoretical models of shockproof material based on double layers graphenes have been constructed, and the electronic structure has been investigated by using semiempirical Extended Hukkel method, which is one of the variant of molecular orbital method. Based on the theoretical models the orbital energies, ionization potentials, full electron's energies etc. of graphene-based materials have been calculated. These materials can be used in military area, for example, for bulletproof vest making.

Table 1

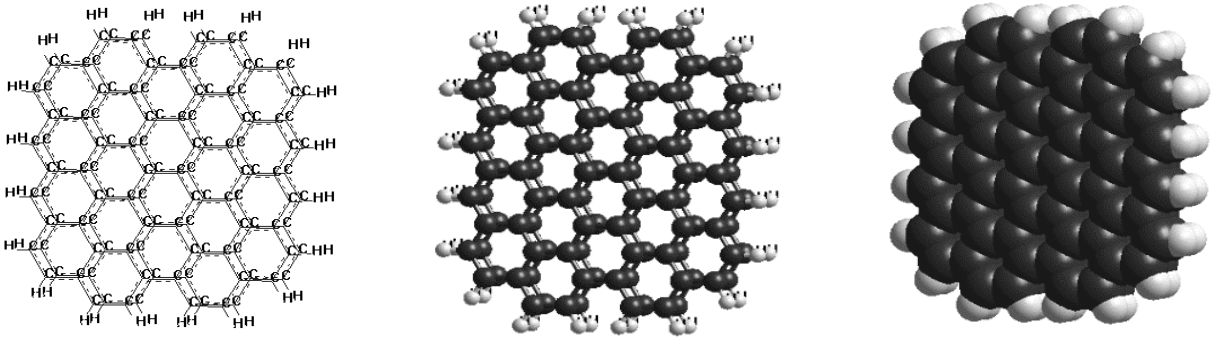
The results for graphene $C_{62}H_{20}$ and two layers graphene $C_{124}H_{40}$

N	Object	Distance between graphene layers D, (nm)	ε_{HOMO}	ε_{LUMO}	Total energy E (amu)	Stability parameter ΔE (amu)	İonization potential I_p (eV)	Band gap E_g (eV)	Strength parameter η (eV)	Wavelength of radiated photon λ(nm)
1	$C_{62}H_{20}$	--	-11,026847	-10,275221	-174,9572207	-126,7	11,03	0,751	0,375	1654
2	$C_{124}H_{40}$	1	-4,36267	-3,256325	-318,5881452	0,3	4,36	1,106	0,553	1124
3	$C_{124}H_{40}$	1.3	-5,164615	-1,469666	-332,7678576	-13,8	5,16	3,694	1,847	336
4	$C_{124}H_{40}$	1.35	-5,083723	-1,180737	-334,0786411	-15,2	5,08	3,902	1,951	319
5	$C_{124}H_{40}$	1.39	-5,012462	-0,969388	-334,9979235	-16,1	5,01	4,043	2,021	307
6	$C_{124}H_{40}$	1.4	-4,96414	-0,913609	-335,1862996	-16,3	4,96	4,050	2,025	307
7	$C_{124}H_{40}$	1.41	-4,957228	-0,869326	-335,4035616	-16,5	4,96	4,087	2,043	304
8	$C_{124}H_{40}$	**1.42**	**-4,927879**	**-0,82677**	**-335,5958942**	**-16,7**	**4,93**	**4,101**	**2,050**	**303**
9	$C_{124}H_{40}$	1.425	-4,957231	-0,869326	-335,4035653	-16,5	4,96	4,087	2,043	304
10	$C_{124}H_{40}$	1.43	-4,897443	-0,990988	-335,7814412	-16,9	4,90	3,906	1,953	318
11	$C_{124}H_{40}$	1.45	-4,814208	-1,476756	-336,115703	-17,2	4,81	3,337	1,668	372
12	$C_{124}H_{40}$	1.5	-4,640948	-2,741458	-336,8882522	-17,9	4,64	1,899	0,949	654
13	$C_{124}H_{40}$	2.0	-9,49594	-9,114124	-344,3934082	-25,5	9,49	0,381	0,190	3256
14	$C_{124}H_{40}$	2.5	-10,530632	-10,252486	-348,5339434	-29,6	10,53	0,278	0,139	4469
15	$C_{124}H_{40}$	2.7	-10,869238	-10,20065	-349,2005579	-30,3	10,87	0,668	0,334	1859
16	$C_{124}H_{40}$	2.8	-10,839393	-10,342786	-349,4107495	-30,5	10,84	0,496	0,248	2503
17	$C_{124}H_{40}$	2.9	-10,751153	-10,468167	-349,5493439	-30,6	349,54	0,282	0,141	4393
18	$C_{124}H_{40}$	3.0	-10,687812	-10,562207	-349,6521241	-30,7	10,69	0,125	0,062	9897



a b c

Fig. 2. The theoretical models of graphene $C_{62}H_{20}$: a-lines, b-lines and spheres, c-spheres.



a b c

Fig. 3. The theoretical models of two layers graphene $C_{124}H_{40}$: a-lines, b-lines and spheres, c-spheres.

CONCLUSION

In the paper, the theoretical models of the electron structure of two layers graphenes $C_{124}H_{40}$ have been investigated by using semiempirical Extended Hukkel method. The calculated results have shown that the strength of two layers graphene material is depended on distance between layers. When this distance is equal D = 0.142 nm then graphene based material is electrophile, semiconductive, stable and the strength of two layers' graphene is much than one layer one in 5 times. These materials can be applied in various areas, for example, for bulletproof vest making.

[1] *Grafen.* https://ru.wikipedia.org/wiki

[2] *J.S. Bunch et. al.* Electromechanical Resonators from Graphene Sheets Science 315, 490,(2007)

[3] *D.A. Abanin, S.V. Morozov, L.A. Ponomarenko, R.V. Gorbachev, A.S. Mayorov, M.I. Katsnelson, K. Watanabe, T. Taniguchi, K.S. Novoselov, S.L. Levitov, A.K. Geim.* Giant Nonlocality Near the Dirac Point in Graphene. – Science. – 15 April 2011: Vol. 332 №. 6027 pp. 328–330

[4] *Ali R.Ranjbartoreh, Bei Wang, Xiaoping Shen and Guoxiu Wang.* Advanced mechanical properties of graphene paper. – Journal of Applied Physics. – 109, pp. 014306-014312 (2011).

[5] *A.G. Gasanov, M.A. Ramazanov, F.G. Pashaev, M.R. Vahabova.* Mathematical modeling of electron structure of PP+$(PbS)_8$+$(CdS)_9$ nanocomposite by semiempiric PM3 method. FİZİKA. Vol. XXIII, №3, Section: Az, October 2017, pp. 9-13

[6] *A.G. Gasanov, A.A. Bayramov, E.G. Hashimov.* Mathematical modeling of the electron structure of SiO_2 nanoparticle. FİZİKA. Vol. XXIII, № 1, Section: En, April, 2017, p.34-39.

[7] *A.G. Gasanov, M.A. Ramazanov, F.G. Pashaev.* Mathematical modelling and investigations of argentum sulphide nanoparticles. FİZİKA Vol. XXIII, № 2, Section: Az July, 2017, s.3-6.

[8] *A.M. Maharramov, M.A. Ramazanov, A.G. Gasanov, F.G. Pashaev.* The Study of Silver Nanoparticles in Basis of Slater Functions // Physical Science International Journal. 10(3): 1-6, 2016.

[9] *M.A. Ramazanov , F.G. Pashaev, A.G. Gasanov, A.M. Maharramov, A.T. Mahmood.* The quantum mechanical study of cadmium sulfur nanoparticles in basis of STO's // Chalcogenide Letters, V11(7), 359-364. (2014).

[10] *F.G. Pashaev, A.G. Gasanov and A.T. Mahmood.* The Study of Gold Nanoparticles in basis of Slater Functions // J. Nano. Adv. Mat., V 2(1), 35-41. (2014).

[11] *A.G. Gasanov.* Mathematical modelling and computer investigation of graphene. BDU reports, phys.-mathm. Ser., № 2, 2011, pp.171-179.

[12] *A.G. Gasanov, F.G. Pashaev.* The Computer Program for the Study of Nanoparticles in Basis of Slater Atomic Orbitals. Romanian Journal of Information Science And Technology Volume 19, Number 4, 2016, 331–337.

[13] *V.I. Minkin, B.Y. Simkin, R.M. Minyaev.* Theory of structure of molecule. Rostov at Don, Feniks, (2010).

[14] *K.S. Novoselov, E. McCann, S.V. Morozov, V.I. Falko, M.I. Katsnelson, U. Zeitler, D. Jiang, F. Schedin, A.K. Geim.* Unconventional quantum Hall effect and Berry's phase of 2in bilayer grapheme. Nature Physics. 2006. Vol. 2. pp. 177—180.

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