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Some electronical properties for Coronene-Y interactions by using density functional theory(DFT)

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Abstract

Density functional theory with hybrid functional (B3LYP) and the basis set 3-21G have been used to investigate the molecular structure for Coronene and Coronene-Y molecules through the geometrical optimization in which (Y=Al, B, C, Ga, In, O). New peaks demonstrate when Y atoms interact with Coronene because new bonds generate between Coronene and Y atoms. Interaction between Coronene and Y atoms lessen the ionization potential but enlarge the electron affinity. Coronene behaves as a donor in Coronene-Y, except Coronene-O. Energy gap becomes similar to semiconductors in Coronene-B and Coronene-C. Coronene behaves as a hard base when interacting with Y atoms. Coronene-In is the most polarizability molecule among all. Coronene-C and Coronene-O are like anti-ferromagnetic materials.

Keywords: DFT, IR, HOMO, LUMO, Energy gap.

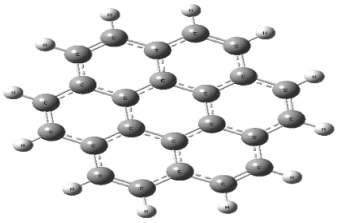
1. Introduction

The density functional methods supply a powerful instrument in quantum mechanics and computational nanoscience of atoms, molecules and solids [1]. It proposes the density function instead of the wave function in order to describe the quantum systems [2]. Born interpretation is one of methods that represent the theoretical basis of density functional theory [3]. It offers an elegant formulation of N electron system and computational efficiency [4]. Electron density plays a vital role in molecular structure, electrostatic potential and contours [5]. Density functional theory is also an approximation for the description of the ground state properties of the metals, semiconductors and insulators [6]. The ground state is unequivocally defined by the electron density [7]. Density functional theory depends tremendously on Schrodinger equation, Hohenberg-Kohn theorm, Kohn-Sham theorm, local density approximation, local spin density approximation and general gradient approximation [8]. In density functional theory the molecular orbitals result in linear combination of atomic orbitals [9]. This leads to new types of orbitals such as sigma and pi [10]. Density functional theory deals with Gaussian orbitals in which Gaussian function changes exponentially with the square value of the position [11]. One of the most popular

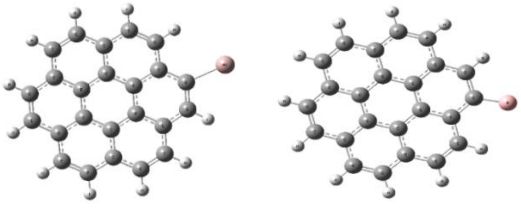
basis sets in density functional theory is the hybrid functional B3LYP [12].

1.2. Molecular structure

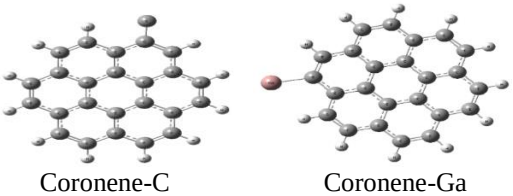
The forces bonding between atoms can be classified into two types: attraction forces and repulsion forces. Attraction forces result between electrons and nuclei, while the repulsion forces result between either couples of electrons or couples of nuclei. When the forces reach an accurate equilibrium, the atoms bond in order to produce stable molecule which has certain molecular structure [13]. Geometrical optimization has been applied so as to find the molecular structure for Coronene and Coronene-Y, where (Y = Al, B, C, Ga, In and O). Molecular structure has been investigated by using density functional theory at ground state level with the basis set having three Gaussian orbitals for inner shell, two Gaussian orbitals for inner valence and one Gaussian orbital for outer valence. Beke three parameters Lee-Yang-Parr(B3LYP) functional has been chosen to investigate the molecular structure of Coronene-Y.



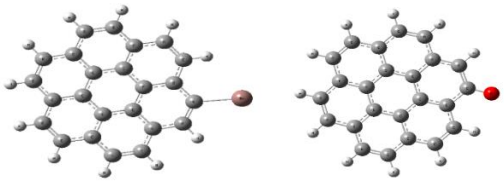
Figure(1) The molecular structure of Coronene.



Coronene-Al Coronene-B



Coronene-C Coronene-Ga

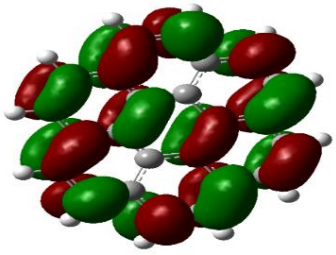


Coronene-In Coronene-O

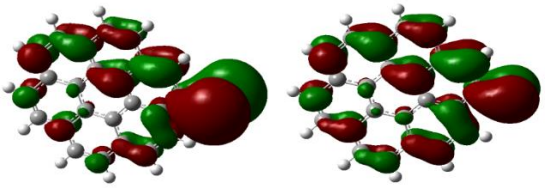
Figure(2) The molecular structure of Coronene-Y

1.3. Current Surface

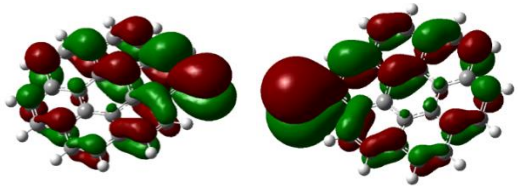
Surface can be expressed by high occupied molecular orbitals (HOMO) and low unoccupied molecular orbitals (LUMO). The abbreviations HOMO and LUMO occasionally refer to the frontier orbitals in frontier molecular orbital theory. Sometimes throughout the geometrical optimization singly or semi occupied molecular orbitals (SOMO) generate in current surface graphs [14]. Current surfaces have been performed for Coronene and Coronene-Y by using density functional theory in Gaussian package.



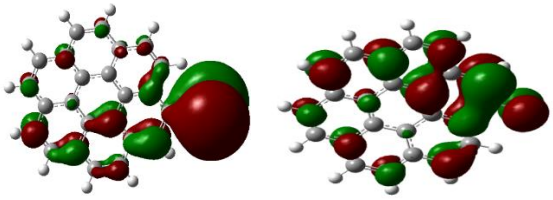
Figure(3) HOMO, LUMO surface of Coronene



Coronene-Al Coronene-B



Coronene-C Coronene-Ga

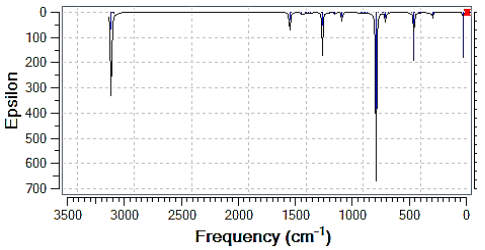


Coronene-In Coronene-O

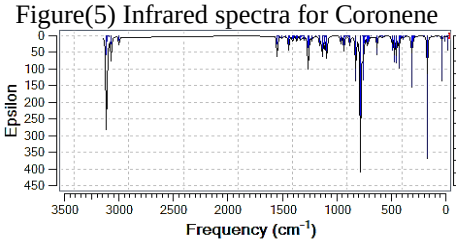
Figure(4) HOMO, LUMO surface of Coronene-Y

1.4. Infrared spectra

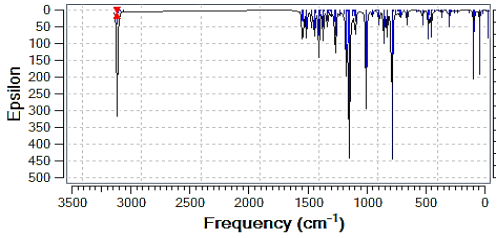
Symmetric and asymmetric vibration can be classified as stretching vibrations. When similar atoms oscillate in the same phase, symmetric stretching takes place, but when the bonds oscillate in different phases asymmetric stretching happen [15]. Harmonic vibrational frequencies are produced throughout infrared spectra. Each value or each range of bond length denotes a vibration mode. Elastic and inelastic vibration can be classified as vibrational modes [16]. Infrared spectra have been achieved after geometrical optimization for Coronene and Coronene-Y.



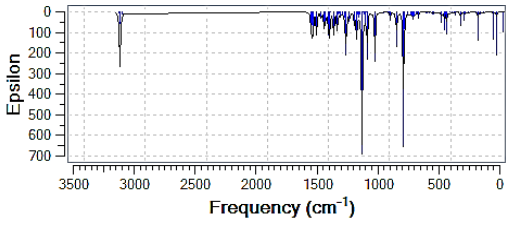
Figure(5) Infrared spectra for Coronene



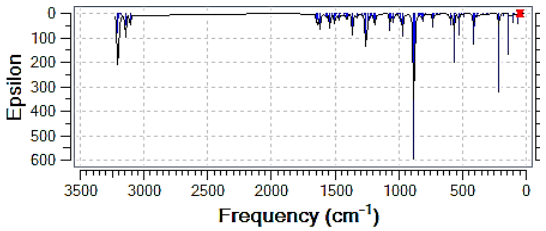
Coronene-Al



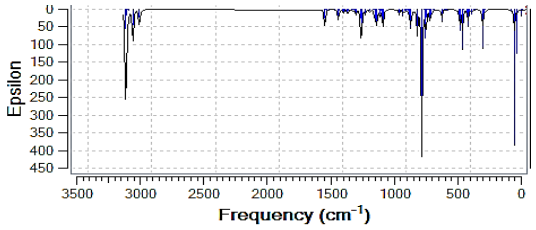
Coronene-B



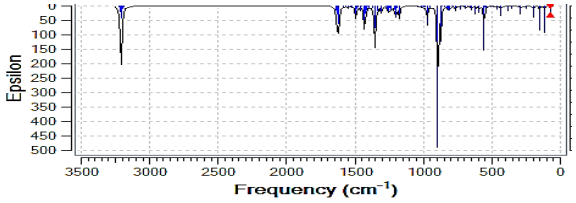
Coronene-C



Coronene-Ga



Coronene-In



Coronene-O

Figure(6) Infrared spectra for Coronene-Y

2. Calculations

2.1. Individual atoms

Table(1) Some electronic properties for individual atoms

atom	HOMO (eV)	LUMO (eV)	Total energy(eV)	Hardness	Softness
Al	-3.5484561	2.0766672	-6558.802772	2.81256165	0.063207106
B	-4.900521	-2.436111 3	-667.1519136	1.23220485	0.329309437
C	-5.153574	-3.483424 2	-1022.359854	0.8350749	0.716999981
G	-3.3242457	-1.930821 6	-52117.89136	0.69671205	1.030061987
In	-3.2262897	-2.012995 8	-155575.2965	0.60664695	1.358619887
O	-8.6565894	-6.499380 6	-2028.639308	1.0786044	0.429779434

2.2. Ionization potential and electron affinity

Ionization potential measures the binding force between the electron and the atom. It is equivalent to the required energy that can remove one electron from neutral atom in the gas state. In Hydrogen there is one ionization energy in the outer shell. The atoms which have more than one electron

in the outer shell will have one ionization energy for electron [17].

Electron affinity may be defined as the energy which releases when an atom acquires, an electron. It is equivalent to the required energy that can remove an electron from negative ion. Sometimes electron affinity is named zero ionization energy. The atoms that have seven electrons in the outer shell have high electron affinity, but the atoms which have closed shells has small electron affinity [18]. According to Koopman's theorm [19]:

$$I.P = -E_{HOMO} \quad \dots (1)$$

$$E.A = -E_{LUMO} \quad \dots (2)$$

I.P & E.A refer to Ionization potential and electron affinity respectivily

Table(2) Ionization potential and electron affinity for Coronene and Coronene-Y.

System	Ionization potential(eV)	Electron affinity(eV)
Coronene	5.614239	1.481857
Coronene-Al	5.572064	1.972453
Coronene-B	5.347037	2.349311
Coronene-C	4.853992	2.911198
Coronene-Ga	5.441184	1.924019
Coronene-In	5.39411	1.941706
Coronene-O	5.403634	1.783888

2.3. Electronic states

The electronic configuration of the atoms or molecules may be a good description to the energy level. When the atoms distribute in orbitals, they must obey Pauli's exclusive principle. According to quantum physics the electrons should have exact value of energies in certain energy levels [20]. Energy gap is a very important property in solids because it allows the prediction of the material whether it is conductor or insulator or semiconductor. It stands for the energy difference between the lower virtual energy level and the higher full energy level [21].

$$E_g = E_{LUMO} - E_{HOMO} \quad \dots (3)$$

Table(3) The electronic states for Coronene and Coronene-Y

System	HOMO(eV)	LUMO(eV)	Eg(eV)
Coronene	-5.6142393	-1.4818566	4.132383
Coronene-Al	-5.5720638	-1.9724529	3.599611
Coronene-B	-5.3470371	-2.3493114	2.997726
Coronene-C	-4.8539919	-2.9111979	1.942794
Coronene-Ga	-5.4411837	-1.9240191	3.517165
Coronene-In	-5.3941104	-1.9417056	3.452405
Coronene-O	-5.4036339	-1.7838876	3.619746

2.4. Total energy

It is the energy of all atoms that form the molecule. In density functional theory the total energy can be given in terms of the boundaries E_T, E_v, E_J and E_{XC} as in the following equation [22]

$$E = E_T + E_v + E_J + E_{XC} \quad \dots (4)$$

Where E_T represents the electronic kinetic energy, E_v represents the electronuclear interaction energy, E_J means electron-electron repulsion energy and E_{XC} means exchange correlation term.

Table(4) The total energy for Coronene and Coronene-Y

System	Total energy (eV)
Coronene	24946.30822
Coronene-Al	-31489.79305
Coronene-B	-25599.05371
Coronene-C	-25956.20618
Coronene-Ga	-77049.89502
Coronene-In	-180506.0842
Coronene-O	-26964.59695

2.5. Hardness Softness Acid Base (HSAB Principle)

This principle includes a description of the behavior of molecules or atoms as the acids and bases in chemistry. In other words, throughout this principle one can distinguish the donors and acceptors. It is necessary to indicate that the soft base and

hard base represent donors, but soft acid and hard acid stand for acceptors.

Hardness and softness can be expressed by the following equations [23]:

$$\eta = \frac{I.P - E.A}{2} \quad \ldots (5)$$

$$\sigma = \frac{1}{2\eta} \quad \ldots (6)$$

η refers to hardness; and σ refers to softness.

Table(5) Hardness and softness for Coronene and Coronene-Y

System	Hardness	Softness
Coronene	4.873311	0.102599649
Coronene-Al	4.58583735	0.109031342
Coronene-B	4.1723814	0.119835641
Coronene-C	3.39839295	0.147128365
Coronene-Ga	4.47917415	0.11162772
Coronene-In	4.4232576	0.113038861
Coronene-O	4.5116901	0.110823215

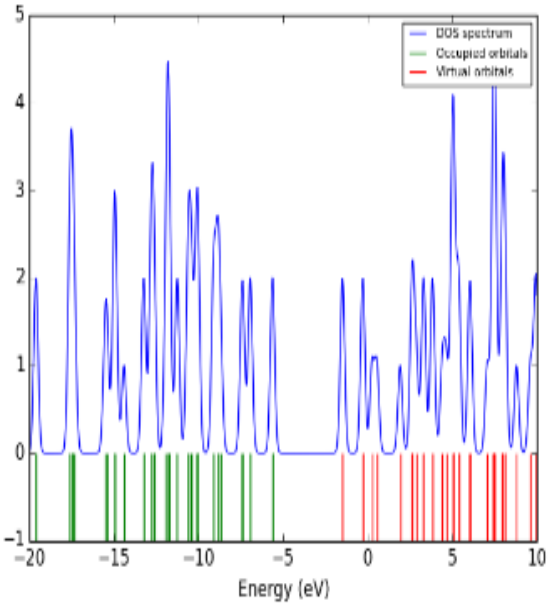
2.6. Polarizability

It shows the capacity of molecules to polarize. It determines the dynamical response of binding system to an external field. It also signifies the linear response of the electron density of an infinite seminal electric field. Polarizability represents a second order variation in the energy [24]. The average polarizability $< \alpha >$ can be calculated throughout the eigen values of the polarizability tensor α_{xx}, α_{yy} and α_{zz} as the following relation [25]:

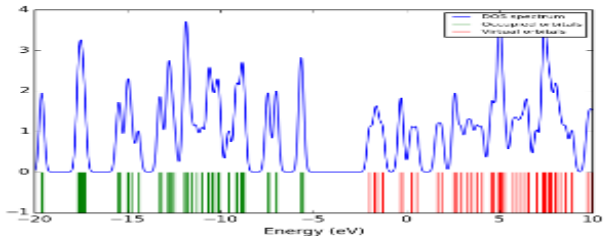
$$< \alpha > = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (7)$$

Table(6) Polarizabilities for Coronene and Coronene-Y

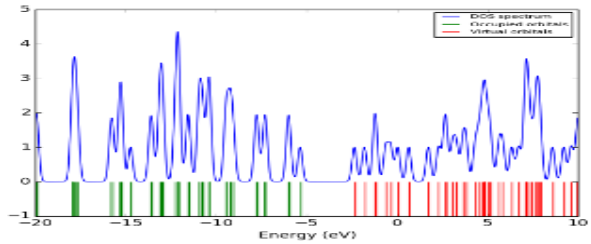
System	α_{xx}	α_{yy}	α_{zz}	$< \alpha >$
Coronene	349.857	349.82	51.266	250.3143
Coronene-Al	457.588	375.678	88.538	307.268
Coronene-B	403.203	359.289	66.027	276.173
Coronene-C	402.27	354.64	56.919	271.2763
Coronene-Ga	450.835	372.974	85.339	303.0493
Coronene-In	480.72	380.742	93.256	318.2393
Coronene-O	390.097	348.419	52.745	263.7536



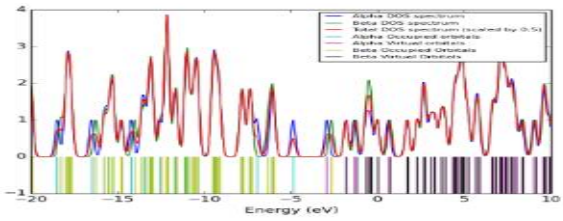
Figure(7) Density of states for Coronene



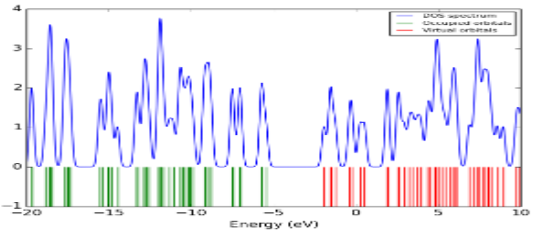
Coronene-Al



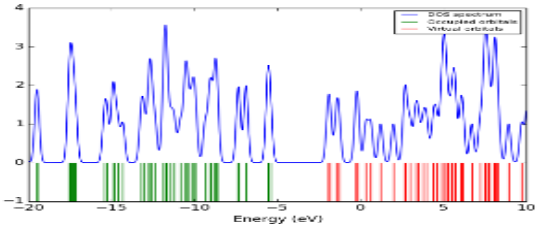
Coronene-B



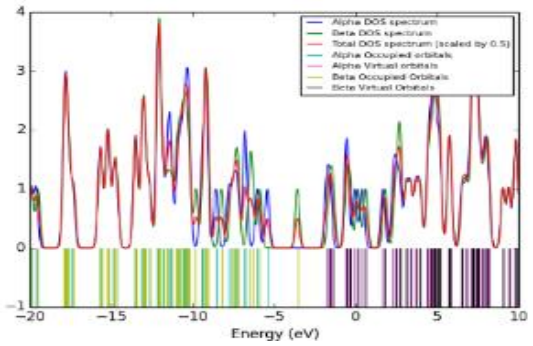
Coronene-C



Coronene-Ga



Coronene-In



Coronene-O

Figure(8) Density of states for Coronene-Y

3. Discussion

Figure(1) and figure(2) show the molecular structure of Coronene and Coronene-Y molecules which are produced through the geometrical optimization. Coronene is one of superbenzene compounds that has the chemical formula $C_{24}H_{12}$. Adding Y atom to Coronene leads to change the electronic configuration of atoms in the molecule. New interactions get in the new molecule (between adding atom and Coronene) cause the change in the electronic configuration, hence new molecular orbitals will generate according to the molecular orbital theory [29].

Figure(3) and figure(4) appear HOMO, LUMO surfaces for Coronene and Coronene-Y. The resulting orbitals may be interpreted according to molecular orbital theory which considers the molecular orbitals as the linear combination to the atomic orbitals. The green color in the figures points out the positive part of the wave function, while the red color denotes to the negative part of the wave function, in which the probability of finding an electron at any position is given by the absolute value of the square of the wave function [30].

Figure(5) and figure(6) represent infrared spectra to the samples under study. In the figures anyone can see peaks that denote the bonds between atoms. Each peak means there is a bond between two neighboring atoms at certain wave number or wavelength. Epsilon in the figure refers to the intensity. One can visualize in figure(6) new peaks that result from the interaction of carbon atom in Coronene molecule and Y atoms, those peaks are denote to C-Al, C-B, C-C, C-Ga, C-In and C-O bonds in Coronene-Y molecules[31].

Table(2) shows the values of ionization potential and electron affinity in (eV) for Coronene and Coronene-Y molecules. Ionization potential and electron affinity result depending on the energies in valence band and conduction band according to Koopman's theorm. From the table one can see adding Y-atom to Coronene makes the ionization potential decrease. This means the electrons will need less energy to escape from the surfaces, this is very advantageous characteristic. On the other hand, the electron affinity increases when, Y atom is added to Coronene.

One can compare between table(1) and table(3) and see that HOMO energy of Coronene is higher than HOMO energy of Al, B, C, Ga and In, hence Coronene will be a donor in Coronene-Y for Y= Al, B, C, Ga, In, while HOMO energy of Oxygen is larger than HOMO energy of Coronene; therefore Coronene will be acceptor in Coronene-O, while Oxygen donor[32]. Table(3) illustrates that adding a Y atom to Coronene lessens the energy gap between valence band and conduction band. Adding Carbon and Boron to Coronene makes the energy gap similar to the energy gap of semiconductors, and this is a very important advantage in the electronic devices [33].

It is very clear from table(4) the total energy increases as the number of atoms increases. The total energy of Coronene-Y

compounds is less than the total energy of the sum of energies for individual coronene and individual Y atom. That is to say the resultant molecule after interaction has total energy less than the energies of interacting particles. So, the orbitals that emerge between Y atoms and Coronene are bonding orbitals [34].

The comparison between table(1) and table(5) shows the hardness of Coronene larger than the hardness of Y atoms, hence Coronene will behave as hard base in Coronene-Y molecules. Aluminum has softness less than Coronene, so it will behave as hard base. The other Y atoms except Aluminum have softness more than Coronene, one can say Y atoms except Aluminum will behave as soft bases [35].

from table(6) one can see adding any Y atom to Coronene makes the average polarizability largest.The molecule which has greater average polarizability has greater reactivity; therefore Coronene-In can be considered the most reactive molecule. Generally, Polarizability becomes larger with increasing the size occupied with electrons. Polarizability is a very important characterstic because it gives vision about the internal structure of the molecule [36].

Figure(7) and figure(8) give density of states for Coronene and Coronene-Y. There will be many available. Electronic states when the density of state is high at any energy level. Electron energy increases with density of state. From the figures one can see Carbon-Coronene and Oxygen-Coronene has beta orbitals. This indicates that those two molecules behaves as anti-ferromagnetic materials because beta orbitals appear in these types of materials, i.e. anti-ferromagnetic Topological properties affect the density of states, so symmetry [37].

4. Conclusions:

When Y atoms are added to Coronene, the electronic configuration changes. New bonds generate throughout the interaction between Coronene and Y atoms, and this is very clear through the change of the intensity with wave number in infrared spectra. Ionization potential of coronene effects when it interacts with y atoms. The ionization potential decrease, but the electron affinity increases. HOMO and LUMO levels demonstrate Coronene behave as donor when it interacts with Y atoms except for its interaction with Oxygen. Both Coronene-B and Coronene-C have semiconductor band gap. Bonding orbitals will originate through Coronene-Y interactions. Aluminum behaves as soft base when it interacts with Coronene. Average polarizabilitty of Coronene-In is the highest value of the average polarizability. So, Coronene-In is the most reactive molecule among Coronene-Y atoms. Anti-ferromagnetic property appears in Coronene-C and Coronene-O.

5. Acknowledgements

I would like to show my deep thanks for Dr. Falah H. Hanoon and Dr.Abbas Sh.Alwan.

6. References

[1] Parr, Robert G., Yang, Weitao, "*Density-Functional Theory of Atoms and Molecules*",Oxford University Press, (1994).

[2] R. Wysokinski, J. Kuduk-Jaworska, D. Michalska, *Electronic structure, Raman and infrared spectra, and vibrational assignment of carboplatin. Density functional theory studies*, J. Mol. Struct.: THEOCHEM 758 (2006).

[3] D.J. Tozer, F.D. Proft, "Computation of the hardness and the problem of negative electron affinities in density functional theory", *J. Phys. Chem.,(2005).*

[4] D. Young," *Computational Chemistry: A Practical Guide for Applying Techniques to Real-World Problems*", NY: John Wiley & Sons, Inc., New York, (2001).

[5] W. Koch, M. C. Holthausen, "*A Chemist's Guide to Density Functional Theory*", 2nd ed., Wiley-VCH Verlag GmbH, Germany, (2001).

[6] A. Szabo,; N.S.Ostlund, "Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory";DoverPublications,Inc.: New York, 1989.

[7] Yao Cong, "*Introduction to quantum chemistry*", (1980).

[8] M. Mueller, "*Fundamentals of Quantum Chemistry: Molecular Spectroscopy and Modern Electronic Structure Computations*", Kluwer Academic/Plenum Publishers, New York, (2001).

[9] M. Oftadeh, S. Naseh, M. Hamadanian, "*Computational and Theoretical Chemistry*" 966, 20- 25, (2011).

[10]I. N. Levine, *Quantum Chemistry vol. 6*: Pearson Prentice Hall: Upper Saddle River, NJ, (2009).

[11] B. Giese, G. B. Deacon, J. Kuduk-Jaworska, D. McNaughton, Densityfunctional theory and surface enhanced Raman spectroscopy characterization of novel platinum drugs, Biopolymers 67 (2002)

[12] Carmer, Christopher J. *"Essential of Computational Chemistry*". Chichester: John Wiley andSons, Ltd. Pp. 154-168, (2002).

[13] J.A. Pople and D.L. Beveridge, "*Approximate molecular orbital theory*", Mc Graw-Hill, (1970).

[14] W. Hehre, L. Radom, P. Schileyer and J. Pople, "*Ab-initio molecular orbital theory*", John Wiely and Sons, (1986).

[15] *H. A. Abbod, Ramla Abdulnaby, "Geometry Optimization And Energies of Donor-Bridge-Acceptor Molecular System", (2014).*

[16] H. I. Abood "Density Functional Theory Calculations of Di-amino naphthalene"Journal of Babylon university, *Pure snd Applied Science. No.3, Vol.22, (2014).*

[17] R. Chang "*Basic principles of spectroscopy*", McGraw-Hill, New York, (1971).

[18] King, G. W., "*Spectroscopy and Molecular Structure*", Holt, Rinehart and Winston, New York, (1964).

[19]C. Lee, W. Yang, R. G. Parr, *Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density*, Phys. Rev. B 37 (1988) .

[20] D. D. FITTS," *Principles of Quantum Mechanics: as Applied to Chemistry and Chemical Physics*", Cambridge University Press, New York, (2002).

[21] H. Ibrahim Aboud, "*Density Functional Theory Calculations for Nitro Benzene Molecules Group*", British Journal of Science Vol. 6 (2) (2012).

[22] M. Totonkoban, M. Oftadeh, N. Farzi *"Study of the Structure Effect on Water Adsorption by a Group of Nano Copper Clusters"* Vol. 1 No 3, 03PCSI03 (3pp) (2012)

[23] Abbas. Sh. Alwan *"Theoretical study of* Na^+ *ion, Na atom and* H_2 *molecule-Ag and Cu surfaces interaction"* Ph.D thesis, Almustansiriyah university, March 2016 A. D.

[24] H. I. Abood& et al."*Study of The Effects of Some Organic Monomers on The Electronic Structure for C20 Cage Fullerene "The* first scientific conference Babylon University. College of science, (2013).

[25] A.M. Ali, "*Investigations of some antioxidant materials by using density functional and semiempirical theories*", *PhD. Thesis*, University of Basra, College of Science, Department of Physics, (2009).

[26] F. C. Brown, , *"The Physics of Solids"*, New York: W. A. Benjamin (1967).

[27] J. D. Patterson, "*Introduction to the Theory of Solid State Physics*", Reading, Mass. Addison-Wesley, (1971).

[28] J.S Blakemore, "*Solid State Physics*", Philadelphia: W. B. Saunders, (1969).

[29] J.A. Pople and D.L. Beveridge, "*Approximate molecular orbital theory*", Mc Graw-Hill, (1970).

[30] Frisch M. J., G. W. Trucks, H. B. Schlegel et al., Gaussian 09, Revision A.02, Gaussian, Inc., PA, Wallingford CT. (2009).

[31] *G. A. H. Jaber, B.A.Ghalib, H. I. Abbood* "STUDY OF THE EFFECT OF CYANO SUBGROUP ON THE ELECTRONIC PROPERTIES OF AZULENE MOLECULE:B3LYP-DFT CALCULATION" European Scientific Journal vol.3 2013.

[32] S. Kaya S. Erkan Kariper, A. Ungördü , C. Kaya "Effect of Some Electron Donor and Electron Acceptor Groups on Stability of Complexes According to the Principle of HSAB", *Journal of New Results in Science, Number: 4, Year 2014, Pages: 82-89.*

[33] L.U. YiZhong W.E.I WenTao and CHEN Wei1,"*Copper nanoclusters: Synthesis, characterization and properties*", (2015).

[34]] Mc Grow- Hill, "*Fundamentals of molecular spectroscopy*", (1972).

[35] F. N. Ajeel, A. M. Khudair, A. A. Mohammed "*Density Functional Theory investigation of the Physical Properties of Dicyano Pyridazine Molecules*", (2015).

[36] D.J. Griffiths, "*Introduction to Electrodynamics*", (3rd Edition), Pearson Education, Dorling Kindersley, (2007).

[37] dachi T. and Sunada. T "*Density of states in spectral geometry of states in spectral geometry*". *Comment. Math. Helvetici 68: 480–493, (1993).*

بعض الخواص الكهربائية لتفاعل مادة كورونين-ص بواسطة استخدام نظرية كثافة الدالة

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الخلاصة

تم استخدام برنامج الكاوسين 09 وبواسطة دالة نظرية كثافة للدالة الهجينة (B3LYP) مع الدالة الاساس 3-21G لبناء مركب الكورونين

ثم تم اضافة بعض الذرات (المنيوم, بورون, كاربون, كاليوم, انديوم,والاوكسجين) الى مركب الكورونين ونمذجتها و دراسة التغيرات على الخواص الالكترونية بواسطة نظرية كثافة الدالة وتم الحصول على الامثلية الهندسية للمركبات و من ثم تم دراسة طيف الاشعة تحت الحمراء لمعرفة مدى التغير في تركيب المركب بعد اضافة الشوائب الى مادة الكورونين وقد ظهرت قمم جديدة ناتجة من الاواصر الجديدة بين الكاربون الموجود في المركب الاصلي (الكورونين) و الذرات المضافة الى المركب. التفاعل بين الكورونين مع الذرات المضافة خفض الجهد الايوني وتكبير الالفة الالكترونية. كل المركبات المتولدة هي مركبات مانحة عدا مركب كورونين- اوكسجين. تم حساب فجوة الطاقة للمركبات لمعرفة نوع المركبات المتولدة, وقد وجد انها تنتمي الى المواد شبة الموصلة لان لها فجوة طاقة مشابة لتلك المواد كما في مركب كورونين- بورون و مركب كورونين-كاربون . المركبات اكتسبت صلابة. ان مركب الكورونين-انديوم له اعظم استقطابية مقارنة مع بقية المركبات. والمركبين كورونين-كاربون و كورونين-اوكسجين تشبه المواد الفيرومغناطيسية.

الكلمات المفتاحية : نظرية كثافة الدالة , الهومو و اللومو , فجوة الطاقة, طيف الاشعة تحت الحمراء