

Calculations of The Effect of Poly-hydroxyl Subgroups on the Electronic Properties of Fullerene C60 Cage Using B3LYP-DFT

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Abstract:

Present work focuses on employing the density functional theory with the B3LYP hybrid functional and 6-31G basis sets to study the effects of the addition of poly-hydroxyl subgroups on the electronic properties of fullerene C60 cage molecule. We used the Koopman's method to calculate some important electronic variables, such as, the ionization energy, electron affinity and electronegativity. The results showed the location and the subgroups number of hydroxyl in fullerene molecule effect on the calculated energies. The addition of the hydroxyl reduces the energy gap, means we construct new molecular electronic structures which can be used in many applications of the organic molecular electronics.

Keywords: DFT, B3LYP, Koopman's theorem, Energy Gap and Polarizability.

حسابات تأثير مجاميع متعدد الهيدروكسيل على الخواص الالكترونية لجزيئة الفولرين 60 باستخدام الدالة الهجينة ذات المعاملات الثلاث من نظرية دالية الكثافة

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الخلاصة:

البحث الحالي يركز على تطبيق نظرية دالية الكثافة مع الدالة المهجنة B3LYP والدوال الاساس 6-31G لدراسة تأثير اضافة مجاميع من متعدد الهيدروكسيل على الخواص الالكترونية لجزيئة الفولرين 60 . استخدمت طريقة كوبمان لحساب بعض المتغيرات الالكترونية مثل طاقة التأين ، اللفة الالكترونية والكهروسالبية. تبين النتائج ان موقع وعدد مجاميع الهيدروكسيل المضافة في جزيئة الفولرين له تأثير على تلك الطاقات المحسوبة. وأن تلك الاضافة قد خفضت فجوة الطاقة وهذا يعني أنه بنيت تراكيب الكترونية جزيئية جديدة يمكن استخدامها في تطبيقات الالكترونيات الجزيئية العضوية.

الكلمات المفتاحية: نظرية دالية الكثافة، الدالة الهجينة، نظرية كوبمان، فجوة الطاقة والاستقطابية.

1. Introduction

Fullerene C60 consists of 60 carbon atoms arranged in twenty hexagons and

twelve pentagons that form a perfectly symmetrical cage structure of a soccer ball with 1 nm size[1]. C60 molecule follows

Euler's theorem where each fullerene consists of twelve pentagons and M hexagons containing $2(10+M)$ carbon atoms[2,3]. Each carbon atom is bonded to three other carbon atoms to form sp^2 hybridization and, consequently, entire C60 molecule is surrounded by electron clouds[4]. C60 has two different types of bonds; 6:6 bond which located in between two hexagon rings and 6:5 bond which located in between a hexagon ring and a pentagon ring and 6:6 bonds are considered as double bonds having shorter bonding length than 6:5 bonds [4]. C60 molecule was first found in 1985 by Kroto et al.[1] from the ablation of a graphite with energetic pulsed laser. However, mass production of these carbon based nanoparticles was not possible until Kratchmer et al.[5-8] succeeded in synthesizing C60 by resistive heating method. Fullerene can be used as organic photovoltaic device[9-13]. Currently, the record efficiency for a bulk heterojunction polymer solar cell is a fullerene-polymer blend. The fullerene acts as the n-type semiconductor (electron acceptor). The n-type is used in conjunction with a p-type polymer (electron donor)[14-17].

2. Theory

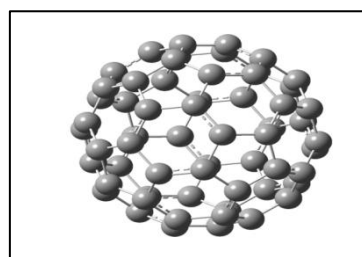
The calculations in present work are performed with the GAUSSIAN 09 suite of programs. Full geometry optimizations of fullerene C60 and hydroxyl fullerene C60 molecules group were performed with Berny optimization algorithm (calculating the energy derivatives with respect to nuclear coordinates analytically, in redundant internal coordinates)[18,19]. The gradient corrected density functional methodology was employed Becke's exchange functional (B) and Becke's three-parameters adiabatic connection (B3) hybrid exchange functional were used in combination with the Lee–Yang–Parr

correlation functional B3LYP. While the BLYP methodology is a 'pure DFT' one (it includes no HF exchange), the B3LYP contains an admixture of HF exchange. The B3 functional contains a linear combination of exact HF exchange, Slater exchange and Becke gradient-corrected exchange[20]. The standard 6-31G basis set was used for orbital expansion to solve the Kohn–Sham equations in all cases. The computed stationary points for which the structures and force fields are presented correspond to real minima on the molecular potential energy hyper surfaces. The DFT (LUMO-HOMO) energy for the poly hydroxyl fullerene C60 molecules group studied in this research was calculated at the same level of theory[21-23].

3. Results and Discussion:

Figure 1 illustrates the optimized structures of the molecules under study in this work. They are six hydroxyl fullerene C60 molecules and labeled (Molecules 2-7), and the fullerene C60 is the reference molecule 1.

The optimized structures of the mentioned molecules are represented by the optimized coordinates in Angstrom ($\text{\AA}$) for all atoms in these molecule 2-7. The optimized parameters of these molecules included bonds in Angstroms ($\text{\AA}$) and angles in degrees calculated from DFT-B3LYP/6-31G (d, p).



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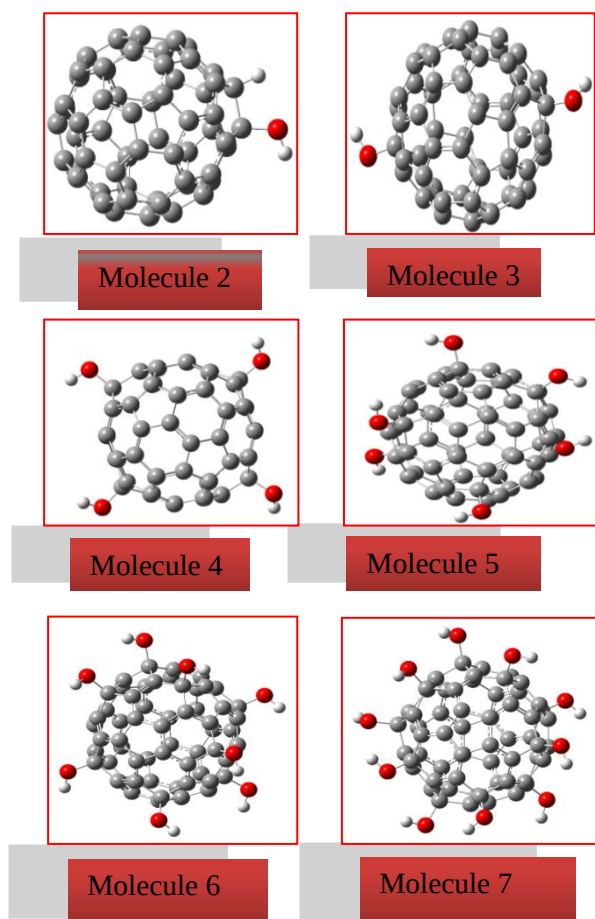


Figure 1: The optimized structures of hydroxyl fullerene molecules group using DFT- B3LYP/6-31G(d, p)

3-1 The Computed Energies

The results of the total energy ET in a.u , and some computed energies in eV of hydroxyl fullerene molecules group are illustrated in table 1, calculated depending on Koopman's theorem. The calculations are carried out by performing B3LYP/6-31G level of density functional theory and included the ionization energy IE, electron affinity EA and electronegativity X.

Table 1 : The calculated energies of hydroxyl fullerene molecules group from DFT-B3LYP/6-31G

Molecule	ET(a.u)	IE(eV)	EA(eV)	X(eV)
1	-2285.5	6.2484	3.3752	4.8118
2	-2361.9	5.6560	3.7551	4.7055
3	-2424.1	4.9170	3.6772	4.2971
4	-2588.5	5.1934	4.2528	4.7231
5	-2740.0	5.1156	4.0402	4.5779
6	-2891.6	5.1042	4.0231	4.5636
7	-3043.1	4.7338	3.9738	4.3538

It is clear from table 1 that the total energy of hydroxyl fullerene molecules group is less than the total energy of the reference fullerene C60. The total energy decreased with increase of OH groups number added to fullerene C60 molecule, as figure 2 illustrates this relation. From the linear relation in figure 2, one can found a simple equation associates the ET of the hydroxyl fullerene molecules group and the OH groups number (n): $ET = ET(\text{fullerene C60}) + nET(\text{OH})$.

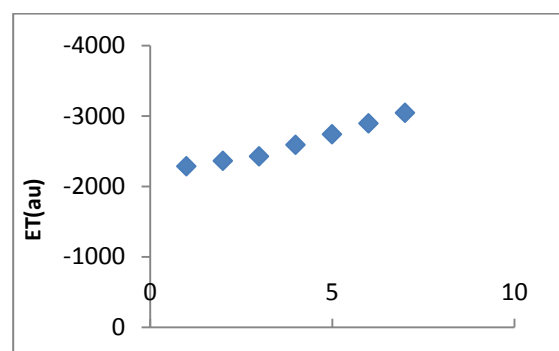


Figure 2 : The relation between the total energy and OH groups number.

The behavior of ionization energy and electron affinity as a function of OH groups number are shown in Figures 3 and 4, respectively. The hydroxyl fullerene molecules group have low values of IE and high values of EA in comparison with the reference molecule 1. Adding the OH group reduced the IE and increased the EA of the fullerene. Molecule 3 has small value of IE but molecule 7 has the smallest, that means these molecules need a small energy to become cations in comparison with the others. Molecule 4 has the higher value of EA in comparison with the others. These results are global properties and they are not coming from the frontier molecular electronic states. This molecule has high ability to acceptance of an electron from the surrounding media.

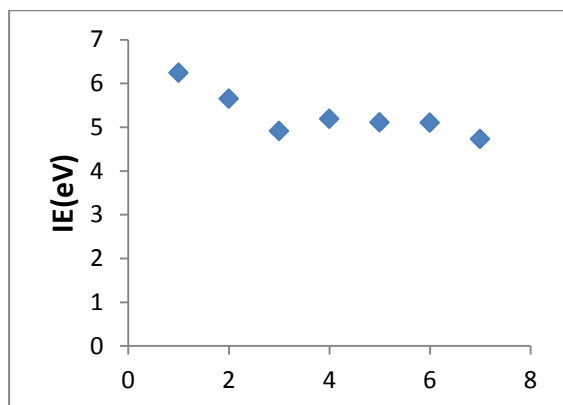


Figure 3 : The relation between the ionization energy and OH groups number

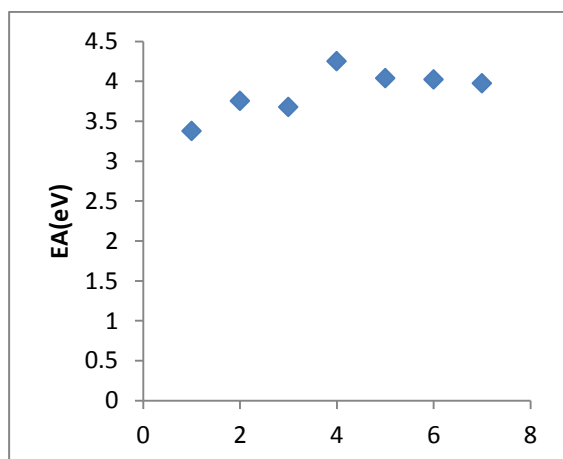


Figure 4 : The relation between the electron affinity and OH groups number.

Figure 5 declares the electronegativity X of the studied molecules 2-7 with the reference fullerene. As seen, all the hydroxy fullerene molecules group have electronegativity less than that for fullerene molecule, that means these molecules have a small escaping tendency comes from the presence of hydroxyl groups in the molecule. It is clear from this result that the electro chemical hardness of all studied molecules is smaller than that for fullerene. The decreasing of electrochemical hardness is the main future and as a sign to that band gap goes to be rather soft and lowering the resistance of these structures to lose an electron.

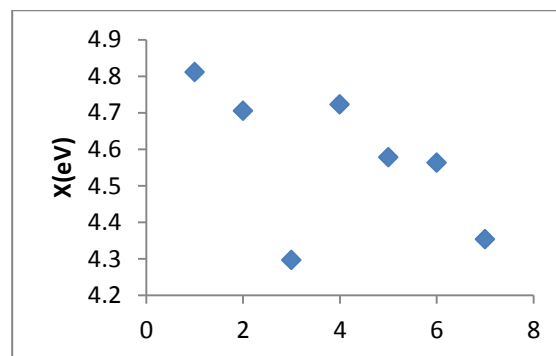


Figure 5 : The relation between the electronegativity and OH groups number.

3-2 Electronic States and Energy Gap

The high occupied molecular orbital energy E_{HOMO} , lower unoccupied molecular orbital energy E_{LUMO} and the energy gap of hydroxyl fullerene molecules group are shown in table 2 calculated from the DFT-B3LYP/6-31G calculations. Figure 6 shows the effect of adding the OH groups on HOMO and LUMO energies. From this figure, the addition of hydroxyl groups has effect on both HOMO and LUMO energies, but its effect on HOMO energy is more than on LUMO energy. The results showed that the energy gap of fullerene C60 decreases with the addition of OH groups, but the least is at molecule 7. Figure 7 shows the variation mode of the energy gap, this variation refers to that the energy gap of fullerene will be soft depends on the number of hydroxyl groups in the molecule.

Table 2 : The E_{HOMO} , E_{LUMO} and E_g of hydroxyl fullerene molecules group

E_g (eV)	E_{LUMO} (eV)	E_{HOMO} (eV)	Molecule
2.873	-3.3752	-6.2484	1
1.9009	-3.7551	-5.6560	2
1.2398	-3.6772	-4.9170	3
0.9406	-4.2528	-5.1934	4
1.0754	-4.0402	-5.1156	5
1.0811	-4.0231	-5.1042	6
0.7600	-3.9738	-4.7338	7

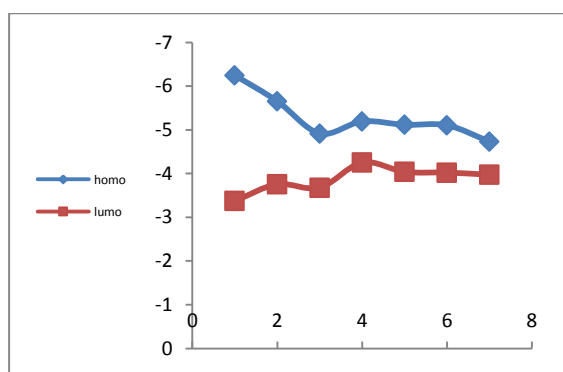


Figure 6 : The effect of OH groups number on the E_{HOMO} and E_{LUMO} .

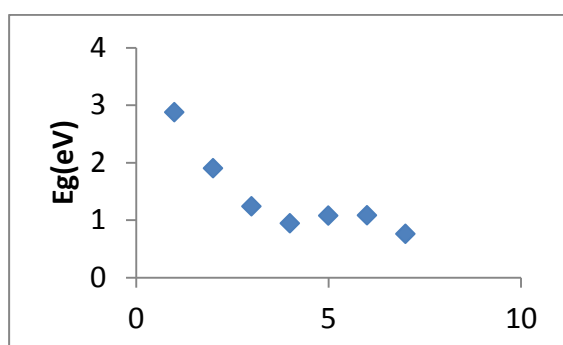
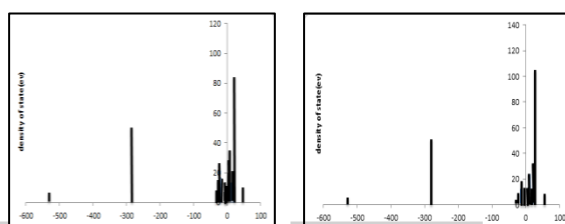


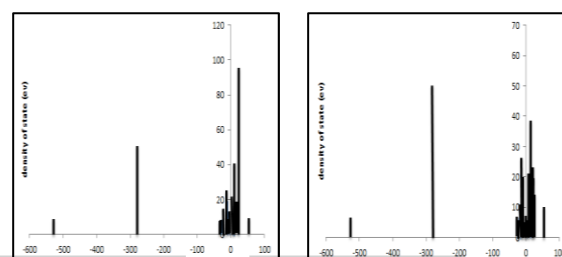
Figure 7 : The relation between the E_g and OH groups number

The effect of hydroxyl subgroups on the density of states of the fullerene molecule was shown in figure 8. Poly hydroxyl fullerene molecules have lower number of degenerate states in comparison with the original fullerene C60 molecule. Also, increasing the number of hydroxyl subgroups added to fullerene leads to lowering the degeneracy, this lowering of degeneracy caused by the existence of the new types of atoms, and leads to varying the bond lengths and angles or changing the geometry of the structure.



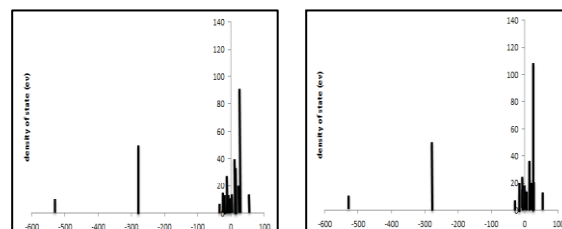
Molecule 2

Molecule 3



Molecule 4

Molecule 5



Molecule 6

Molecule 7

Figure 8: The density of states as a function of energy levels of hydroxyl fullerene molecules group

3-3 Polarizability

The calculated average Polarizability and its components as shown in table 3 declare that all hydroxyl fullerene molecules group have large values of Polarizability in comparison with the reference fullerene C60 molecule and that indicates these molecules are more reactive in charge transfer with the surrounding media. This may be a result of the presence of OH groups in the molecule. The distribution of the Polarizability components is in good agreements with the experimental data, in which, they are in the order of $\alpha_{zz} > \alpha_{yy} > \alpha_{xx}$ for all molecules. The values of the polarizability depend on both the number and the position of the subgroups added to the molecule.

Table 3: The calculated total dipole moment and Polarizability of hydroxyl fullerene molecules group

Molecule	Total D.M (Debye)	Polarizability(a.u)			
		α_{xx}	α_{yy}	α_{zz}	$\langle\alpha\rangle$
1	0.00	460.664	460.693	460.719	460.692
2	0.649	460.168	475.351	505.371	480.296
3	9.691	444.510	460.972	538.475	481.319
4	5.245	479.815	579.606	620.723	560.048
5	3.991	498.383	600.902	646.272	581.852
6	5.060	481.328	650.640	707.994	613.320
7	8.034	479.576	723.067	768.892	657.178

4. Conclusions

The total energy of the hydroxyl fullerene C60 molecules group is a linear function of fullerene subgroups added to the molecule. The total energy was linearly decreased with increasing the number of fullerene subgroups in the molecule. All the hydroxyl fullerene molecules group have low ionization energy and high electron affinity, which gave these structures the high ability to play role in the electron transfer process from the interaction with the surrounding media. Adding the fullerene subgroups to the fullerene C60 molecule leads to change both the HOMO and LUMO energies, and therefore, reduced the energy gap of the molecule, but this decrease of energy gap depends on the number and the location of fullerene subgroups in the molecule. This result is a sign of constructing new organic molecular structures have new molecular electronic applications. The molecular polarizability was increased with increasing the number of fullerene subgroups in the molecule, this is an indication to the new constructing molecules have high reactivity to interact with the surrounding.

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