



Study of the Ionization Potential, Electron Affinity and HOMO-LUMO Gaps in the Small Fullerene Nanostructures

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ABSTRACT

In this work, the theoretical investigations on the buckyball systems including C₂₀, C₂₄, C₂₆, C₂₈, C₃₀ and C₁₉Si were done to study the structures and properties of different carbon nanoclusters. The geometries of all species were performed at the B3LYP and PBE1PBE levels using the 6-31+G (d) basis set. The HOMO-LUMO energy gap, ionization potential, electron affinity, chemical potential, electronegativity, global hardness and softness, electrophilicity and maximum amount of electronic charge of studied clusters were computed. The results showed that the computed electronic properties were considerably influenced by the size of different carbon nanoclusters. The Si atom doped instead of the carbon atom in C₂₀ was investigated

1. Introduction

The use of nanomaterials is extensively increased in many aspects [1]. A molecule of carbon in the shape of a hollow sphere, ellipsoid, tube and many other forms, is called buckyballs [2]. In 1985, Kroto and co-workers discovered the first fullerene molecule that called buckminsterfullerene (C₆₀) [3]. The fullerene has opened the new area of appropriate designing of nanomaterials with full of novel attributes [4-7]. Important thermodynamic properties including ionization potentials, electron affinity and other parameters have been carried out on fullerene and its different derivatives [8-12].

Experimental research of the vertical ionization potentials of fullerene and its hydrogenated derivatives namely C₆₀H₁₈ and C₆₀H₃₆ have performed [8], which the results indicated that the first ionization potentials of the hydrogenated fullerenes are lower than that of the fullerene C₆₀. Recently, the theoretical study of size dependence of ionization potential and dissociation energies of neutral and charged carbon clusters (C_n; n=40-70) have investigated at the B3LYP/6-31G(d)

level [9]. The fullerene C₅₀, C₆₀ and C₇₀ have known as magic number fullerenes, because of the largest ionization potentials and dissociation energies. The aim of this research is to investigate the effect of size on the ionization potentials, electron affinities and other electronic properties of different carbon clusters with hybrid density functional B3LYP and PBE1PBE using 6-31+G(d) basis set at gas phase and 1atm pressure. It has been shown that the size has notable influence on the electronic properties of nanostructures.

2. Computational details

The ground state geometries were optimized at the DFT level using the B3LYP and PBE1PBE functionals and the 6-31+G(d) basis set. The energy required to release an electron from the system at the ground state is defined to the vertical ionization potentials (IP). The energy difference between the neutral and the anionic species is defined as the vertical electron affinity. The quantum molecular descriptors for nanocarbons were determined as follows:

$$E_{\text{gap}} = E_{\text{LUMO}} - E_{\text{HOMO}} \quad (1)$$

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$$\mu = (E_{\text{LUMO}} + E_{\text{HOMO}})/2 \quad (2)$$

$$\eta = (E_{\text{LUMO}} - E_{\text{HOMO}})/2 \quad (3)$$

$$\omega = \mu^2 / 2\eta \quad (4)$$

$$S = 1/2\eta \quad (5)$$

$$\Delta N_{\text{max}} = -\mu/\eta \quad (6)$$

The electronegativity (χ) is determined as the negative amount of the chemical potential (μ), as follows: $\chi = -\mu$. Furthermore, global hardness (η) can be approximated using the Koopmans theory. The electrophilicity (ω) and softness (S) were calculated from Eqs. (4) and (5). The maximum amount of the electronic charge, ΔN_{max} , is given by Eq. (6) [13]. All calculations were performed using the GAUSSIAN 03 program [14].

3. Results and discussion

The optimized geometries of different types of carbon clusters, C_{20} , C_{24} , C_{26} , C_{28} , C_{30} and $C_{19}\text{Si}$ were presented (Fig. 1). Table 1 was presented the computed different electronic properties at the B3LYP and PBE1PBE levels.

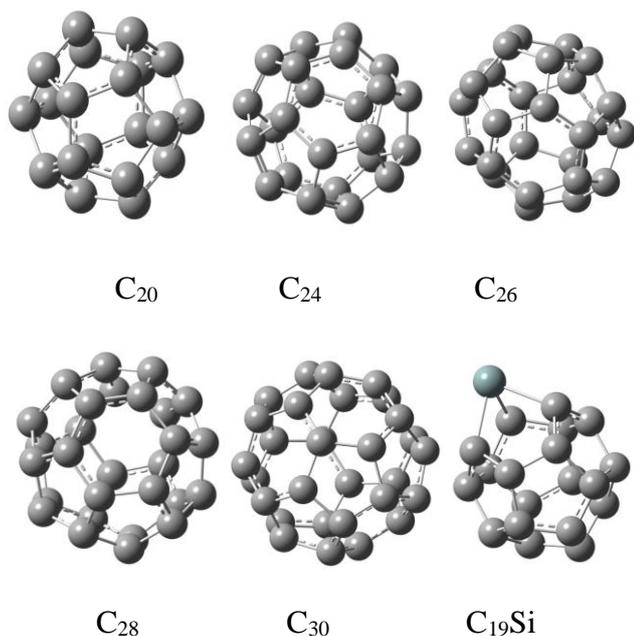


Fig. 1. Structure of different types of the carbon clusters: C_{20} , C_{24} , C_{26} , C_{28} , C_{30} and $C_{19}\text{Si}$

3.1 Cohesive energy and HOMO–LUMO energy gap

The important quantity for understanding the trends in the formation of fullerene-like molecules is the cohesive energy, defined as the difference of the total molecular energy and the sum of the energies of the isolated atoms [15]. The cohesive energy from C_{20} to C_{30} calculated with B3LYP and PBE1PBE are in the range from -4.9 to -9.0 a.u. and -6.2 to -9.6 a.u., respectively (Table 1).

Table 1. Different electronic properties at the B3LYP and PBE1PBE levels.

Struct	E_{HOMO} (eV)	E_{LUMO} (eV)	T_{E} (au)	IP (eV)	EA (eV)	E_{coh} (au)	E_{coh}/A (au)	Egap (eV)
C_{20}	-5.50	-3.62	-761.46798	7.78	-2.32	-4.9	-0.247	1.89
C_{20}	-5.64	-3.47	-760.64400	6.91	-2.37	-6.2	-0.308	2.17
C_{24}	-6.08	-4.30	-913.86587	7.47	-2.98	-7.0	-0.293	1.78
C_{24}	-6.24	-4.19	-912.87402	5.17	-3.06	-7.5	-0.312	2.05
C_{26}	-6.07	-4.45	-990.08507	2.95	-3.34	-7.7	-0.295	1.61
C_{26}	-6.21	-4.38	-989.01166	2.47	-3.49	-8.2	-0.314	1.83
C_{28}	-6.050	-4.64	-1066.33299	2.26	-3.51	-8.4	-0.298	1.41
C_{28}	-6.22	-4.54	-1065.17908	2.10	-3.56	-8.9	-0.317	1.68
C_{30}	-6.18	-4.85	-1142.58672	2.09	-3.62	-9.0	-0.301	1.33
C_{30}	-6.35	-4.75	-1141.35229	2.05	-3.69	-9.6	-0.320	1.60
$C_{19}\text{Si}$	-5.92	-3.68	-1012.91445	7.47	-2.41	–	–	2.24
$C_{19}\text{Si}$	-6.07	-3.53	-1011.99634	7.18	-2.43	–	–	2.55

The DFT calculations indicated that the cohesive energy increased when the size of the carbon nanoclusters increased from C_{20} to C_{30} . The cohesive energy per atom (in magnitude) also found to increase with increase in the size of the carbon nanostructure. The results of Table 1 also indicate that the PBE1PBE cohesive energies slightly overestimate in comparison with the more reliable B3LYP ones.

The calculated HOMO-LUMO energy gaps for nanostructures indicates that the HOMO-LUMO gaps decrease from C_{20} to C_{30}

In Table 1, all calculations indicate that $C_{19}\text{Si}$ has the largest HOMO-LUMO gap and is perhaps the most stable isomeric structure with high chemical stability. The HOMO–LUMO energy gap overestimate in the Si atom doped instead of the carbon atom in C_{20} positive slightly in comparison with the more reliable C_{20} ones. We conclude that the present results suggest that with changing the shape and size of carbon clusters one can get material of different conducting properties i.e. insulator, semiconductor or conductor.

The dipole moments of all studied nanostructures were found to be zero

3.2 vertical ionization potentials (IP) and electron affinities (EA)

The DFT calculations indicated that the vertical ionization potentials (IP) increased when the carbon nanoclusters size increased at both studied levels of theory. The vertical ionization potentials were computed as the energy required to release an electron from the system at the ground state reference geometry. The

computed vertical ionization potentials for C₂₀, C₂₄, C₂₆, C₂₈, C₃₀ and C₁₉Si at were found to be 7.78, 7.47, 2.95, 2.26, 2.09 and 7.47eV with the **B3LYP** method and 6.91, 5.17, 2.47, 2.10, 2.05 and 7.18 eV with the **PBE1PBE** level, respectively. The (IP) becomes more positive in the order C₂₀ > C₁₉Si > C₂₄ > C₂₆ > C₂₈ > C₃₀ (Table 1). Thus, the calculated values indicate that C₂₀ has the largest vertical ionization potential and Thus, the ionization potential is decreased in going from C₂₀ to other carbon nanostructures; the largest decrease is revealed for the C₃₀ structure at both studied functionals.

3.3 Electron affinities (EA):

The computed electron affinities (EA) of studied systems were also computed at the B3LYP and PBE1PBE levels. The calculations showed that the EA decreased with the increase in the size of nanostructures. The computed EA for C₂₀, C₂₄, C₂₆, C₂₈, C₃₀ and C₁₉Si with **B3LYP** functional at were found to be -2.32, -2.98, -3.34, -3.51, -3.62 and -2.41 eV and with the **PBE1PBE** level at were found to be -2.37, -3.06, -3.49, -3.56, -3.69 and -2.43 eV, respectively. For nanostructures, the electron affinities becomes more negative in the order C₃₀ > C₂₈ > C₂₆ > C₂₄ > C₁₉Si > C₂₀. This is the order with the increase in the size of nanostructures. Similar results were also found in an earlier theoretical investigation [15].

3.3 the electronegativity (χ), chemical potential (μ), electrophilicity(ω), global hardness (η), softness(S) and the maximum amount of electronic charge (ΔN_{max})

Table 1 lists the calculated other parameters including the electronegativity (χ), chemical potential (μ), electrophilicity(ω), global hardness (η), softness(S) and the maximum amount of electronic charge (ΔN_{max}) for C₂₀, C₂₄, C₂₆, C₂₈, C₃₀ and C₁₉Si at the B3LYP and PBE1PBE functionals. For nanostructures, the electronegativity (χ), softness(S) and the maximum amount of electronic charge (ΔN_{max}) values becomes more positive in the order C₃₀ > C₂₈ > C₂₆ > C₂₄ > C₁₉Si > C₂₀. The chemical potential (μ) and hardness values decreased in the order C₃₀ < C₂₈ < C₂₆ < C₂₄ < C₁₉Si < C₂₀. According to the results obtained from Table 1, the electronegativity (χ), softness(S) and the maximum amount of electronic charge (ΔN_{max}) were increased when the size of the carbon nanoclusters increased while the chemical potential (μ) and global hardness (η) decreased when the size of the carbon nanoclusters increased. The electrophilicity (ω) not affected significantly in the increase of the size of the carbon nanoclusters. results showed that the cohesive energy was increased when one silicon atom doped instead of a carbon atom in C₂₀. The results showed that the total energy (T_E) was increased when one silicon atom doped instead of a carbon atom in C₂₀. Other parameters like

full carbon nanocluster, for B3LYP level including η , ω , E_{gap} and less than PBE1PBE level and for μ and χ are equal and for IP, EA, S and ΔN_{max} more than PBE1PBE level. Comparison studies between last theoretical work about C₂₀ and C₂₀high-level ab initio calculations including B3LYP and PBE1PBE levels [16] and our paper were done and it indicated that calculated total energies and relative energies had good agreement with our results. At B3LYP and PBE1PBE methods gap energy had reasonable relationship with cage forms of C₂₀.

Table 2. Different electronic properties at the B3LYP and PBE1PBE levels

Structure	μ (eV)	χ (eV)	η (eV)	ω (eV)	S (eV)	ΔN_{max} (eV)
C ₂₀	-4.56	4.56	0.94	0.0133	391.87	131.38
C ₂₀	-4.55	4.55	1.09	0.0152	340.51	114.04
C ₂₄	-5.19	5.19	0.89	0.0162	414.95	158.40
C ₂₄	-5.21	5.21	1.02	0.0188	361.13	138.47
C ₂₆	-5.26	5.26	0.81	0.0151	458.38	177.31
C ₂₆	-5.29	5.29	0.91	0.0173	404.76	157.58
C ₂₈	-5.35	5.35	0.70	0.0136	526.21	206.90
C ₂₈	-5.38	5.38	0.84	0.0165	439.42	173.88
C ₃₀	-5.51	5.51	0.66	0.0136	557.95	226.21
C ₃₀	-5.55	5.55	0.80	0.0167	462.66	188.96
C ₁₉ Si	-4.80	4.80	1.12	0.0174	330.70	116.78
C ₁₉ Si	-4.80	4.80	1.27	0.0198	290.35	102.46

Hydrogen atom energy at the B3LYP/6-31G(d) level is 0.50027 Hartree; E_{iso} (C) = -37.7850283; E_{iso}(Si) = -289.3313739

Hydrogen atom energy at the PBE1PBE/6-31G(d) level is 0.50027 Hartree; E_{iso} (C) = -37.7246732; E_{iso} (Si) = -289.1824926

4. Conclusions

This paper presents the results of theoretical investigations to determine the properties of different size of carbon nanoclusters by using B3LYP and PBE1PBE levels at the 6-31+G* basis set. The following conclusions can be drawn from the present study:

- 1) Results show that with increase in the size of nano structure at both studied levels; HOMO-LUMO energy, vertical electron affinity, cohesive energy per atom, chemical potential and global hardness decreased but vertical ionization potentials, cohesive energy, electronegativity, softness and maximum amount of electronic charge increased and electrophilicity had no reasonable outside among all sizes.
- 2) Finding clearly indicated that downtrend or uptrend for all parameters was same and also different values of energy were not significant at two levels.

- 3) The total energy (T_E) was increased when one silicon atom doped instead of a carbon atom in C_{20} .
- 4) Finally, the total energy of $C_{19}Si$ structure is similar to C_{26} at both levels.

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