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Density Functional Study on Stability and Structural Properties of Cu_n clusters

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ABSTRACT

In this research DFT/B3LYP method has been employed to investigate the geometrical structures, relative stabilities, and electronic properties of Cu_n (n=3–10) clusters for clarifying the effect of size on the properties. Through a careful analysis of the successive binding energies, second-order difference of energy and the highest occupied-lowest unoccupied molecular orbital energy gaps as a function of cluster size, an odd-even alternative phenomenon has been observed. The results show that the clusters with even number of copper atoms present relatively higher stabilities.

Keywords: Cu cluster; Density Functional Theory; Geometric configuration; Relative stability

INTRODUCTION

In recent years, a lot of researches have been put on the study of the physical and chemical properties of atomic clusters, which, consisting of a few to a few thousand atoms. The characteristics of atomic clusters, such as geometrical arrangements and electronic properties, can be tuned up by altering the clusters' size and composition, which are generally inaccessible in the bulk phase. There has been a significant increase in the research focused on the synthesis, characterization, and theoretical analysis of clusters and nanoparticles. Their ability to guide, enhance, emit, and modify optical fields puts them on the center stage for applications such as photonic crystals, biosensors, and optical materials [1, 2].

Among the various studies on clusters, metal clusters have attracted considerable attention from both experimental and theoretical researchers [3-10]. The goal of most of these studies is to examine how the properties of a cluster evolve with size. These properties include the geometric structures, binding energies, ionization energies, and the highest occupied-lowest unoccupied molecular orbital (HOMO-LUMO) energy gaps, etc.

Cluster properties are very sensitive to the number of atoms, and they can sometimes change dramatically with the addition or removal of one atom from the cluster. The research in cluster chemistry has been guided to study the dependence of different properties upon the size of the cluster, and how these properties tend to the bulk values. Properties such as ionization potentials, electron affinities, chemical reactivity, investigations of ion abundances, and dissociation energies of alkali-metal and transition-metal clusters

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have been reported [11-15].

Since the closed sub shell and limited number of valence electrons can greatly simplify theoretical simulation and spectroscopic measure, investigations of alkali metal series have been an active field to understand the structural and physicochemical properties in depth [16-20].

Transition metal clusters are particularly interesting for their potential application in many processes like heterogeneous catalysis, in organometallic chemistry or new electronic materials [21–23]. Moreover, much attention has been paid to the melting behaviour and thermodynamic properties of Cu nanoclusters [24].

Thus, characterization of geometrical structures, various energetic and electronic-structure related properties of the Cu clusters should be a meaningful project. Such a study on the metal clusters would also provide useful information on how the properties of a cluster evolve with size.

In this paper, we present a systematic study of the Cu_n clusters (n=3-10) at their neutral states. Relative energy and successive binding energy of Cu_n clusters are analysed to provide the effect of cluster size on their geometrical arrangements and stabilities.

COMPUTATIONAL METHOD

The lowest energy configurations of Cu_n (n=2-10) clusters are investigated by means of GAUSSIAN 09[25] program package. Each species was optimized by the DFT/B3LYP method using the LANL2DZ [26] basis set for effective core potentials. In searching for the lowest energy structures, lots of possible initial configurations have been extensively explored without any symmetry constraint, and different spin multiplicities are also taken into account by considering the spin polarization in geometry optimizations. Vibrational analysis was performed in order to be sure that the structures obtained correspond to stable clusters. In this way, for each cluster size, a large number of stable isomers are obtained, but here we only report the lowest energetically ones. Relative energies, the HOMO-LUMO energy gaps, the successive binding energy (sBE) and the second difference energies of Cu_n clusters were obtained.

RESULTS AND DISCUSSION

1. Structural characteristics

The lowest energy structures of the Cu_n (n=3-10) clusters are shown in Fig. 1. The geometrical parameters of these structures are collected in Table 1. In this section, we will discuss the structures of the Cu_n clusters according to the increasing order of n. All of the 8 clusters considered in this study are planar. From Fig. 1, each Cu_n structure can be gained by adding a Cu atom on the geometry of the former Cu_{n-1} cluster. Besides, the introduction of one more Cu atom influences the Cu_{n-1} geometry in an interesting way. Specifically, if a Cu′ atom in Cu_{n-1} bonds with the added Cu atom, then the Cu′-Cu bond will elongate.

The global minimum of Cu_3, exhibits a structure with C_{2v} symmetry. From Table 2, the Cu-Cu bond lengths are 2.32 Å, which are longer than that of Cu2 (2.22 Å) [27, 28]. As mentioned before, it is due to the bonding of a Cu′ atom in Cu_2 cluster with the added Cu atom. The distance from Cu (1) and Cu (3) is 2.81 Å and so these atoms do not connect with each other.

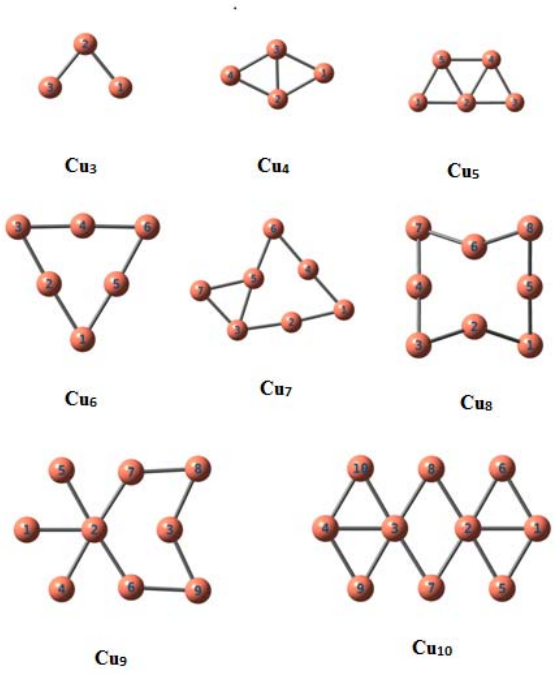

Fig. 1. The lowest energy structures of the Cu_n clusters.

Table1. The bond lengths of the Cu_n clusters in their lowest energy configurations

Cluster	Type	Bond length(Å)	Cluster	Type	Bond length(Å)
Cu_3	1,2	2.32	Cu_8	1,2	2.41
	1,3	2.81		1,5	2.4
Cu_4	1,2	2.45		5,8	2.4
	3,4	2.31		6,8	2.41
Cu_5	1,2	2.47	Cu_9	1,2	2.43
	2,3	2.42		2,7	2.46
	4,5	2.31		3,8	2.42
Cu_6	1,2	2.41		7,8	2.41
	2,3	2.41	Cu_{10}	1,2	2.45
	3,4	2.41		1,5	2.46
Cu_7	1,2	2.43		2,5	2.44
	1,4	2.42		2,7	2.47
	2,3	2.45		2,8	2.47
	3,5	2.42		3,9	2.44
	3,7	2.43		3,10	2.44
	4,6	2.41			
	5,6	2.41			

From Table 1, the average Cu-Cu bond length varies in the order 2.32 Å for Cu_3<2.38 Å for Cu_4< 2.40 Å for Cu_5<2.41 Å for Cu_6 ≈ 2.41 Å for Cu_7 ≈2.41 for Cu_8 < 2.43 for Cu_9 < 2.45 for Cu_{10}. So The Cu-Cu bond lengths are slightly increased with increasing of the cluster size n. This behavior is due to the binding force in planar structure of the larger clusters.

2. Electronic properties and relative stabilities

Table 2 indicate total energies, relative energies and HOMO- LUMO energy gaps for the optimized Cu_n clusters. The results of relative energies are also presented in figure 2.

From Figure 2, the relative energy data do not yield a monotonic variation. In the curve, the minimums occur when the number of copper atoms is even. In fact Cu_4, Cu_6, Cu_8, Cu_{10} clusters are possess relative higher relative energies than their neighboring ones.

The gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is an effective measurement for assessing the stability of clusters. The HOMO-LUMO energy gap reflects the ability for electrons to jump from occupied molecular orbital to unoccupied molecular orbital, which

Table 2. Total energies, relative energies and HOMO-LUMO energy gaps for the lowest energy configurations

cluster	E(a.u.)	E/n(eV)	relative energy(eV)	HOMO-LUMO gap(eV)
Cu_3	-588.4612	-5338.3410	0.7228	0.0513
Cu_4	-784.6592	-5338.6407	0.4230	0.0700
Cu_5	-980.8178	-5338.6128	0.4510	0.0576
Cu_6	-1177.0517	-5338.9337	0.1301	0.1192
Cu_7	-1373.2151	-5338.8842	0.1796	0.0757
Cu_8	-1569.4133	-5338.9716	0.0922	0.0871
Cu_9	-1765.5892	-5338.9675	0.0963	0.0660
Cu_{10}	-1961.8011	-5339.0638	0	0.0813

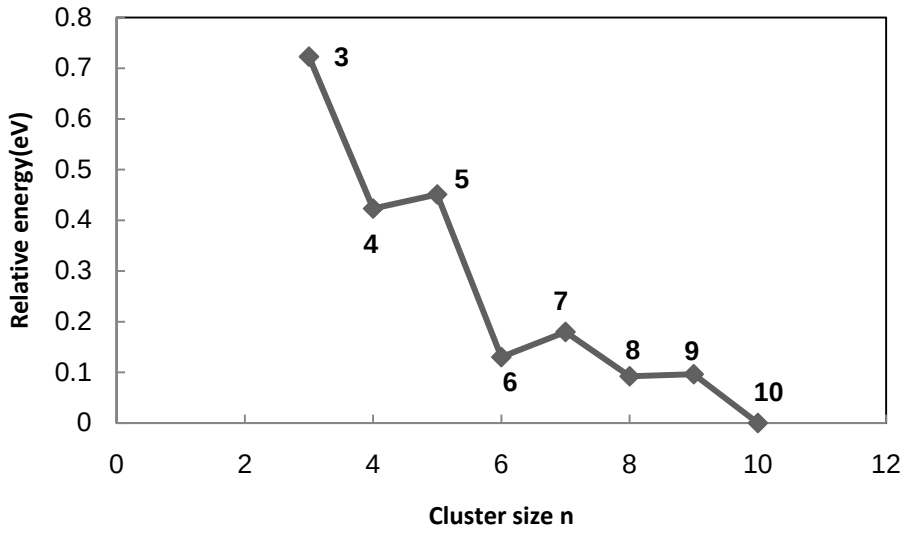

Fig. 2. The relative energies of the most stable structures of the Cu_n clusters.

indicates the ability of a molecule to participate in chemical reaction to some degree. For the lowest energy structures of Cu_n (n=3–10) clusters, the trends of HOMO-LUMO energy gaps with respect to cluster size are plotted in Figure 3. It can be seen that the HOMO-LUMO energy gaps of Cu_n clusters present a similar odd-even oscillatory behavior as observed in the relative energies. The clusters with even-number valence electrons have large HOMO-LUMO energy gaps and are relatively weaker in chemical activity (more stability and so the less relative energy) than those with odd-number valence electrons.

The relative stabilities of different sized Cu_n clusters can be represented by the comparison of binding energies, the successive binding energies, and the second difference of the total energy.

The binding energies (E_b), Successive binding energies (sBE) and second-order difference of energy (Δ^2E) are defined as

$$E_b = nE_{Cu} - E_{Cu_n} \quad (1)$$

$$(sBE)_{Cu} = E(Cu_{n-1}) + E(Cu) - E(Cu_n) \quad (2)$$

$$\Delta^2 E(Cu_n) = E(Cu_{n-1}) + E(Cu_{n+1}) - 2E(Cu_n) \quad (3)$$

Based on the above formulas, the calculated results of binding energies, successive binding energies(with respect to removing one Cu atom from cluster), and second-order difference of energies are obtained, which are summarized in Table 3, and Figures 4 and 5 respectively, describe their dependences with respect to cluster size.

Figure 4 is display binding energies as a function of the cluster size. As can be seen, E_b has an increasing tendency with the cluster size growing. It is well known that the magnitude of E_b gives information about the strength of chemical bonds in clusters. Therefore, it might help to determine the stability and reactivity of the cluster. In metallic clusters the increase of binding energy is due to a high electronic delocalization which is originated by the high coordination of the atoms.

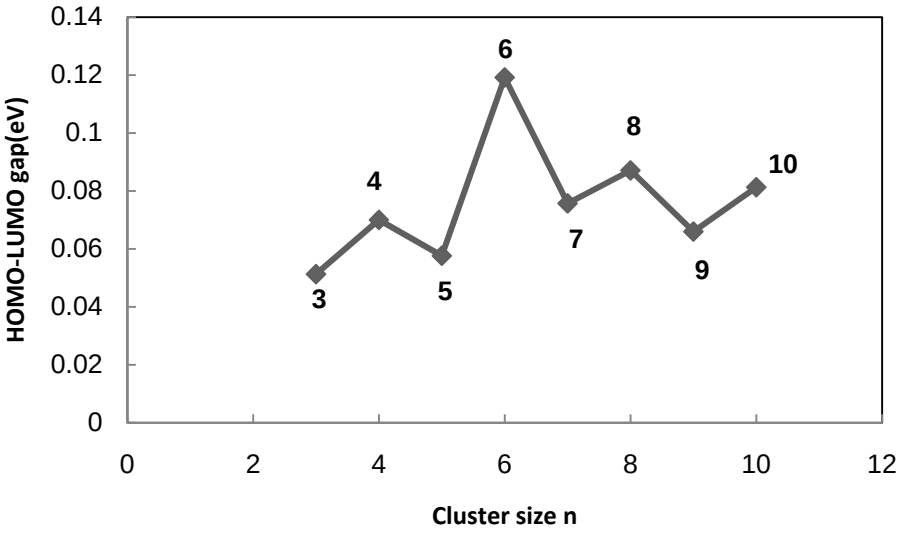

Fig.3. Size dependence of the HOMO-LUMO energy gaps for the Cu_n clusters.

Table3 . binding energies (E_b), Successive binding energies (sBE) and second-order difference of energy(Δ^2E) for the Cu_n clusters

cluster	E_b(eV)	sBE(eV)	Δ^2E (eV)
Cu_3	3.003	0.9902	-1.2097
Cu_4	5.203	2.2	1.039
Cu_5	6.364	1.161	-2.0374
Cu_6	9.5624	3.1984	1.9517
Cu_7	10.8092	1.246	-0.997
Cu_8	13.053	2.243	0.6496
Cu_9	14.6472	1.5942	-0.9966
Cu_{10}	17.238	2.5908	-

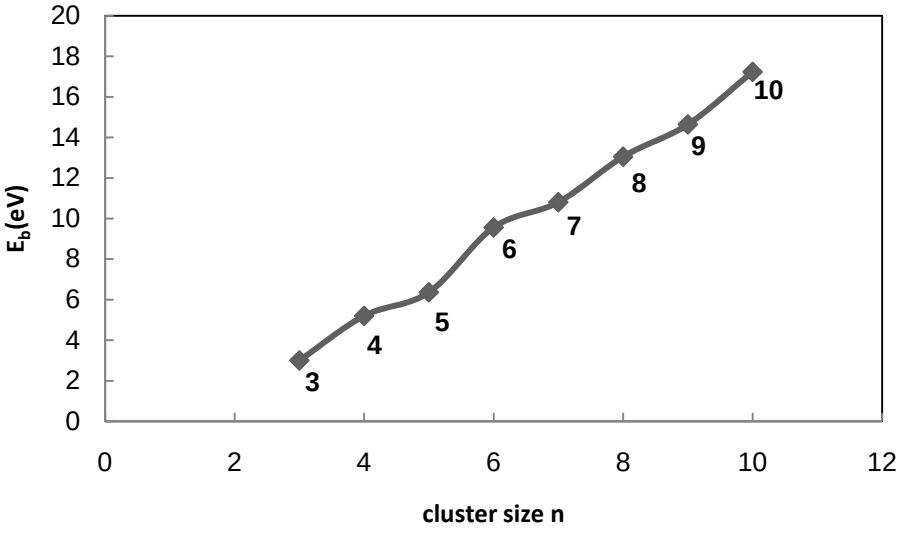

Fig. 4. Binding energies of Cu_n clusters.

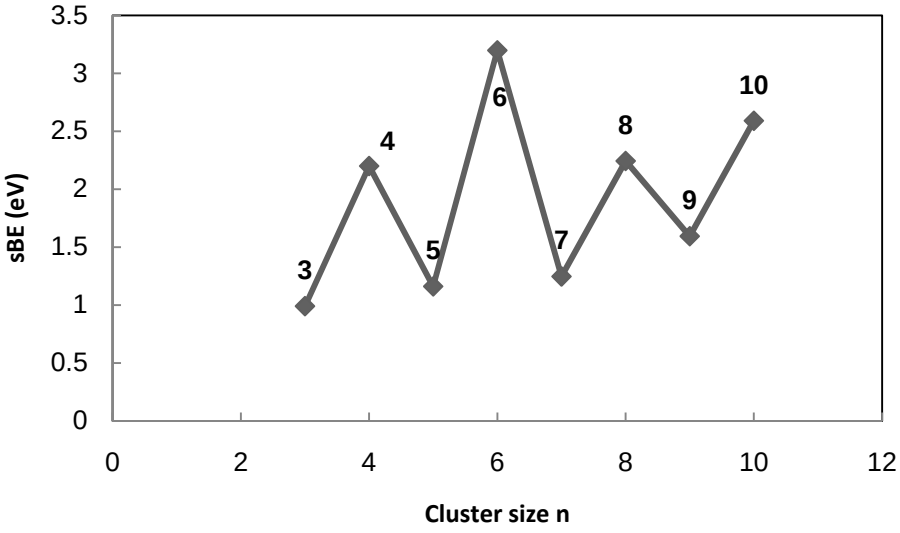

Fig. 5. Successive binding energies (sBECu) for the Cu_n clusters.

In view of the successive binding energies with respect to single Cu dissociation and second-order difference of energies, they are quite sensitive quantities that reflect the relative stability of cluster. In the figure 5, the sBE curves for the Cu_n clusters exhibit odd-even oscillatory behavior. Particularly prominent sBE peaks are found at n= 4, 6, 8 and 10.

The clusters containing even Cu atoms have relative higher stabilities as compared with their neighbors. The Cu_6 cluster exhibits the largest sBE value of 3.1984 eV, implying its stability with respect to loss of Cu atom. The second difference energy is a sensitive quantity to evaluate the relative stability of the clusters. Positive Δ^2E value indicates that the dissociation of Cu_{n+1} into Cu_n is a more favorable process than the fragmentation of Cu_n into Cu_{n-1}. Therefore $\Delta^2E > 0$ means that the Cu_n clusters are particularly stable. From table 3, Δ^2E presents a clear odd-even alternation again. Positive values are presented for Cu_4(1.0390 eV), Cu_6(1.9517) and Cu_8 (0.6496 eV). The largest Δ^2E value for Cu_6 indicates its high stability. Based on the above analyses, Cu_6 exhibits the highest relative stability among the Cu_n clusters and may be used as the building block for cluster-assembled materials due to its special stability.

CONCLUSION

Based on the first principle method, we have presented a systematic study on geometrical structures and relative stabilities of the neutral Cu_n clusters. The binding energies, Successive binding energies, second-order difference of energies, and HOMO-LUMO energy gaps are studied as a function of cluster size in details for each ground state cluster. The calculated results show that there exhibit an odd-even alternative phenomenon and the clusters with even number of copper atoms are more stable than the others. Particularly, the Cu_6 configuration exhibits the most stability among the Cu_n clusters.

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