Isomers of the Cu_5 cluster: a density function theory study*

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In this work, a systematic study of some possible isomer structures of the Cu_5 cluster obtained from density functional theory methods is presented. The polarisation and pseudopotential basis sets are employed in the calculations. The results show that the binding energies, frequencies, coordination numbers and average bond lengths are in reasonable agreement with reported experimental data. Moreover, four isomers of the Cu_5 cluster are obtained according to calculations, in which the most stable configuration is the planar structure. Meanwhile, two three-dimensional structures of the Cu_5 cluster are obtained in this work, which might be valuable for further theoretical and experimental studies. In addition, our study proves the possibility of the isomer structures of the Cu_5 cluster.

Keywords: density function theory, Cu_5 cluster, isomer structure

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1. Introduction

Atomic clusters provide a bridge between molecular and condensed matter physics. Thus, by studying the properties of clusters with different sizes, one can learn how they evolve towards bulk and find some unique properties for specific cluster sizes that differ greatly from their bulk counterparts. In fact, the properties of clusters are very sensitive to the number of atoms. When an atom is added or removed from a small cluster, its properties undergo dramatic changes. The transition from bulk to nano-structure, as the dimensionality changes from volume to surface to wires to molecules, is known to exhibit some fascinating and unconventional properties. These facts indicate the enormous potential of cluster studies for a wide range of applications. In particularly, metal clusters have many potential applications in the construction of new nanodevices for electronics and novel nanocatalysis systems. Therefore, many researchers trying to find stable structures of clusters in the ground state.[1] The properties of small metal clusters have been regarded as a research subject of great interest in recent decades.[2−10] In particular, the copper cluster has unique characteristics with atomic structures $3d^{10}4s^1$, which can be regarded as a bridge between the 'simple' s-only alkali metal and the more complicated s-d transition metals.[11]

Over the last 20 years, a considerable amount of theoretical studies about different properties of metal copper clusters have been conducted and reported. For example, copper clusters with up to 5 atoms were studied a few years ago in terms of the density functional theory (DFT) using the Demon program.[12,13] Jug *et al.*[14] investigated the structure and stability of small copper clusters with up to 10 atoms by DFT. Kabir and Mookerjee[15] studied the structure and stability of Cu_n clusters (n = 3–5) with proposed tight-binding molecular dynamics with parameters, which fitted to first-principles calculations. Massobrio *et al.*[16] studied neutral and anionic Cu_n clusters (Cu_2, Cu_3, Cu_6 and Cu_7) with DFT via the local density approximation (LDA) and Perdew and Wang's generalised-gradient approximation (GGA) for exchange and correlation. Erkoc and Shaltaf[17] investigated the structural stability and energy for small copper clusters $Cu_n(3, \ldots, 55)$ using a Monto Carlo technique at room temperature (T = 300 K). Cao *et al.*[18] and Fernández *et al.*[19] studied the stable structures and possible isomers of small copper clusters, respectively. Recently, Guvelioglu[20] systematically searched for possible isomers of small copper clusters Cu_n ($n \leq 15$) using first-principles. Jia *et al.*[21] studied the possible isomer structures of the Cu_6 cluster using DFT. A lot of work about the isomers of small copper clusters has been done with the different potential functional.[22−28]

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In addition, a number of experimental features of copper clusters were qualitatively described in terms of a simple electron shell model. Other experimental studies have indicated that localised d electrons in the copper clusters play a significant role in the geometrical and electronic structures through the hybridisation with more extended valence s electrons.[16−19] However, many properties of a copper cluster are extremely difficult to be measured directly in reality. Hence, theoretical studies of copper clusters are essential in cluster science.

The present work aims to search for some possible isomers of the Cu_5 cluster in order to prove their existence. In our calculations, the stability of the structures of the Cu_5 cluster is tested at the ground state. Furthermore, the binding energy (BE), coordination number (CN) and the average Cu–Cu bond length ($< r_{\mathrm{Cu-Cu}} >$) of the Cu_5 cluster are obtained in our study.

2. Computational methods

All the presented calculations were carried out using Gaussian 03 packages.[29] The program uses the formalism of the self-consistent Kohn–Sham equations and analytic energy gradients for the structure optimisation.[30] It works with polarisation basis sets, pseudopotentials basis sets and auxiliary functions, which is used to avoid four-centre integrals. In addition, an adaptive grid is used for the numerical calculation of the exchange–correlation potential.[31] In our calculations, the optimisations of the Cu_5 cluster structure were performed using three methods: (i) the local spin density approximation (LSDA) with the exchange–correction functional of Vosko–Wilk–Nusair(VWN) and polarisation basis set 6-31G*;[32] (ii) the non-local functional method with gradient-corrected exchanged functional of Becke–Lee–Yang–Parr (B3LYP) and pseudopotentials basis set SDD; and (iii) the hybrid-exchanged functional method with exchanged functional of Perdew86 and Perdew–Wang 91(B3PW91) and pseudopotentials basis set LANL2DZ.[33,34] The reliability of all these methods have already been proven for small copper clusters with up to five atoms and, therefore, they are used to calculate some possible isomer structures for the Cu_5 cluster. The same functional is used for the frequency analysis in order to distinguish the stable structures and transition structures.

In addition, tight convergence criterion (TCC) with a force of 0.000450 (in unit of Hartree/Bohr, 1 Hartree/Bohr = $8.2387225(14) \times 10^{-8}$ N), 0.000300 for the root-mean-square (RMS) of forces, 0.001800 Å for the displacement and 0.001200 Å (1 Å = 0.1 nm) for the root-mean-square of the displacement was employed in our simulation. The TCC is critical to determine the lowest energy structure for a given cluster. In most cases, there are several local minima within a small energy range. The structure is regarded as stable if no imaginary frequency is found. Thus, it is necessary to analyse the frequency to estimate the structure stability.

The DFT includes electron correlation for the instantaneous interaction of pairs of electrons with opposite spin. The DFT divides the electronic energy into several components, *e.g.* the electron–nuclear interaction, kinetic energy, the coulomb repulsion and an exchange–correlation term accounting for the remainder of the electron–electron interaction. All these components are computed separately. It is noted that the form of functional of each component has not been defined. However, due to the consideration of approximate functional in DFT by Kohn and Sham, the electronic energy can be expressed by the following equation:

$$E = E^{\mathrm{T}} + E^{\mathrm{V}} + E^{\mathrm{J}} + E^{\mathrm{XC}}, \tag{1}$$

where E^{T} is the kinetic energy, E^{V} describes the potential energy of the nuclei–electrons attraction as well as the repulsion between pairs of nuclei, E^{J} is the electron–electron repulsion and E^{XC} is the exchange–correlation term, which includes the residual part of the electron–electron interactions. Every term can be formulated with the electron density ρ functional except for the nucleus–nucleus repulsion terms E^{V}. Therefore, n-electron system energy is given by

$$\begin{aligned} E = & -\frac{1}{2}\sum_i \int \psi_i(r_i)\nabla^2\psi_i(r_i)\mathrm{d}r_1 \\ & + \sum_A \int \frac{Z_{\mathrm{A}}}{|R_{\mathrm{A}} - r_1|}\rho(r_1)\mathrm{d}r_1 \\ & + \frac{1}{2}\int \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|}\mathrm{d}r_1\mathrm{d}r_2 + E^{\mathrm{XC}}, \end{aligned} \tag{2}$$

where E^{XC} is divided into two parts, e.g. exchange–functional $E^{\mathrm{X}}(\rho)$ and correlation-functional $E^{\mathrm{C}}(\rho)$, which correspond to the interactions of identical spin and mixture spins, respectively. Since the ground electron configuration of the copper atom is $3d^{10}4s^1$ and the outermost shell possesses an unpaired electron, it

is possible to choose the relativistic effective core potential (RECP). The RECP can replace the inner shell 18 ($(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6$) electrons and the outer shell 11($(3d)^{10}(4s)^1$) electrons to contract the basic functional. Due to the properties of vast electrons and atoms depending mainly on valence electrons, we adopt the effect of amending RECP and use the idea of RECP of expansion orbit to replace nuclear and inner electronic electrostatic potential. Thus, we can not only explain the importance of RECP correctly, but also decrease computing time drastically. In this work, we study the possible isomer structure of Cu_5 cluster by DFT with RECP. The cluster geometries are fully optimised without symmetry constraints.

3. Results and discussion

Although there are a large number of theoretical works about the Cu_5 cluster,[36−44] there are few experimental results concerned with the ground state of the copper pentamer. Howard *et al.*[45−47] used matrix electron spin resonance(ESR) to study Cu_5 and Ag_5 clusters, and interpreted that the ground state geometry is a distorted trigonal bipyramid. However, those results about the tetramers and the pentamers are far from certain, much further verification with both experimental and theoratical methods will be needed .

In this work, The structural optimisations of the Cu_5 cluster are performed by the LSDA, B3LYP and B3PW91 methods, respectively, with DFT. Our optimised structural parameters and frequencies of the low-lying minima for the ground state of the Cu_5 cluster are listed in Table 1. The corresponding stable isomer structures of Cu_5 cluster are displayed in Fig. 1. Both the 2D and 3D isomer structures of the Cu_5 cluster were obtained in our calculations. In order to characterise the calculated ground state isomer structures of the Cu_5 cluster and give clues for further desirable experimental investigations, the harmonic vibration frequencies have been calculated by two-point numerical differentiation of the energy gradients.[48] The results also are listed in Table 1. Comparisons of the frequencies calculated by LSDA, B3LYP and B3PW91 methods show no significant differences. All the ground state isomer structures have no imaginary frequency and, therefore, they are real minima on the potential energy surface. We can see the vibrational frequencies of Cu_5 cluster in Table 1.

Table 1. Point group (PG), structural parameters [Å] and frequencies [cm^{-1}] for the Cu_5 cluster.

cluster	PG	structures		frequencies				
$Cu_5$①	C_{2v}	$r13 = 2.33912$	$r14 = 2.47907$	68	74	94	115	118
		$r15 = 2.47907$	$r23 = 2.33912$	154	157	206	255	
		$r24 = 2.47907$	$r25 = 2.47907$					
		$r34 = 2.43879$	$r35 = 2.43879$					
$Cu_5$②	C_2	$r12 = 2.37328$	$r15 = 2.39312$	41	50	104	110	139
		$r13 = 2.43005$	$r14 = 2.37516$	164	202	214	254	
		$r25 = 2.43096$	$r23 = 2.39134$					
		$r45 = 2.43339$						
$Cu_5$③	D_{3h}	$r12 = 2.47669$	$r13 = 2.27279$	83	96	138	155	158
		$r14 = 2.36687$	$r15 = 2.36687$	170	180	243	298	
		$r23 = 2.27279$	$r24 = 2.36687$					
		$r25 = 2.36687$	$r34 = 2.35167$					
		$r35 = 2.35167$						
$Cu_5$④	C_2	$r12 = 2.33670$	$r13 = 2.27662$	38	54	117	128	160
		$r23 = 2.30450$	$r24 = 2.27662$	191	236	247	298	
		$r34 = 2.33670$	$r35 = 2.33610$					
		$r45 = 2.30450$						
$Cu_5$⑤	C_{2v}	$r13 = 2.36907$	$r23 = 2.36907$	69	72	83	101	113
		$r34 = 2.47372$	$r35 = 2.47372$	147	148	199	245	
$Cu_5$⑥	C_2	$r12 = 2.41559$	$r13 = 2.40056$	39	40	99	112	135
		$r23 = 2.45199$	$r24 = 2.46891$	161	196	213	251	
		$r34 = 2.45151$	$r35 = 2.39849$					
		$r45 = 2.41539$						

Table 2. Binding energy (BE), binding energy per atom(BE/n), coordination number (CN), the average Cu–Cu bond length ($< r_{\mathrm{Cu-Cu}} >$) and experimental corrected binding energy per atom(CBE/n).

cluster	E	BE/eV	(BE/n)/eV	CN	r(Cu–Cu)/Å	BE(exp.)	CBE/n(exp.)
$Cu_5$①	−986.830	6.0724	1.214	3.2	2.4340		
$Cu_5$②	−986.850	6.6045	1.321	2.8	2.4040		
$Cu_5$③	−8190.910	10.4236	2.188	3.6	2.3548	$7.76 + 0.37$[23]	1.49296[14]
$Cu_5$④	−8190.910	10.4236	2.188	2.8	2.3102	$6.19 + 1.13$[24]	
	0						
$Cu_5$⑤	−981.018	6.7105	1.342	1.6	2.4214		
$Cu_5$⑥	−981.034	7.1380	428.1	2.8	2.4289		
bulk metal				12	2.556		

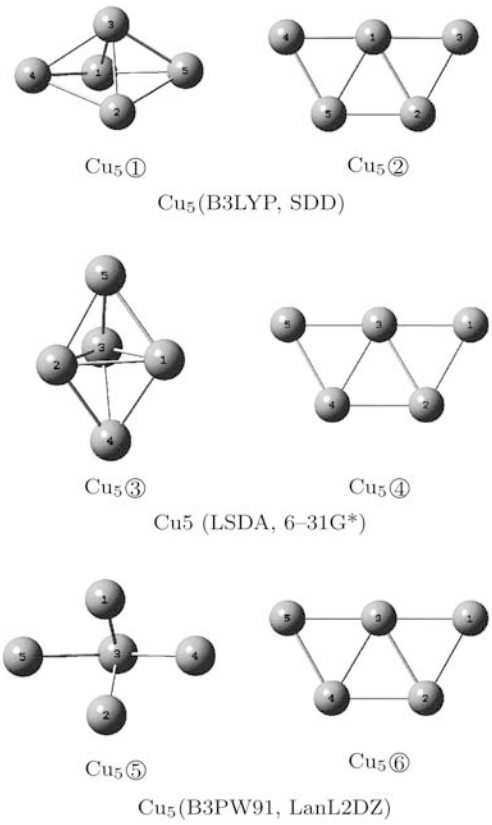


Fig. 1. The isomers of Cu_5 cluster on the LSDA and Hybrid-function level.

The binding energy can be calculated by the following formula

$$\mathrm{BE} = [E(\mathrm{Cu}_n) - nE(\mathrm{Cu})]\,. \tag{3}$$

In Table 2, the values of binding energy are listed and compared with the experimental values for the Cu_5 cluster. Moreover, the BE/n is also given in Table 2. As expected the LSDA values overestimate the binding energies considerably. The BE of the Cu_5 cluster using the B3PW91 method is 0.6220 eV for the planar geometry, which is lower than the corresponding experimental value. The BE of the Cu_5 cluster by B3LYP method is 1.5555 eV for the planar structure, which is also lower than the corresponding experimental value. However, the experimental value is 0.1176 eV higher than the corresponding computational BE for the 3D structure by B3LYP method. The experimental value is 0.5205 eV lower than the corresponding computational BE for the 3D geometry by B3PW91 method. By comparing and analysis, it is indicated that the B3LYP method is a better one to calculate the stable structure of copper cluster.

It is found that the trapezoidal C2v structure is the most stable neutral structure. The bond distances of both LSDA and B3PW91 are almost the same. However, the difference in bond distances between LSDA and B3LYP is about 0.1 Å. In our B3LYP computational results, the BE/n of the 3D geometry is 1.214 eV, which is less than the planar structure one in the ground state. The BE/n of the 3D structure lies 1.342 eV below one of the planar configuration in our B3PW91 computational results. Therefore, it can be concluded that the trapezoidal planar structure is the most stable structure. Our result agrees with those obtained by Powers *et al.*[24] In addition, the BEs of both planar and 3D structures are determined by LSDA method with 6-31G* basis set in our simulation. The BE are much higher than the experimental value,[23,24] as illustrated in Table 2. Thus, the LSDA method may give some uncertainties. However, the results obtained from the B3LYP and B3PW91 methods agree with the experimental values.[23,24] It is indicated that these two methods could provide more accurate results for the possible isomers of the Cu_5 cluster than the LSDA method in the simulation.

In addition, we list the values of the average Cu–Cu bond length ($< r_{\mathrm{Cu-Cu}} >$) and the mean CN of the Cu_5 clusters in Table 2. The CN was calculated as the arithmetic mean of the bond lengths of the

first neighbours at each site. As shown in Table 2, by comparing the two structures of Cu_5 cluster obtained by LSDA method with 6-31G* basis set, the average bond length varies slightly from 2.3548 to 2.3102 Å. By using B3LYP method with SDD basis set, the average bond length of the planar structure was almost 0.03 Å below that of the 3D configuration and BE/n increased from 1.214 eV to 1.321 eV accordingly. In comparison of the two structures of the Cu_5 cluster obtained by the B3PW91 with LanL2DZ basis set, it can be found that the average bond length is slightly prolonged from 2.4214 to 2.4289 Å. Furthermore, BE/n values increases from 1.342 to 1.428 eV. It also can be found that BE/n for the planar structure of the Cu_5 cluster is higher than that of the corresponding 3D structure. Therefore, the planar structure is much more stable than 3D structure.

In this study, we report the existence of the possible isomer structures of the Cu_5 cluster. The 3D structure of $Cu_5$③ has been reported by Calaminici *et al.*[12] However, the other two 3D stable structures of $Cu_5$① and $Cu_5$⑤, as shown in Fig. 1, have not been reported in other published works.

4. Summary

Based on the DFT, we have performed the optimisation of the Cu_5 clusters. It is found that out of four possible isomer structures of the Cu_5 cluster, the planar structure is the most stable structure. By analysing the BE, frequency, CN and average bond length, our results are in good agreement with the experimental data. The two 3D structures $Cu_5$① and $Cu_5$⑤ have also been obtained in this work. Finally, we confirmed that the Cu_5 clusters have isomer structures and enrich the structures of copper clusters.

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