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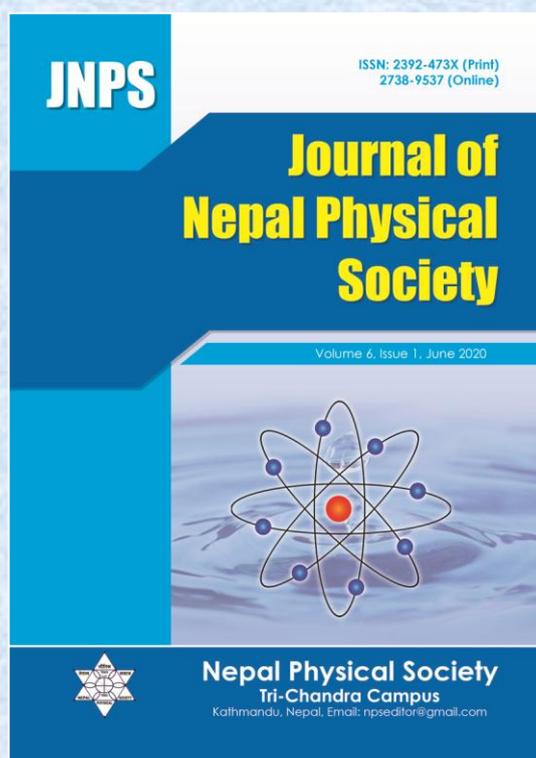
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Computational Study of the Structural, Electronic and Magnetic Properties of Nanoclusters of Cu₂O and CuO: Ab-Initio Approach

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Abstract

The structural, electronic and magnetic properties of the nanoclusters of (Cu₂O) n = 1, 2, 3 and (CuO) m = 2, 4, 6 have computationally studied. Density Functional Theory incorporated in Atomistic tool kit (ATK-DFT) calculators with exchange-correlation functional (SGGA+U) based ab-initio approach is applied for simulation and calculation of these nanoclusters. In the computational study, the nanoclusters (Cu₂O)₁, (Cu₂O)₃, (CuO)₂ and (CuO)₆ show semiconducting behavior whereas (Cu₂O)₂ and (CuO)₄ show semi-metallic behaviors. The nanoclusters (Cu₂O)₁ and (Cu₂O)₃ show diamagnetic, (Cu₂O)₂ and (CuO)₄ show ferromagnetic, (CuO)₂ and (CuO)₆ show antiferromagnetic behaviors. The magnetic moments 0.28μ_B and 0.03 μ_B are observed in the nanoclusters (Cu₂O)₂ and (CuO)₄ while others are found to be as nonmagnetic. The total energy of nanoclusters have found to be decreasing towards total minimum energy with increasing number of atoms of copper oxides. The nanoclusters (Cu₂O) n = 1, 2, 3 and (CuO) m = 2, 4, 6 are used in various applications as in the synthesis of technological materials. The analysis of the effects of bond length and binding energy with the size of nanoclusters have been presented.

Keywords: Density of States, Magnetic moments, Nanoclusters, Semi-metals, Binding energy.

1. INTRODUCTION

The copper oxides Cu₂O and CuO exist as stable in the bulk phase. They are transition-metal compound in general and the high-T, superconductors in particular [1]. Cu₂O and CuO are expected to have the essentially full Cu-3d shell (3d¹⁰4s¹) and open Cu-3d shell (3d⁹4s²) respectively. The shape-sizes and dimensions of both copper oxides play very important role on their structural, electronic and magnetic properties in nanosystem. As experimentally and theoretically, the bulk Cu₂O is found to be diamagnetic and p-semiconductor with a band gap 2.17 eV where as the bulk CuO be the antiferromagnetic and p-semiconductor with a band gap 1.2-1.9 eV [2, 3]. They are widely used in various catalytic reactions, semiconducting materials, environmental protection, and energy storage and conversion systems [4]. In comparison to bulk, nano-sized clusters (NCs) are more active and selective due to their large specific surface area and

quantum-confinement effects. The nanoclusters (0-dimension) of Cu₂O and CuO are applied to examine the remarkable physical and chemical properties of atomic or molecular species in the condensed phases. They can play a key role in various environmental processes and contribute to health hazards associated with airborne fine particles [5, 6]. They play an important role in the synthesis of technological materials [7]. The nanoclusters of both copper oxides Cu₂O and CuO can be formed by proper synthesis of copper and oxygen in the plane oriented substrates or other process [8]. An extensive experimental investigation is powerful probe to study their structural, electronic and magnetic properties and are given invaluable insight on the changes of their properties with shape-size [9]. Their physical and chemical properties are closely related to the crystalline quality, structure and stoichiometry [10]. In electrochemical reaction, the measurement reports that surface CuO clusters acts as a promoter for the

reduction of O_2 [11]. The CuO nanoclusters coated with mesoporous SiO_2 also are highly active and stable catalysts for olefin epoxidation [12]. That is why we are interested to study the various properties of clusters $(Cu_2O)_{n=1,2,3}$ and $(CuO)_{m=2,4,6}$. The SGGA+U exchange correlation with hubbard parametrization based on ab-initio approach is employed for their optimization and analyzing perpose.

Our present paper is organized as follows: The method and computational details are described in section-2 after completion of the introduction in section-1. The results and discussion are written in section-3 before the conclusive remarks explained in section-4. Acknowledgments and references are listed at the end of the sections.

2. METHOD AND COMPUTATIONAL DETAILS

A powerful set of modeling tools Atomistix ToolKit (ATK) is used for investigating a variety of nanoscale systems as molecules, bulk and two-probe systems. We have applied the ATK-DFT calculator with exchange-correlation functional SGGA+U ($U=7.5eV$) with review-Perdew-Burke-Ernzerhof (rPBE) parameterization based on density-functional theory through first-principle approach for simulation of the nanoclusters (NCs) of both $(Cu_2O)_{n=1,2,3}$ and $(CuO)_{m=2,4,6}$. The structures of all nanoclusters have been optimized and analyzed before the estimation of our

calculations. In the present calculation, we have calculated the physical properties like total energy, the bond length of Cu-O, the molecular energy spectrums (MES), the density of states (DOS), magnetic moment, spin polarization, etc using ATK toolKit. We have chosen the basic settings such as electron temperature 300K, grid mesh cut off 75, exchange correlation SGGA+U and spin polarized through ATK-DFT [13-16] toolkits. The computational structures of nanoclusters, calculated values of various parameters, total energy/bond length vs total atoms and the molecular energy spectrums (MES) with density of states (DOS) are reported in Fig. 1(1-f), Table 1, Fig. 2, 3 and, Fig. 4 (a-c) and 5(a-c), respectively.

3. RESULTS AND DISCUSSION

The structures, electronic and magnetic properties of the nanoclusters (NCs) of the both $(Cu_2O)_{n=1,2,3}$ and $(CuO)_{m=2,4,6}$ are described in following subsections .

3.1 Nanocluster Structures

In computational method, the molecular structures of copper oxide nanoclusters $(Cu_2O)_{n=1,2,3}$ and $(CuO)_{m=2,4,6}$ have been found as shown in Fig. 1 (a-f), where the yellow and the red colors spheres represent copper and oxygen atoms respectively.

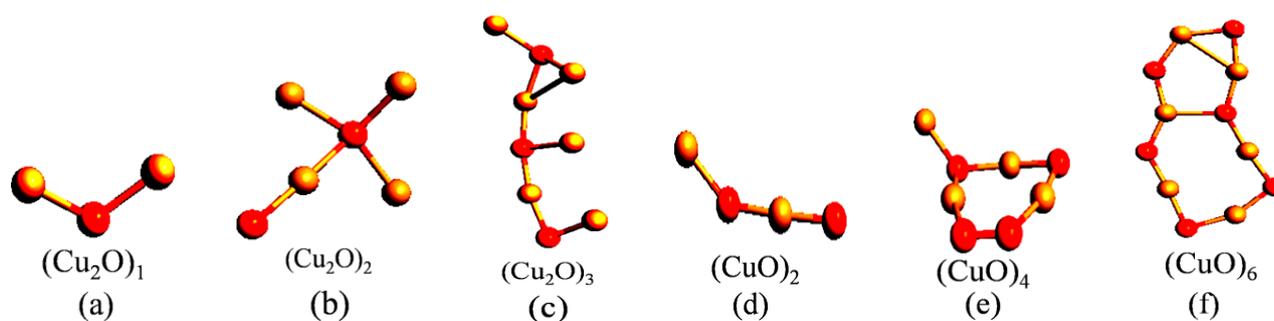


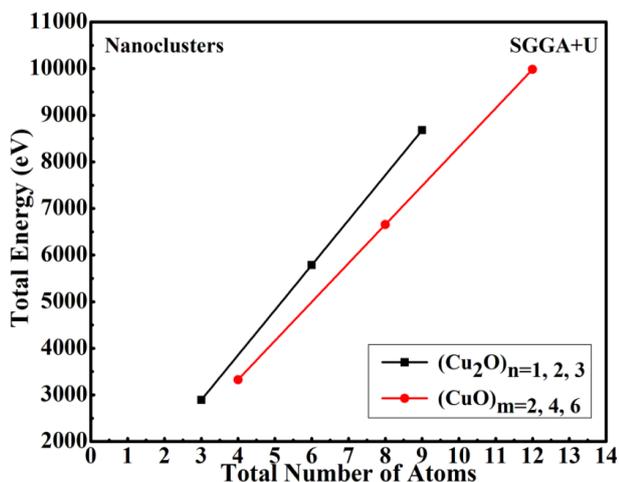
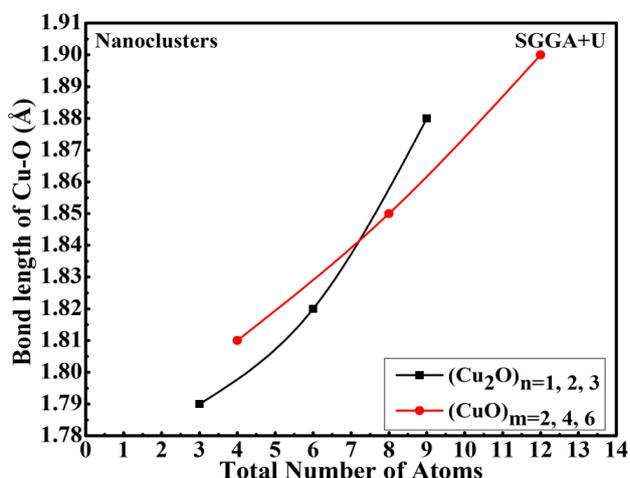
Fig. 1 (a-f): The molecular structures of the nanoclusters $(Cu_2O)_{n=1,2,3}$ and $(CuO)_{m=2,4,6}$

In the present calculation, the nanoclusters $(Cu_2O)_{n=1,2,3}$ and $(CuO)_{m=2,4,6}$ have been used as samples contain 3, 6, 9 and 4, 8, 12 atoms respectively as in Table 1. The binding energy and total energy of both type of nanoclusters have found to be increasing with the increasing number of atoms indicating that the nanoclusters (NCs) of more molecules are more stable than

that of less atoms as in Table 1 and Fig. 2 respectively and approaches towards the bulk behavior. Similarly, the bond length between Cu and O have found to be increasing with the increasing number of atoms in the nanoclusters of both types of copper oxides as in figure 3. All parameters are comparable with previously calculated available data [17-19].

Table 1: The calculated parameters of the nanoclusters $(\text{Cu}_2\text{O})_{n=1,2,3}$ and $(\text{CuO})_{m=2,4,6}$

Nano-Clusters (NCs)	Total No. of Atoms	Total Energy (eV)	Binding Energy/Atom (eV)	Bond Lengths (Cu-O)	Band Gap (eV)	HUMO - LUMO (eV)	Magnetic Moment (μ_B)	Spin Polarization	Natures
$(\text{Cu}_2\text{O})_1$	3	2892.65	1.38	1.79	1.00	1.40	0	indefinable	Dia, Semiconductor
$(\text{Cu}_2\text{O})_2$	6	5785.94	1.58	1.82	0	0.28	0.28	1	Ferro, Half-metal
$(\text{Cu}_2\text{O})_3$	9	8682.47	1.82	1.88	0.20	0.56	0	indefinable	Dia, Semiconductor
$(\text{CuO})_2$	4	3325.89	1.30	1.81	0.80	2.00	0	indefinable	Antiferro Semiconductor
$(\text{CuO})_4$	8	6656.35	1.55	1.85	0	0.40	0.03	1	Ferro Half-metal
$(\text{CuO})_6$	12	9985.65	1.57	1.90	0.1	0.60	0	indefinable	Antiferro Semiconductor


Fig. 2: The total energy vs total number of atoms in nanoclusters $(\text{Cu}_2\text{O})_{n=1,2,3}$ and $(\text{CuO})_{m=2,4,6}$

Fig. 3: The bond length vs total number of atoms in nanoclusters $(\text{Cu}_2\text{O})_{n=1,2,3}$ and $(\text{CuO})_{m=2,4,6}$

3.2 Electronic Properties

We have investigated the molecular energy spectrum (MES) with density of states (DOS) of both the nanoclusters $(\text{Cu}_2\text{O})_{n=1,2,3}$ and $(\text{CuO})_{m=2,4,6}$ for the study of their electronic properties as depicted in Fig. 4 (a-c) and Fig. 5 (a-c) respectively. In this calculation $(\text{Cu}_2\text{O})_1$, $(\text{Cu}_2\text{O})_3$, $(\text{CuO})_2$ and $(\text{CuO})_6$ are showing semi-

conducting properties whereas $(\text{Cu}_2\text{O})_2$ and $(\text{CuO})_4$ found to be as half-metals. The nanoclusters $(\text{Cu}_2\text{O})_2$ and $(\text{CuO})_4$ have found as same molecular structures of unit cells of the bulks copper (I) and copper (II) oxides respectively. But both bulk forms of copper oxide are P-type semiconductors of band gaps 2.17eV and 1.2-1.9 eV experimentally [1-3].

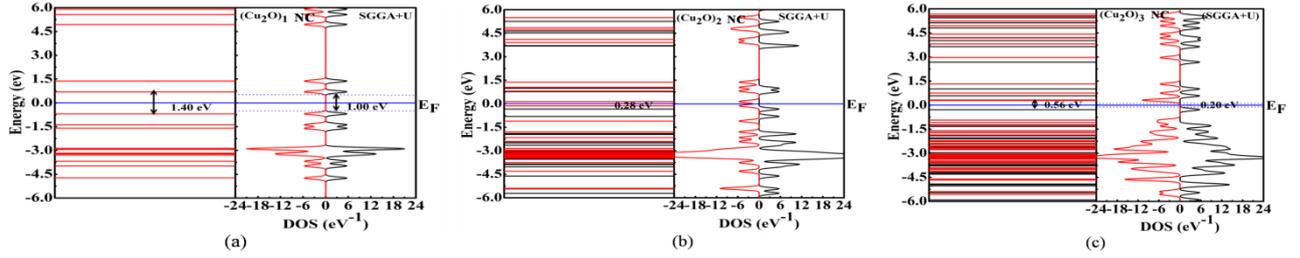


Fig. 4 (a-c): The molecular energy spectrums of the nanoclusters $(Cu_2O)_n$, $n = 1, 2, 3$ with DOS profiles

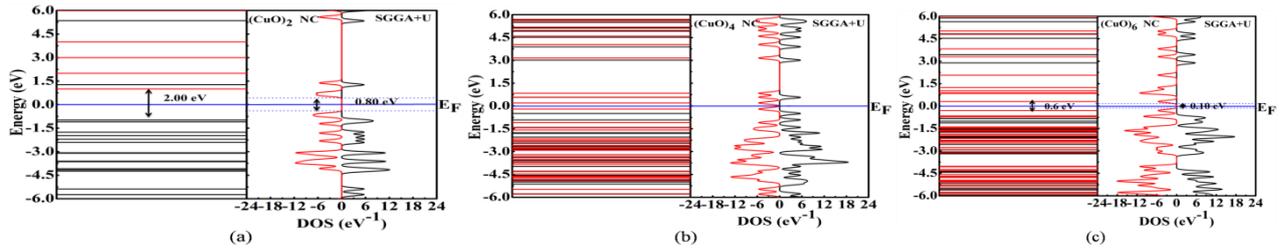


Fig. 5 (a-c): The molecular energy spectrums of the nanoclusters $(CuO)_m$, $m = 2, 4, 6$ with DOS profiles

3.3 Magnetic Properties

In our observation, the clusters $(Cu_2O)_1$ and $(Cu_2O)_3$ show diamagnetic behaviors because each individual atomic moment for both cases are found separately to be zero where cluster $(Cu_2O)_2$ as ferromagnetic. The clusters $(CuO)_2$ and $(CuO)_6$ behave as antiferromagnetic being magnetic moments of unit cell is zero but individual atoms have some polarization. Similarly $(CuO)_4$ has found to be as ferromagnetic. But the bulk forms of Cu_2O and CuO are diamagnetic and anti ferromagnetic materials respectively. The magnetic moments of nanoclusters $(Cu_2O)_2$ and $(CuO)_4$ are $0.28\mu_B$ and $0.03\mu_B$, and their matching spin polarization unity. The useful physical equations to calculate the magnetic moment per atom and spin polarization expressed as equations (1) and (2) which explains the magnetic properties [20-25].

$$\mu_{total} = \frac{m_B}{atom} = [n \uparrow (E_F) - n \downarrow (E_F)] \mu_B / atom \quad (1)$$

and

$$P = \frac{[n \uparrow (E_F) - n \downarrow (E_F)]}{[n \uparrow (E_F) + n \downarrow (E_F)]} \quad (2)$$

where, μ_{total} = magnetic moment per atom, m_B = magnetic moment, μ_B = magnetic moment per electron, P = spin polarization, $n \uparrow (E_F)$ = spin up and $n \downarrow (E_F)$ = spin down electrons density at Fermi level.

4. CONCLUSION

The bulks of copper oxides Cu_2O and CuO are transition-metal p-type semiconductors in general and the high- T_C , superconductors in particular. They show dia-magnetic and anti ferromagnetic behaviors as experimentally and theoretically. In the present calculations using ATK-DFT have found that nanoclusters of bulks Cu_2O and CuO found as half-metal ferromagnetic nano- materials, the clusters $(Cu_2O)_1$, $(Cu_2O)_3$ and $(CuO)_2(CuO)_6$ as semiconductors behave as diamagnetic and anti ferromagnetic nano-materials respectively. The magnetic moments of clusters $(Cu_2O)_2$ and $(CuO)_4$ have found to be $0.28\mu_B$ and $0.03\mu_B$ respectively with spin polarization unity. The total maximum energy and also binding energy increase with increasing number of atoms or molecules in these nano-clusters. Similarly, the bond length between Cu-O is found to be directly proportional to the number of atoms / molecules . It clarifies the stability of nanocluster depends on its number of atoms tend towards bulk properties. They can be used in various environmental processes, health hazards and synthesis of technological materials gas sensors etc..

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