

Density Functional Theory Investigation for Sodium Atom on Copper Clusters

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Abstract: *Density functional theory has been performed for NaCu_n clusters, ($n=4, 5, 6, 7$). Optimization plus frequency at the ground state level, B3LYP, 3-21G basis sets has been investigated. The charges for all clusters are equal to zero (neutral charges). Molecular orbital theory has been used to find HOMO and LUMO energies. Total energy, dipole moment have been computed. Koopman's theorem has been used to calculate the ionization potential and electron affinity. Also the electronegativity has been evaluated for sodium atom, pure copper clusters and NaCu_n clusters. Surfaces (HOMO and LUMO) and contours (electrostatic potential) have been carried out. All calculations have been investigated by using Gaussian 09 software package.*

Keywords: DFT, B3LYP, Koopman's theorem, Total Energy, Dipole moment, Electronegativity.

1. Introduction

1.1 Density Functional Theory (DFT)

DFT is a computational quantum mechanical modeling method used in physics, chemistry and material science to investigate the electronic structure (principally the ground state) of many body systems, in particular atoms, molecules and condensed phases[1][2]. With this theory the properties of a many electron system can be determined by using functional i.e. functions of another function which in this case is the spatially dependent electron density [3]. Hence the name density functional theory comes from the use of functional of the electron density [4]. DFT is among the most popular and versatile methods available in condensed-matter physics, computational physics and computational chemistry[5]. DFT has been very popular for calculations in solid state physics since 1970s[6]. However, DFT was not considered accurate enough for calculations in quantum chemistry until the 1990s, when the approximations used in the theory were greatly refined to better model the exchange and correlation interactions[7][8]. In many cases the results of DFT calculations for solid state systems agree quite satisfactorily with experimental data[9]. Computational costs relatively low when compared to traditional methods such as Hartree Fock theory and its descendants based on the complex many electron wave function despite recent improvements [10].

1.2. Basis Sets

A basis set in theoretical and computational chemistry is a set of functions called basis functions which are combined in linear combinations (generally as part of quantum chemical calculations) to create molecular orbitals[11]. For convenience these functions are typically atomic orbitals centered on atoms, but can theoretically be any function plane waves are frequently used in material calculations [12][13]. 3-21G means three Gaussian Type Orbitals for

inner shell, two Gaussian Type Orbitals for inner valence and one Gaussian Type Orbital for outer valence [14]. B3LYP means Becke three parameter Lee-Yang-Parr and it has been called the hybridization method to obtain the approximations of DFT. This method was introduced by Axel Becke in 1993 to describe correlation-exchange energies[15].

1.3. Geometry Optimization

Geometry optimization is name for the procedure that attempt to find the configuration of minimum energy of the molecule[16]. The procedure calculates the wave function and the energy at starting geometry and then proceeds to search a new geometry of a lower energy. This is repeated until the lowest energy geometry is found the procedure calculates the force on each atom by evaluating the gradient (first derivative) of the energy with respect to atomic positions sophisticated algorithms are then used at each step to select a new geometry[17]. Aiming for rapid convergence to the geometry of the lowest energy. In the final minimum energy geometry the force on each atom is zero[18]. It is important to recognize that this procedure will not necessarily find the global minimum i.e. the geometry with the lowest energy[19][20].

2. Molecular Structure

Optimization plus Frequency has been carried out to optimize sodium atom and pure copper clusters. Also Optimization plus Frequency has been applied to optimize sodium on copper clusters NaCu_n . DFT has been used at 3-21G, B3LYP basis sets at the ground state with Gaussian 09 software package. Below figures of the optimized sodium atom, pure copper clusters and NaCu_n copper clusters.

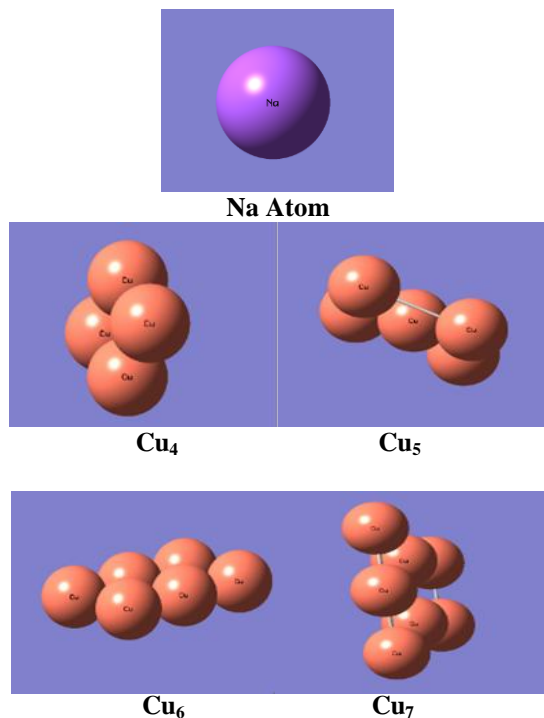


Figure 1

Molecular structure for Na atom and pure copper clusters.

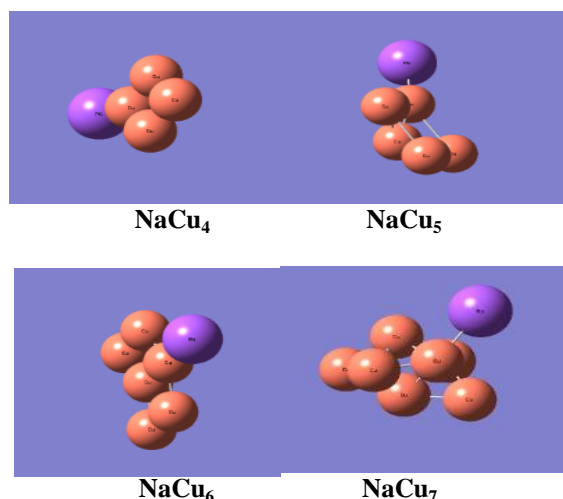


Figure 2

Molecular structure for NaCu_n clusters.

3. Calculations

3.1 Total energy

DFT partition the total energy as:

$$E = E_T + E_v + E_j + E_{xc} \quad \dots \dots (1)$$

E_T : electronic kinetic energy

E_v : electronuclear interaction energy

E_j : electron-electron repulsion

E_{xc} : exchange correlation term [21].

Total energy for Na atom, Cu_n, NaCu_n Clusters has been computed.

Table 1: Total energy for Na atom, Cu_n, NaCu_n Clusters

system	Total energy(eV)*10 ⁵
Na	-0.043881
Cu ₄	-1.7768
Cu ₅	-2.2210
Cu ₆	-2.6653
Cu ₇	-3.1095
NaCu ₄	-1.8207
NaCu ₅	-2.2650
NaCu ₆	-2.7092
NaCu ₇	-3.1535

3.2. Dipole Moment

Dipole moment appears in the heteronuclear molecules. Homonuclear molecules have very small dipole moment as compared with heteronuclear, some homogenous molecules have no dipole moment[22].

Table 2: Dipole moment for Na atom, Cu_n, NaCu_n Clusters

system	Dipole moment (Debye)
Na	0.0000
Cu ₄	0.0000
Cu ₅	0.0000
Cu ₆	0.0002
Cu ₇	0.4936
NaCu ₄	5.1930
NaCu ₅	4.5814
NaCu ₆	2.7313
NaCu ₇	4.7614

3.3. Electronic State

HOMO and LUMO energies represent the electronic states.

HOMO : High Occupied Molecular Orbital

LUMO : Low Unoccupied Molecular Orbital[23].

Table 3: Electronic states for Na atom, Cu_n, NaCu_n Clusters

system	E_{HOMO} (eV)	E_{LUMO} (eV)
Na	-3.4783	-0.5586
Cu ₄	-4.7435	-3.0992
Cu ₅	-4.4048	-2.5863
Cu ₆	-4.7854	-3.1349
Cu ₇	-4.1950	-3.0037
NaCu ₄	-3.9406	-2.4682
NaCu ₅	-4.3566	-3.0570
NaCu ₆	-3.4603	-2.7629
NaCu ₇	-4.7598	-2.8772

3.4. Ionization potential and electron affinity

The ionization energy of an atom or molecule describes the minimum amount of energy required to remove an electron (to infinity) from the atom or molecule in the gaseous state. Electron affinity is defined as the change in energy of a neutral atom in the gaseous phase when an electron is added to the atom to form a negative ion. In other words, the natural atom's likelihood of gaining an electron[24].

According to Koopman's theorem in which the frontier orbital energies are given as:

$$E_{HOMO} = -I.P \quad \dots \dots (2)$$

$$E_{LUMO} = -E.A \quad \dots \dots (3)$$

$I.P$: Ionization potential

E.A : electron affinity[25].

Table 4: Ionization potential and electron affinity for Na atom, Cu_n, NaCu_n Clusters

system	<i>I.P</i> (eV)	<i>E.A</i> (eV)
Na	3.4783	0.5586
Cu ₄	4.7435	3.0992
Cu ₅	4.4048	2.5863
Cu ₆	4.7854	3.1349
Cu ₇	4.1950	3.0037
NaCu ₄	3.9406	2.4682
NaCu ₅	4.3566	3.0570
NaCu ₆	3.4603	2.7629
NaCu ₇	4.7598	2.8772

3.5. Electronegativity and Chemical Potential

Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons[26]. Within the framework of DFT on of the global quantities are chemical potential (μ) which is measures the escaping tendency of an electronic cloud and the electronegativity (χ) which is characterized the escaping tendency of electrons from the equilibrium system (e.g.atoms or molecules). Let $E(N)$ represent a ground state electronic energy as a function of the number of electrons (N). It is well-known the derivative of $E(N)$ with respect to (N) at a constant external potential $V(r)$ is the chemical potential or the negative of the absolute negativity. where:

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{V(r)} \approx -\chi \quad \dots\dots\dots(4)$$

The electronegativity can be done by using the method which is based on the difference between the energies of HOMO and LUMO of the neutral molecules and is known as orbital vertical.

$$\chi = \frac{E_{HOMO} + E_{LUMO}}{2} \dots\dots\dots(5)$$

Or by using the equation:

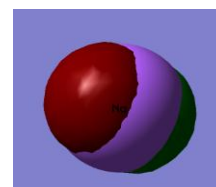
$$\chi = \frac{I.P + E.A}{2} \dots\dots\dots(6)[27].$$

Table 5: Eletronegativity for Na atom, Cu_n, NaCu_n Clusters

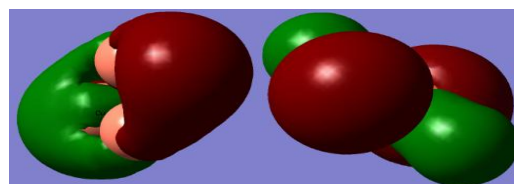
system	Electronegativity
Na	2.0184
Cu ₄	3.9214
Cu ₅	3.4955
Cu ₆	3.9601
Cu ₇	3.5993
NaCu ₄	3.2044
NaCu ₅	3.7068
NaCu ₆	3.1116
NaCu ₇	3.8125

4. Surfaces and Contours

Surfaces have been carried out by using molecular orbitals for HOMO and LUMO orbitals. Contours have been carried out with electrostatic potential type (ESP).

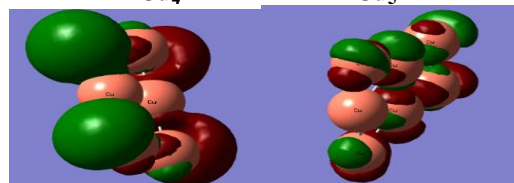


Na atom



Cu₄

Cu₅

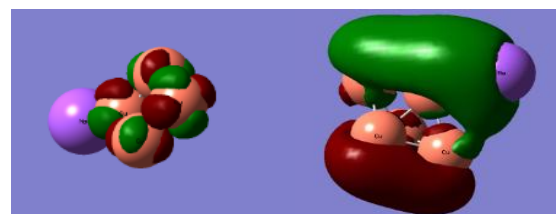


Cu₆

Cu₇

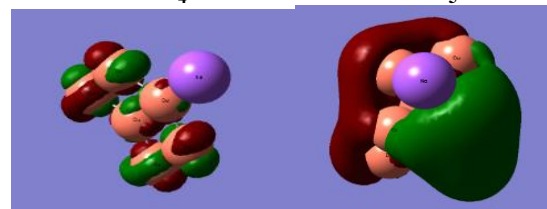
Figure (3)

HOMO surfaces for Na atom and pure copper clusters.



NaCu₄

NaCu₅

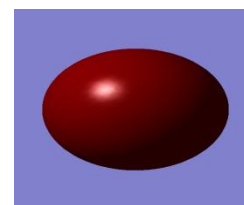


NaCu₆

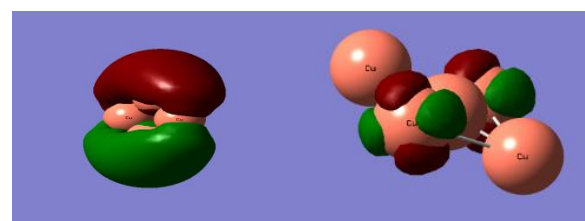
NaCu₇

Figure 4

HOMO surfaces for NaCu_n clusters.



Na atom



Cu₄

Cu₅

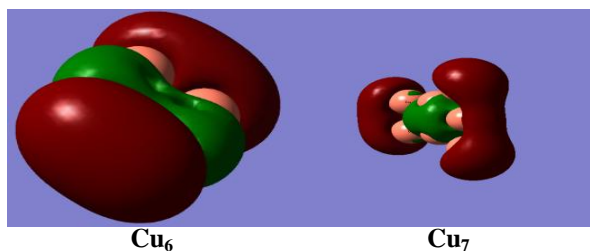


Figure 5

LUMO surfaces for sodium atom and pure copper clusters.

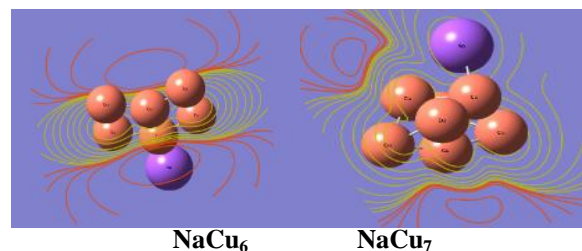
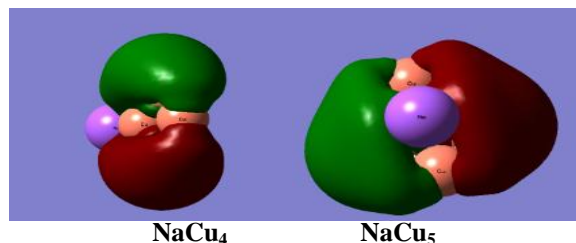


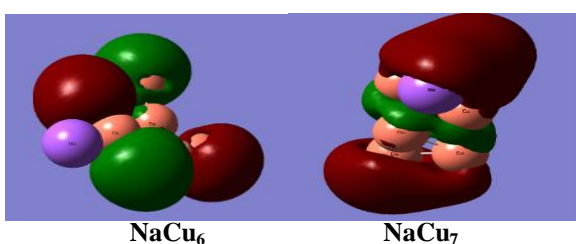
Figure 8

Contours for NaCu_n clusters.



NaCu_4

NaCu_5

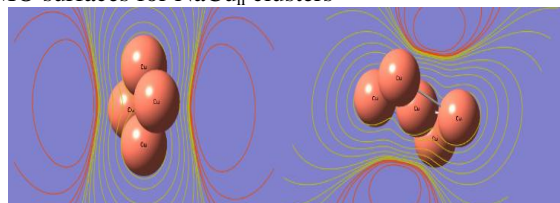


NaCu_6

NaCu_7

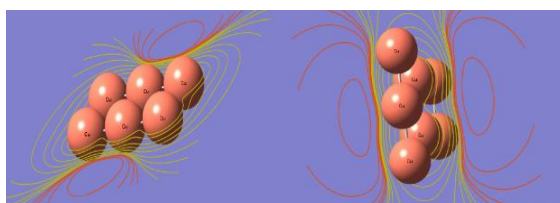
Figure 6

LUMO surfaces for NaCu_n clusters



Cu_4

Cu_5

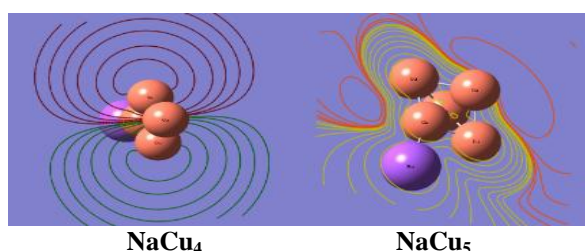


Cu_6

Cu_7

Figure 7

Contours for copper clusters.



NaCu_4

NaCu_5

5. Results and Discussion

Table (1) represents the total energy for Na atom, Cu_n clusters, NaCu_n clusters. The total energy for NaCu_n clusters is less than the total energy for sum of the individual Na atom plus individual Cu_n clusters, and this means that the molecules have been resulted and the bonding between sodium atom and copper clusters has been found. this results agree with results of the molecular physics[28][29].

Table(2) represents the dipole moment for Na atom, Cu_n clusters, NaCu_n clusters. The dipole moment for Cu_4, Cu_5 clusters equal to zero, so this molecules have no dipole moment. The dipole moment for Cu_6 equal to (0.0002 Debye), so this molecule has very small dipole moment. The dipole moment for Cu_7 equal to (0.4936 Debye), so this molecule has small dipole moment. In general the dipole moment for Cu_n clusters is much smaller than the dipole moment for NaCu_n clusters, as shown in table (2), for example, the dipole moment for NaCu_4 cluster equal to (5.1930 Debye), the dipole moment for (NaCu_5) equal to (4.5814 Debye). Cu_n clusters are homonuclear, thus these molecules have no interact with the electromagnetic rays and don't give rotational spectrum, so these molecules don't have dipole moment changes during the rotation. But NaCu_n clusters have dipole moment varies during the rotation and this dipole moment generates because this molecules heteronuclear, so this molecules have a rotation and during process of absorption the molecule to the radiation the dipole moment interact with the electric field of the electromagnetic rays, so the rotation has been generated with the dipole moment.

This results are in general agreement with the basics of the spectroscopy science[30][31].

Table(3) stands for HOMO and LUMO energies for Na atom, Cu_n clusters, NaCu_n clusters. HOMO energies for copper clusters is higher than the HOMO energies for sodium atom, so the electrons will release to the unoccupied orbitals, therefore, copper represents the accepto, sodium represents the donor . and this results are in a good agreement with that obtained from reference [32].

Table(4) stands for the ionization potential and electron affinity for Na atom, Cu_n clusters, NaCu_n clusters. the ionization potential is close to work function for the solid Cu[33]. The work function for the transition metals decrease dramatically when the alkali-metal adds to transition metal, also adding alkali-metal to transition metals tend to

adsorption the alkali metal on the transition metal, and this procedure causes reduction of the work function of the transition metals. The correlation obtained only between the covalent electrons i.e. between 3s in Na and 4s in Cu. The size of cluster affect on the work function and this is very clearly in table(4), note that the work function of NaCu₇ closes to the work function of Cu₄, and this means when we increase the number of Cu atoms in NaCu_n clusters, the work function of NaCu_n back to similar the work function of the pure copper clusters. So the values of the work function of Cu_n clusters decreases when we add sodium atom to Cu_n clusters except NaCu₇ and this is because of increasing number of copper atoms with respect to sodium. Many experimental and theoretical works have been devoted to investigating Cu clusters[34][35][36]. The experimental data for copper approximately (4.59eV)[37].

Table(5) represents the electronegativity for Na atom, Cu_n clusters, NaCu_n clusters. Note that the electronegativity for Cu_n clusters is greater than the electronegativity of Na atom so sodium atom will adsorb on copper clusters. Although copper and sodium are metals and they have a low electronegativity because all metals have low electronegativity but the atomic size of Na is greater than the atomic size for Cu, thus sodium will adsorb on copper clusters because the electronegativity decrease as the atomic size increase.

This result agree with basics of physical chemistry [38].

6. Conclusions

When we use density functional theory at ground state level with B3LYP, 3-21G basis sets for Na atom, Cu_n clusters, NaCu_n clusters, we conclude that the sodium atom adsorbs on copper clusters, we know this through the values HOMO energies because the molecule which has high HOMO energy release the electrons to the unoccupied orbitals. also we conclude the work function decrease when we add alkali-metal to transition metal except NaCu₇ cluster, the work function for NaCu₇ closes to Cu₄ cluster. another quantity prove that sodium atom adsorbs on copper clusters is the electronegativity, all copper clusters have electronegativity greater than Na atom, and this means sodium adsorbs on copper.

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