# Geometrical Optimization and Some Physical Properties For Sodium on Copper Clusters

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***Abstract:*** *The optimized coordinates has been investigated at ground state, B3LYP, 3-21G basis sets with density functional theory (DFT). Also geometrical parameters such as bond lengths, bond angles and dihedral angles have been calculated by using (DFT) at ground state with B3LYP, 3-21G basis sets. Polarizability and density of states(DOS) also performed for pure copper clusters and also for sodium on copper clusters. $NaCu_6$ cluster has the highest polarizability($\alpha=398.6493a.u$) and this means this cluster is more active than the other clusters because of the highest polarizability means the highest activity. Infrared spectra has been carried out for pure copper clusters and also for sodium on copper clusters. So in $NaCu_6$ cluster shielding procedure has been occurred. All calculations have been investigated by using Gaussian 09 program.*
***Keywords:*** *Geometrical optimization, DFT, Polarizability, density of states, Infrared spectra.*

## I. Introduction

### 1.1. Density Functional Theory:

Density functional theory method becomes more and more popular because of the obtaining results are comparable to the ones obtained using the other methods, however CPU time is drastically reduced[1]. DFT differs from that the methods based on Hartree Fock calculations in the way that the electron density that it is used to compute the energy instead of the wave function[2]. DFT was introduced in the two seminal papers in the 60's by Hohenberg-Kohn in 1964 and Kohn-Sham in 1965[3]. DFT predicts a great variety of molecular properties, molecular structure, vibrational frequencies[4]. in this original formulation, the density functional theory provides the ground state properties of a system, and the electron density plays a key role[5].

### 1.2. Basis Sets:

A basis set is a set of wave functions that describes the shape orbitals(AOs). The molecular orbitals are computed by using the selecting theoretical model by linearly combining the AOs (LCAO)[6]. Density functional theory requires abasis set specification. The level of approximation of the calculation is directly related to the basis set used[7]. The choice to make is trade-off between accuracy of results and CPU time[8]. B3LYP is the most popular DFT model, this method called to be a hybrid, because of using corrections for both gradient and exchange correlations[9]. The basis set 3-21G represents three Gaussian Type Orbitals for inner shell, two Gaussian Type Orbitals for inner valence and one Gaussian Type Orbital for outer valence[10].

## II. Molecular Geometry

Optimization and Frequency has been used to obtain the molecular structure for Na atom, copper clusters($Cu_n$) and also for sodium on copper clusters($NaCu_n$), (n= 4,5,6,7). Density functional theory has been carried out to investigate the molecular geometry for copper clusters($Cu_n$) and also for sodium on copper clusters($NaCu_n$). Becke three Parameter Lee-Yang-Parr, three Gaussian Type Orbitals for inner shell, two Gaussian Type Orbitals for inner valence and one Gaussian Type Orbital for outer valence basis sets has been applied at the ground state to geometry optimized the molecular structure for Na atom, $Cu_n$ clusters, $NaCu_n$ clusters. The following figures stand fot the molecular structure for Na atom, $Cu_n$ clusters, $NaCu_n$ clusters.



| Na atom | Cu₄ | Cu₅ | Cu₆ | Cu₇ |
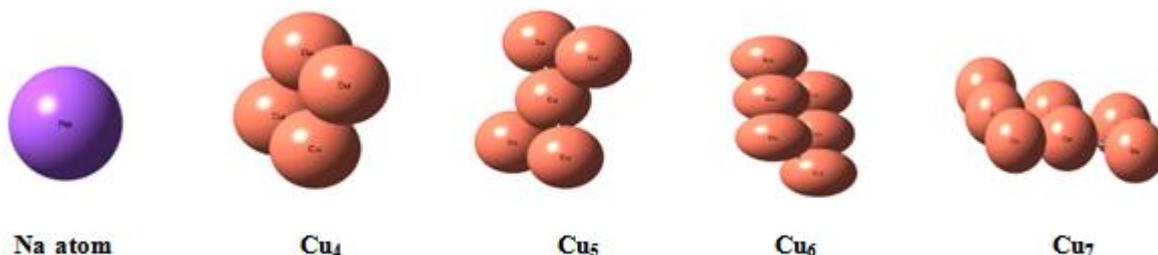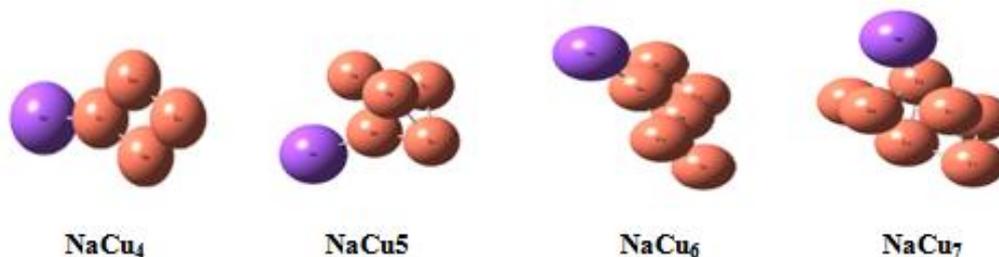
**Figure(1):** Molecular structure For Na atom, $Cu_n$ Clusters, $NaCu_n$ Clusters**.**

## III. Calculations

### 3.1. The optimized coordinates:

In this procedure it has been found the configuration of minimum energy for the clusters[11]. the force on each atom was calculated during the procedure[12]. by computing the gradient (first derivative) of the energy with respect to atomic positions to converge to the geometry of the lowest energy[13]. Also, the second derivative with respect to atomic positions have been applied by using sophisticated algorithms with Gaussian 09 software package[14]. The geometry optimization stops when the force resultant on atoms equal to zero[15]. The optimized coordinates stand for the positions of atoms in the molecule in space, the best optimized positions have been gotten during geometry optimization[16].

**Table 1:** The optimized coordinates for $Cu_4$ Cluster.

| atom | X($A^o$) | y($A^o$) | z($A^o$) |
|---|---|---|---|
| Cu1 | 0.000000 | 1.069763 | 0.000000 |
| Cu2 | 0.000000 | 0.000000 | 1.777227 |
| Cu3 | 0.000000 | 0.000000 | -1.777227 |
| Cu4 | 0.000000 | -1.069763 | 0.000000 |

**Table 2:** The optimized coordinates for $Cu_5$ Cluster.

| atom | X($A^o$) | y($A^o$) | z($A^o$) |
|---|---|---|---|
| Cu1 | 0.000000 | 1.977795 | 0.000000 |
| Cu2 | 0.000000 | 0.000000 | 2.081241 |
| Cu3 | 0.000000 | 0.000000 | 0.000000 |
| Cu4 | 0.000000 | 0.000000 | -2.081241 |
| Cu5 | 0.000000 | -1.977795 | 0.000000 |

**Table 3:** The optimized coordinates for $Cu_6$ Cluster.

| atom | X($A^o$) | y($A^o$) | z($A^o$) |
|---|---|---|---|
| Cu1 | 1.026808 | 0.000000 | 0.000000 |
| Cu2 | -1.026931 | 0.000000 | 0.00000 |
| Cu3 | 1.023593 | 2.041750 | 0.000000 |
| Cu4 | 1.023593 | -2.041750 | 0.000000 |
| Cu5 | -1.023531 | 2.041765 | 0.000000 |
| Cu6 | -1.023531 | -2.041765 | 0.000000 |

**Table4:** The optimized coordinates for $Cu_7$ Cluster.

| atom | X($A^o$) | y($A^o$) | z($A^o$) |
|---|---|---|---|
| Cu1 | 0.000000 | 2.093143 | 1.566297 |
| Cu2 | 0.00000 | -2.093143 | 1.566297 |
| Cu3 | 0.000000 | 1.052217 | -0.198354 |
| Cu4 | 0.000000 | -1.052217 | -0.198354 |
| Cu5 | 0.000000 | 0.000000 | 1.731545 |
| Cu6 | 0.000000 | 1.042138 | -2.233716 |
| Cu7 | 0.000000 | 1.042138 | -2.233716 |

**Table5:** The optimized coordinates for $NaCu_4$ Cluster.

| atom | X($A^o$) | y($A^o$) | z($A^o$) |
|---|---|---|---|
| Cu1 | 0.000000 | 1.117883 | -0.359355 |
| Cu2 | 0.000000 | 0.000000 | -1.340762 |
| Cu3 | 0.000000 | 0.000000 | 2.075369 |
| Cu4 | 0.000000 | -1.117883 | 0.359355 |
| Na | 0.000000 | 0.000000 | -3.831471 |

**Table6:** The optimized coordinates for NaCu$_5$ Cluster.

| atom | X(A°) | y(A°) | z(A°) |
|------|-------|-------|-------|
| Cu1 | 0.998971 | -1.309077 | -0.000439 |
| Cu2 | -0.801787 | -0.598485 | -1.031978 |
| Cu3 | -0.800277 | -0.597091 | 1.033404 |
| Cu4 | 0.712842 | 0.746898 | -0.000185 |
| Cu5 | -1.267269 | 1.284219 | -0.000602 |
| Na | 3.051644 | 1.248415 | -0.000528 |

**Table7:** The optimized coordinates for NaCu$_6$ Cluster.

| atom | X(A°) | y(A°) | z(A°) |
|------|-------|-------|-------|
| Cu1 | 0.000000 | 0.000000 | -0.660241 |
| Cu2 | 0.000000 | 0.000000 | 1.421643 |
| Cu3 | 0.000000 | 1.777729 | -1.607760 |
| Cu4 | 0.000000 | -1.777729 | -1.607760 |
| Cu5 | 0.000000 | 1.880172 | 0.487758 |
| Cu6 | 0.000000 | -1.880172 | 0.487758 |
| Na | 0.000000 | 0.000000 | 3.898135 |

**Table8:** The optimized coordinates for NaCu$_7$ Cluster.

| atom | X(A°) | y(A°) | z(A°) |
|------|-------|-------|-------|
| Cu1 | -0.580652 | 1.226028 | -0.360498 |
| Cu2 | -2.228283 | -0.086815 | -0.665908 |
| Cu3 | 0.738830 | 0.257753 | 1.065707 |
| Cu4 | -0.342194 | -1.100803 | -0.383696 |
| Cu5 | -1.326344 | -0.110943 | 1.308779 |
| Cu6 | 1.124500 | 0.251164 | -1.208458 |
| Cu7 | 1.800689 | -1.283461 | 0.117560 |
| Na | 2.144440 | 2.249022 | 0.333555 |

## 3.2. Geometrical parameters:

The geometrical parameters that were calculated in this paper: bond lengths, bond angles and dihedral angles. Bond length represents the average distance between nuclei of two bonded atoms in a molecule[17]. Molecular geometry depends on orbital configuration with respect to other through center of the atom, in other words depends on angles, which the orbitals make between them angles in space through center of the atom, this angles called bond angles[18]. Dihedral angle is the angle between two planes, this angle can be seen at edge on levels along intersection line[19].

**Table9:** Geometrical Parameters for Cu$_4$ Cluster.

| Bond Length(A°) | | Bond Angle(Degree) | | Dihedral Angle(Degree) | |
|------|-------|------|-------|------|-------|
| Bond | Value | Bond | Value | Bond | Value |
| R(1,2) | 2.0743 | A(2,1,3) | 117.9102 | D(3,1,2,4) | 0.0 |
| R(1,3) | 2.0743 | A(1,2,4) | 62.0898 | D(2,1,3,4) | 0.0 |
| R(2,4) | 2.0743 | A(1,3,4) | 62.0898 | D(1,2,4,3) | 0.0 |
| R(3,4) | 2.0743 | A(2,4,3) | 117.9102 | D(1,3,4,2) | 0.0 |

**Table10:** Geometrical Parameters for Cu$_5$ Cluster.

| Bond Length(A°) | | Bond Angle(Degree) | | Dihedral Angle(Degree) | |
|------|-------|------|-------|------|-------|
| Bond | Value | Bond | Value | Bond | Value |
| R(1,2) | 2.8711 | A(2,1,4) | 92.9198 | D(4,1,2,5) | 0.0 |
| R(1,3) | 1.9778 | A(1,2,5) | 87.0802 | D(2,1,4,5) | 0.0 |
| R(1,4) | 2.8711 | A(1,4,5) | 87.0802 | D(1,5,2,4) | 0.0 |
| R(2,3) | 2.0812 | A(2,5,4) | 92.9198 | D(1,4,5,2) | 0.0 |
| R(2,5) | 2.8711 | | | | |
| R(3,4) | 2.0812 | | | | |
| R(3,5) | 1.9778 | | | | |
| R(4,5) | 2.8711 | | | | |

**Table11:** Geometrical Parameters for Cu$_6$ Cluster.

| Bond Length(A°) | | Bond Angle(Degree) | | Dihedral Angle(Degree) | |
|------|-------|------|-------|------|-------|
| Bond | Value | Bond | Value | Bond | Value |
| R(1,2) | 2.0537 | A(2,1,3) | 89.9098 | D(3,1,2,5) | 0.0 |
| R(1,3) | 2.0418 | A(2,1,4) | 89.9098 | D(3,1,2,6) | 180.0 |
| R(1,4) | 2.0418 | A(1,2,5) | 89.9046 | D(4,1,2,5) | 180.0 |
| R(2,5) | 2.0418 | A(1,2,6) | 89.9046 | D(4,1,2,6) | 0.0 |
| R(2,6) | 2.0418 | A(1,3,5) | 90.0906 | D(2,1,3,5) | 0.0 |

| R(3,5) | 2.0417 | A(1,4,6) | 90.0906 | D(5,3,4,6) | 0.0 |
| R(4,6) | 2.0417 | A(2,5,3) | 90.095 | D(2,1,4,6) | 0.0 |
| | | A(2,6,4) | 90.095 | D(1,2,5,3) | 0.0 |
| | | | | D(3,5,6,4) | 0.0 |
| | | | | D(1,2,6,4) | 0.0 |
| | | | | D(1,3,5,2) | 0.0 |
| | | | | D(1,4,6,2) | 0.0 |

**Table12:** Geometrical Parameters for Cu$_7$ Cluster.

| Bond Length(A°) | | Bond Angle(Degree) | | Dihedral Angle(Degree) | |
|---|---|---|---|---|---|
| Bond | Value | Bond | Value | Bond | Value |
| R(1,2) | 4.1863 | A(2,1,3) | 59.4646 | D(3,1,2,4) | 0.0 |
| R(1,3) | 2.0488 | A(1,2,4) | 59.4646 | D(2,1,3,4) | 0.0 |
| R(1,5) | 2.0997 | A(1,3,4) | 120.5354 | D(2,1,6,7) | 0.0 |
| R(2,4) | 2.0488 | A(4,3,6) | 89.7163 | D(1,2,4,3) | 0.0 |
| R(2,5) | 2.0997 | A(5,3,6) | 151.1163 | D(1,2,7,6) | 0.0 |
| R(3,4) | 2.1044 | A(2,4,3) | 120.5354 | D(1,3,4,2) | 0.0 |
| R(3,5) | 2.1981 | A(3,4,7) | 89.7163 | D(1,3,4,7) | 180.0 |
| R(3,6) | 2.0354 | A(5,4,7) | 151.1163 | D(6,3,4,2) | 180.0 |
| R(4,5) | 2.1981 | A(3,6,7) | 90.2837 | D(6,3,4,7) | 0.0 |
| R(4,7) | 2.0354 | A(4,7,6) | 90.2837 | D(4,3,6,7) | 0.0 |
| R(6,7) | 2.0843 | | | D(5,3,6,7) | 0.0 |
| | | | | D(3,4,7,6) | 0.0 |
| | | | | D(5,4,7,6) | 0.0 |
| | | | | D(3,6,7,4) | 0.0 |

**Table13:** Geometrical Parameters for NaCu$_4$ Cluster.

| Bond Length(A°) | | Bond angle(Degree) | | Dihedral Angle(Degree) | |
|---|---|---|---|---|---|
| Bond | Value | Bond | Value | Bond | Value |
| R(1,2) | 2.0347 | A(2,1,3) | 113.5919 | D(3,1,2,4) | 0.0 |
| R(1,3) | 2.048 | A(1,2,4) | 66.6525 | D(3,1,2,5) | 180.0 |
| R(2,4) | 2.0347 | A(1,2,5) | 146.6738 | D(2,1,3,4) | 0.0 |
| R(2,5) | 2.2907 | A(4,2,5) | 146.6738 | D(1,2,4,3) | 0.0 |
| R(3,4) | 2.048 | A(1,3,4) | 66.1638 | D(5,2,4,3) | 180.0 |
| | | A(2,4,3) | 113.5919 | D(1,3,4,2) | 0.0 |

**Table14:** Geometrical Parameters for NaCu$_5$ Cluster.

| Bond Length(A°) | | Bond angle(Degree) | | Dihedral Angle(Degree) | |
|---|---|---|---|---|---|
| Bond | Value | Bond | Value | Bond | Value |
| R(1,2) | 2.1963 | A(2,1),4) | 64.2815 | D(4,1,2,5) | -27.4338 |
| R(1,3) | 2.1939 | A(1,2,5) | 103.3415 | D(2,1,4,5) | 31.4524 |
| R(1,4) | 2.0758 | A(1,3,5) | 103.3233 | D(2,1,4,6) | -148.5232 |
| R(2,3) | 2.0654 | A(2,3,4) | 63.0031 | D(1,2,5,4) | 27.7024 |
| R(2,5) | 2.1966 | A(1,4,5) | 113.1051 | D(2,3,4,6) | -128.7751 |
| R(3,4) | 2.2725 | A(1,4,6) | 94.1799 | D(1,4,5,2) | -31.3105 |
| R(3,5) | 2.1969 | A(3,4,6) | 140.8153 | D(6,4,5,2) | 148.6363 |
| R(4,5) | 2.0517 | A(5,4,6) | 152.715 | | |
| R(4,6) | 2.392 | A(2,5,4) | 64.6031 | | |

**Table15:** Geometrical Parameters for NaCu$_6$ Cluster.

| Bond Length(A°) | | Bond angle(Degree) | | Dihedral Angle(Degree) | |
|---|---|---|---|---|---|
| Bond | Value | Bond | Value | Bond | Value |
| R(1,2) | 2.819 | A(2,1,3) | 118.0573 | D(3,1,2,5) | 0.0 |
| R(1,3) | 2.0145 | A(2,1,4) | 118.0573 | D(3,1,2,6) | 180.0 |
| R(1,4) | 2.0145 | A(3,1,4) | 123.8853 | D(4,1,2,5) | 180.0 |
| R(2,5) | 2.0993 | A(1,2,5) | 63.5863 | D(4,1,2,6) | 0.0 |
| R(2,6) | 2.0993 | A(1,2,6) | 63.5863 | D(2,1,3,5) | 0.0 |
| R(2,7) | 2.4765 | A(5,2,6) | 127.1726 | D(4,1,3,5) | 180.0 |
| R(3,5) | 2.098 | A(5,2,7) | 116.4137 | D(2,1,4,6) | 0.0 |
| R(4,6) | 2.098 | A(6,2,7) | 116.4137 | D(3,1,4,6) | 180.0 |
| | | A(1,3,5) | 64.7414 | D(1,2,5,3) | 0.0 |
| | | A(1,4,6) | 64.7414 | D(6,2,5,3) | 0.0 |
| | | A(2,5,3) | 113.6149 | D(7,2,5,3) | 180.0 |
| | | A(2,6,4) | 113.6149 | D(1,2,6,4) | 0.0 |
| | | | | D(5,2,6,4) | 0.0 |

| | | | | D(7,2,6,4) | 180.0 |
|---|---|---|---|---|---|
| | | | | D(1,3,5,2) | 0.0 |
| | | | | D(1,4,6,2) | 0.0 |

**Table16:** Geometrical Parameters for NaCu$_7$ Cluster.

| Bond Length(A°) | | Bond angle(Degree) | | Dihedral Angle(Degree) | |
|---|---|---|---|---|---|
| Bond | Value | Bond | Value | Bond | Value |
| R(1,2) | 2.125 | A(2,1,3) | 107.0639 | D(3,1,2,4) | -36.017 |
| R(1,3) | 2.1682 | A(1,2,4) | 65.977 | D(2,1,3,4) | 34.961 |
| R(1,5) | 2.2624 | A(1,3,4) | 63.5234 | D(2,1,3,6) | 100.5176 |
| R(2,4) | 2.1599 | A(1,3,6) | 56.9411 | D(2,1,3,8) | 171.7307 |
| R(2,5) | 2.171 | A(1,3,8) | 78.4413 | D(1,2,4,3) | 33.5272 |
| R(3,4) | 2.2616 | A(4,3,6) | 56.3834 | D(1,2,4,7) | 9.9029 |
| R(3,5) | 2.1119 | A(4,3,8) | 123.3416 | D(1,3,4,2) | -33.5303 |
| R(3,6) | 2.3066 | A(5,3,6) | 106.0505 | D(1,3,4,7) | 135.2747 |
| R(3,8) | 2.545 | A(5,3,8) | 135.2193 | D(6,3,4,2) | -99.9096 |
| R(4,5) | 2.1938 | A(6,3,8) | 68.0534 | D(6,3,4,7) | 68.8953 |
| R(4,7) | 2.2083 | A(2,4,3) | 102.657 | D(8,3,4,2) | -86.9718 |
| R(6,7) | 2.1379 | A(2,4,7) | 156.3269 | D(8,3,4,7) | 81.8331 |
| | | A(3,4,7) | 55.9716 | D(6,3,5,2) | -6.9682 |
| | | A(5,4,7) | 107.3083 | D(8,3,5,2) | 67.8314 |
| | | A(1,5,4) | 63.1387 | D(1,3,6,7) | -152.1115 |
| | | A(2,5,3) | 107.4339 | D(4,3,6,7) | -74.0035 |
| | | A(3,6,7) | 56.1807 | D(5,3,6,7) | -109.4965 |
| | | A(4,6,7) | 59.53.6 | D(8,3,6,7) | 117.6303 |
| | | | | D(7,4,5,1) | 92.0647 |
| | | | | D(2,4,7,6) | -48.3881 |
| | | | | D(3,4,7,6) | -76.5385 |
| | | | | D(5,4,7,6) | -101.4676 |
| | | | | D(3,6,7,4) | 72.03 |

### 3.3. Polarizability($\alpha$):

   Polarizability describes ability of molecule for polarization[20]. Also polarizability determines the linear response of the electron density in the presence of an infinite seminal electric field F, and stands for a second order variation in the energy.

$$\alpha = -\left(\frac{\partial^2 E}{\partial F_a \partial F_b}\right)_{a,b} = x, y, z \dots \dots \dots (1)[21].$$

The mean polarizability $< \alpha >$ is evaluated by using the equation:

$$< \alpha > = \frac{1}{3}\left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right) \dots \dots .. (2).$$

Where $\alpha_{xx}, \alpha_{yy}, \alpha_{zz}$ are the eigen values of the polarizability tensor[22].

**Table16:** Polarizability for Na atom, Cu$_n$ Clusters, NaCu$_n$ Clusters.

| System | $\alpha_{xx}$ | $\alpha_{yy}$ | $\alpha_{zz}$ | $< \alpha >$ |
|---|---|---|---|---|
| Na | 152.529 | 152.529 | 152.529 | 152.529 |
| Cu$_4$ | 104.277 | 142.340 | 232.140 | 159.5857 |
| Cu$_5$ | 137.197 | 251.768 | 327.356 | 238.7737 |
| Cu$_6$ | 247.661 | 315.661 | 135.248 | 232.8567 |
| Cu$_7$ | 151.112 | 324.127 | 328.120 | 267.7863 |
| NaCu$_4$ | 139.827 | 219.171 | 425.778 | 261.5920 |
| NaCu$_5$ | 331.921 | 269.672 | 169.427 | 257.0067 |
| NaCu$_6$ | 230.692 | 339.437 | 625.819 | 398.6493 |
| NaCu$_7$ | 341.490 | 281.033 | 258.331 | 293.6180 |

### 3.4. Density of states:

         In solid state and condensed matter physics, the density of states(DOS) of a system describes the number of states per interval of energy at each energy level that are a vailable to be occupied[23]. A high density of state at a specific energy level means that there are many states available for occupation[24]. A density of state zero means that no state can be occupied at the energy level. In general a density of state is an average over the space and time domains occupied by the system[25]. In quantum mechanics systems, waves, or wave-like particles can occupy modes or states with wavelengths and propagation directions dictated by the system often only specific states are permitted[26]. In some systems the interatomic spacing and the atomic charge of the material allows only electrons of certain wavelengths to exist. In other systems, the crystalline

structure of the material allows waves to propagate in one direction while suppressing wave propagation in another direction[27]. Thus it can happen that many states are possible at a specific wavelength, and therefore at this associated energy, while no states are available at other energy levels, this distribution is characterized by the density of states[28] [29].
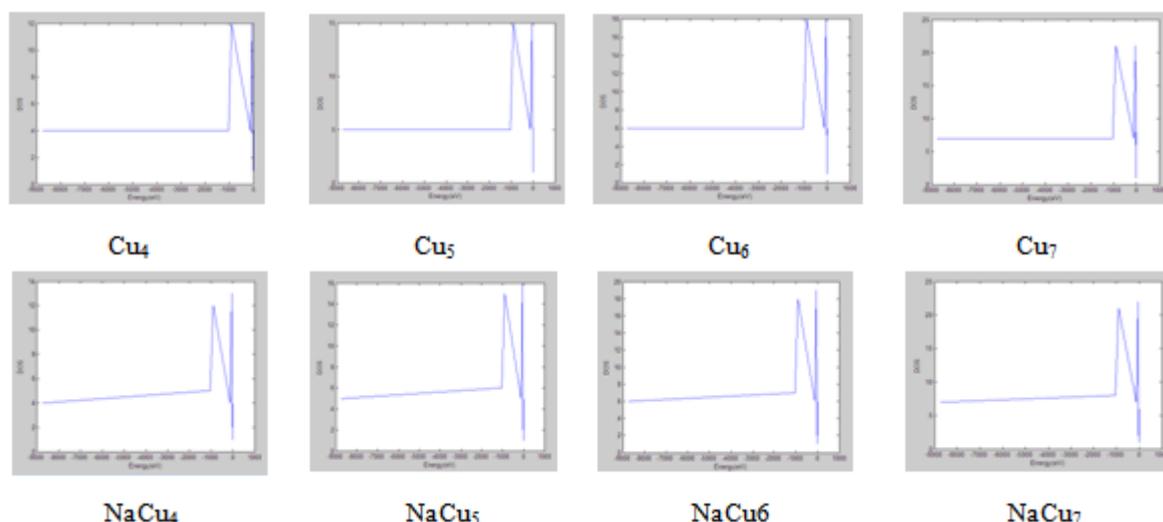


**Figure(2):** Density of States For $Cu_n$ Clusters, $NaCu_n$ Clusters.

## IV.    Infrared Spectra

The harmonic vibrational frequencies have been investigated for pure copper clusters and sodium on copper clusters, at ground state, B3LYP, 3-21G basis sets[30]. There are two types of stretching variations, symmetric and asymmetric, the symmetric stretching is happening when the same atoms vibrate in the same phase, and the asymmetric stretching is happening when the bonds vibrate in different phases[31].
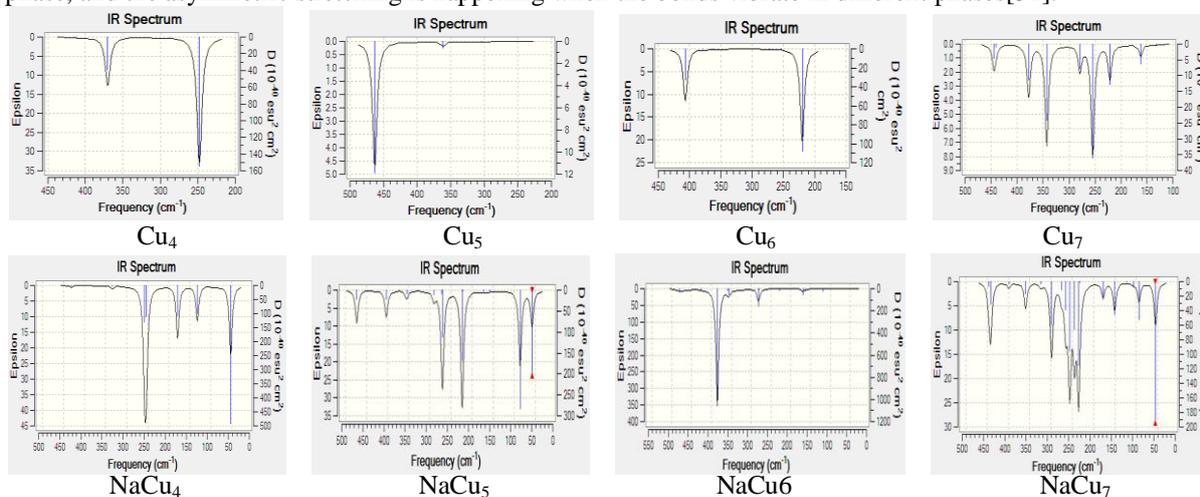


**Figure(3):** Infrared Spectra For $Cu_n$ Clusters, $NaCu_n$ Clusters.

## V.    Results And Discussion

Table(1)-Table(8) stands for optimized coordinates for $Cu_n$ clusters and $NaCu_n$ clusters by using DFT at ground state ,B3LYP,3-21G basis sets. The optimized coordinates have been   investigated by using sophisticated algorithms with Gaussian 09 program. This geometrical optimization stops when the program finds fixed point(static) and in this case the force resultant on the atom equal to zero. So, it has been seen there is no imaginary frequency and that means that using DFT at ground state ,B3LYP,3-21G basis sets is suitable for study the optimized coordinates for these clusters. Typically Gaussian 09 calculate the freguencies according to harmonic oscillator model(the second derivative with respect to nuclei movement). It is clear that from these tables the method that used to optimize coordinates in the present study had been used in[32].

Table(9)-Table(16) represents bond lengths($A^o$), bond angles(Degrees) and dihedral angles(Degrees) respectively. From these tables one can note small difference in bond lengths for $Cu_n$ clusters because these bond between atoms have the same atomic number. sometimes it has been seen there is difference between the

theoretical and experimental data, this occurs because the theoretical data deal with isolated molecules in gaseous phase, but experimental results study the molecules in solid state. Also positions of atoms affects on bond lengths. It has been observed when another atom have different atomic number i.e. $NaCu_n$ Clusters affect on geometrical parameters, for example it has been seen in $NaCu_7$ cluster there is small dihedral angle and this results from the electrostatic repulsion between atoms. Therefore adding alkali metal to transition metal affect on geometrical parameters, and this appears clearly in the tables. Also orbital hypridization cause difference in geometrical parameters. This method that used to optimize geometrical parameters in this paper had been used in [33].

Table(16) stands for polarizability for Na atom $Cu_n$ clusters, $NaCu_n$ clusters. it has been observed the difference number of atoms affect on the polarizability values, in this table it has been appeared that $NaCu_6$ cluster has the highest polarizability(398.6493a.u) and this means this cluster is more active than the other clusters because of the highest polarizability means the highest activity.the polarizability is very important property, it gives a sight about internal structure for the molecule. In general the polarizability increase with increasing of the size occupied with electrons. This results is in agreement with reference[34].

Figure(2) represents density of states for $Cu_n$ clusters and $NaCu_n$ clusters. A high density of state at an certain energy level means there is many available states to occupied. But when the density of state equal to zero, that means there is no available energy level to occupied. The local vibrations results from distortion of the original system and it is called local density of state(LDOS). If the density of state for a system undistributed is zero, LDOS will probably be not zero, and this is because of the local potential is found. When the electron energy increase, density of state increase, and many states become available to occupied. Also the topological properties affect on density of state. Density of states is a very important property in solid state physics. As one can see from this figures DOS become rise when sodium atom adds to $Cu_n$ clusters i.e in $NaCu_n$ clusters and this means there are many orbitals have been generated under approximately (-2 eV). This results is in general agreement with reference[35].

Figure(3) represent IR spectra for $Cu_n$ clusters and $NaCu_n$ clusters. IR spectra gives harmonic vibrational frequencies at B3LYP, 3-21G basis set. The number of atomic modes depend on number of atoms in the cluster. Each value or each range stands for vibration mode, the vibration either elastic or inelastic. In the figures it has been observed peaks, and the peaks refers to the bonds between atoms. Torsion vibrations appears at low frequencies. It has been seen also adding atoms to molecules affect on vibration modes and this is very clearly from tables. When we compare between $Cu_n$ clusters and $NaCu_n$ clusters it has been observed anew active groups because of adding sodium to copper. For example, $Cu_7$ cluster has seven clear peaks, but $NaCu_7$ cluster has ten clear peaks, so it is clearly, we see the effect of adding alkali metal to transition metal, from increasing of number of peaks which refers to existence of (Na-Cu bond) in $NaCu_n$ cluster. Also one can note after adding Na atom to $Cu_6$ cluster, structure $NaCu_6$ cluster has one clear peak since the geometrical optimization makes the interaction with at least two Cu atoms more than the other four atoms, and this limit peak appears because of the shielding procedure. And this results agree with reference [36].

## VI. Conclusions

Using DFT method, B3LYP, 3-21G basis set have been suitable to investigate the optimized coordinates and geometrical parameters for $Cu_n$ clusters and $NaCu_n$ clusters. The highest polarizability appears to $NaCu_6$ cluster($\alpha$=398.6493a.u) and this means $NaCu_6$ cluster have a highest activity than the other clusters. Density of state increase as the electron energy increase, and many states become available to occupied. So many orbitals generate under approximately(-2 eV) in $NaCu_n$ clusters. The topological properties affect on density of state.IR spectra appears existence new peaks in clusters belong to (Na-Cu bond) when sodium adds to copper clusters, i.e. in $NaCu_n$ clusters.

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## References

[1]. W. Koch and M. C. Holthausen, A chemist's guide to density functional theory: Wiley-VCH, 2000.
[2]. Vignale, G. Mark Rasolt (1987). "Density functional theory in strong magnetic fields". Physical Review Letters (American Physical Society) 59 (20): 2360-2363.
[3]. Grimme, Stefan (2006). "Semiemperical hyprid density functional with perturbative second order correlation". Journal of Chemical Physics 124 (3): 034108.
[4]. R. G. Parr, "Density functional theory," Annual Review of physical chemistry, vol. 16: Oxford university press, 1989.
[5]. M. Orio, D. A. Pantazis, and F. Neese,"Density functional theory," Photosynthesis research, vol. 102, pp. 433-453, 2009.
[6]. An introduction to computational chemistry using G09W and Avogadro software anna.tomberge@mail.mcgill.com.
[7]. Jensen, Frank(1999). Introduction to computational chemistry. JohnWiley and Sons. Pp. 68-77.
[8]. A. Frisch, Gaussian 09: User's Reference: Gaussian, 2009.

[9].    Carmer, Christopher J. (2002). Essential of Computational Chemistry. Chichester: John Wiley and Sons, Ltd. Pp. 154-168.
[10].   H.B. Schlegel (1982), J. Comput. Chem. 3, 214.
[11].   Trucks, M. J. G. W.; Schlegel, H. B. et al., Gaussian 09, Revision A.02, Gaussian, Inc., PA, Wallingford CT. 2009.
[12].   C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 , 785, 1988.
[13].   A.D. Becke, Phys. Rev. A 38 , 098, 19883.
[14].   A.D. Becke, J. Chem. Phys. 98, 5648, 1993.
[15].   M. Oftadeh, S. Naseh, M. Hamadanian, Computational and Theoretical Chemistry 966,20-25, 2011.
[16].   R. Chang "Basic principles of spectroscopy",  McGraw-Hill, New York (1971) .
[17].   "Fundamentals of molecular spectroscopy", (Mc Grow-Hill (1972).
[18].   ] King, G. W. (1964) Spectroscopy and Molecular Structure, Holt, Rinehart and Winston, New York.
[19].   F. K. Richtmyer, E-H-Kennard and J. N. Cooper, "Introduction to Modern Physics", Tata McGraw-Hill, 1976.
[20].   Elementary Solid State Physics Principles and Applications M.Ali Omar.
[21].   M. Oftadeh, S. Naseh, M. Hamadanian, Computational and Theoretical Chemistry 966.
[22].   P. Udhayakala, T. V. Rajendiran, S. Seshadri, and S. Gunasekaran, J. Chem. Pharm. Res., 3 (2011)610-625.
[23].   "Introduction to Solid State Physics", Charles Kittel.
[24].   J.S Blakemore, 1969, Solid State Physics, Philadelphia: W. B. Saunders.
[25].   P.L. Taylor, 1970, A Quantum Approach to Solid State, Englewood Cliffs, N. J. : Prentice-Hall.
[26].   j. Ziman, 1972, Principles of the Theory of Solids, second edition, Cambridge: Canbridge University Press.
[27].   F. C. Brown, 1967, The Physics of Solids, New York: W. A. Benjamin.
[28].   J. D. Patterson, 1971, Introduction to the Theory of Solid State Physics, Reading, Mass. : Addison-Wesley.
[29].   W. A. Harrison, 1970, Solid State Theory, New York: McGraw-Hill.
[30].   T. Clark, A handbook of computational chemistry: A practical guide to chemical structure and energy calculations: Wiley New York, 1985.
[31].   S. Gumus, Turk. J. Chem., 35, 803-808, 2011.
[32].   H.B. Schlegel, J. Comput. Chem. 3 (1982) 214.
[33].   Geometry Optimization And Energies of Donor-Bridge-Acceptor Molecular System, Ramla Abdulnaby, H. A. Abbod, Journal of Kufa-Physics, Vol.6/ No.1 (2014).
[34].   M. Oftadeh, S. Naseh and M. Hamadanian, Computational and theoretical chemistry, Chemical Physics Letters, 966(2011), 20-25.
[35].   Adachi T. and Sunada. T. (1993). "Density of states in spectral geometry of states in spectral geometry". Comment. Math. Helvetici **68**: 480–493.
[36].   Int. J. Pure Appl. Sci. Technol., 15(1) (2013), pp. 1-13, Mohsin K. AL-Khaykanee[1], and H. Ibrahim Aboud[2].