Geometrical Optimization and Electronic Properties of Li on Xn Nanoclusters

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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 optimized parameters such bond lengths, bond angles and dihedral angles have been calculated for all nanoclusters under study. Density of states (DOS) also performed for pure Xn nanoclusters, Lithium on Xn nanoclusters. Infrared spectra has been carried out for pure Xn nanoclusters and Lithium on Xn nanoclusters, in which (X = Copper (Cu), Chromium (Cr)) and (n = 4 , 6). Some electronically properties have been achieved in this study like electronic states, energy gap, ionization potential and electron affinity. All calculations have been investigated by using Gaussian 09 package.**

Index Terms— **DFT, Geometrical optimization, IR, Energy gap, DOS.**

INTRODUCTION

I. DENSITY FUNCTIONAL THEORY

DFT is one of the quantum mechanics methods which is used to investigate the electronic structure of atoms, molecules, nanoclusters and condensed phases and solid materials. DFT deals with systems, have many particles through the electron density. Electron density can be defined as the probability to determine locations of the electrons at certain space. Currently DFT considers very important to investigate the ground state properties of many body systems of materials, insulators and semiconductors. With DFT the properties of many electron systems can be expressed by using functional, i.e. functions of another function which in this case is the spatially dependent electron density. DFT is among the most popular and versatile methods available in computational physics and computational chemistry. DFT has become very popular the calculation in solid state physics since 1970's. DFT was not considered accurate enough for calculations in quantum chemistry until 1990's when the approximations used in the theory were greatly refined to better model the exchange and correlation interactions. In most cases, the results of DFT for solid state systems agree quite satisfactorily with experimental data. In DFT the electron density is used to calculate the energy instead of the wave function. However in DFT CPU time is drastically reduced [1-3].

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II. BASIS SETS

In general, the basis set is a collection of vectors which spans a space in which a problem is solved. The basis set in theoretical and computational chemistry is a set of functions which called basis functions. It is functional in which used to describe the shape of orbitals in atoms. In quantum chemistry the basis set usually refers to the sets of non-orthogonal one particle functions which is used to build molecular orbitals, in which the molecular orbitals result from linear combination of atomic orbitals. These functions are naturally atomic orbitals centered on atoms. The atomic orbital has one electron function. The choice must take accuracy of results and CPU time in account. Molecular orbitals and entire wave functions are created by linear combination of the basic functions and angular functions. Most semi-empirical methods use predefined basis sets. But DFT calculations require specified basis sets, i.e. in DFT methods the basis set should specify. B3LYP is the most popular DFT model, this method called to be a hybrid, because of using corrections for both gradient and exchange correlations. 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 [4-9].

III. GEOMETRY OPTIMIZATION

Geometry optimization is the name for the procedure that attempts to find the configuration of minimum energy of the molecule. The procedure finds the wave function and calculates the energy at starting geometry and then search a new geometry of a lower energy. This is repeated until the lowest energy geometry on the potential surface is found. The procedure evaluates the force on each atom by evaluating the gradient first derivative of the energy with respect to atomic positions (gradient), aiming for rapid convergence to the lowest energy geometry. Sophisticated algorithms are then used at each step to select a new geometry. Finally, in the minimum energy geometry, the force on each atom is zero. Typically, a successive search for a minimum finds a local minimum but not necessarily the lowest. In fact, the optimization procedure stops when it finds a stationary point, i.e. a point when the forces resultant on the atoms are zero, and this may be also a saddle point. If the symmetry of the molecule is restricted, it does not allow the program to search the full space of molecular configurationally degrees of freedom. It is always a good idea to start a procedure of a geometry optimization calculation with a small basis set and a relatively poor method before the movement of choice for a particular problem. It can then start the final geometry optimization from the geometry selected by the simpler and

less accurate approach. During the optimization, also the second derivatives of the energy with respect to atomic coordinates are used. Geometry optimization goals are to find the local minimum structure, the global minimum structure and the transition state structure. In the geometrical optimization procedure, the optimized coordinates and optimized parameters are investigated [10, 11].

MOLECULAR STRUCTURE

Optimization plus Frequency have been carried out to optimize Cr_4, Cu_4, Cr_6, Cu_6, $LiCr_4$, $LiCu_4$, $LiCr_6$, $LiCu_6$. DFT has been used at 3-21G and B3LYP basis sets at the ground state with Gaussian 09 software package.
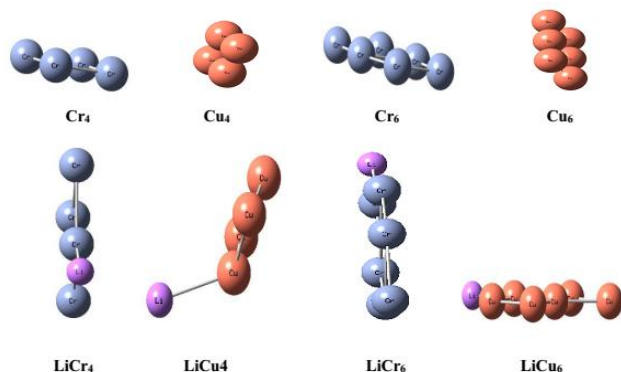

Figure. 1: Molecular structure for Cr_4, Cu_4, Cr_6, Cu_6, $LiCr_4$, $LiCu_4$, $LiCr_6$, $LiCu_6$ nanoclusters

CALCULATIONS

IV. THE OPTIMIZED COORDINATES

According to procedure, it has been found the configuration of minimum energy for the nanoclusters. The force on each atom was calculated during the procedure by evaluating the gradient (first derivative) of the energy with respect to atomic positions to converge to the lowest energy geometry. The second derivative with respect to atomic positions has been applied by using sophisticated algorithms with Gaussian 09 software package too. The geometry optimization stops when the force resultant on atoms equal to zero. The optimized coordinates stand for the positions of atoms in the nanocluster in the space. The best optimized positions have been found during geometry optimization [12].

Table. 1: The optimized coordinates for Cr_4 nanocluster.

atom	$X(A^o)$	$y(A^o)$	$z(A^o)$
Cr1	0.000000	1.292656	0.000000
Cr2	1.292656	0.000000	0.000000
Cr3	-1.292656	0.000000	0.000000
Cr4	0.000000	-1.292656	0.000000

Table. 2: The optimized coordinates for Cu_4 nanocluster.

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. 3: The optimized coordinates for Cr_6 nanocluster.

atom	$X(A^o)$	$y(A^o)$	$z(A^o)$
Cr1	0.000000	1.910010	0.875011
Cr2	0.000000	1.910010	-0.875011
Cr3	0.000000	0.000000	-1.121169
Cr4	0.000000	0.000000	1.121169
Cr5	0.000000	-1.910010	0.875011
Cr6	0.000000	-1.910010	-0.875011

Table. 4: The optimized coordinates for Cu_6 nanocluster.

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

Table. 5: The optimized coordinates for $LiCr_4$ nanocluster.

atom	$X(A^o)$	$y(A^o)$	$z(A^o)$
Cr1	0.000000	1.928579	0.003922
Cr2	0.000000	0.000000	1.514378
Cr3	0.000000	0.000000	-1.062895
Cr4	0.000000	-1.928579	0.003922
Li	0.000000	0.000000	-3.674611

Table. 6: The optimized coordinates for $LiCu_4$ nanocluster.

atom	$X(A^o)$	$y(A^o)$	$z(A^o)$
Cu1	-0.000732	1.014972	0.000000
Cu2	- 0.000732	-0.038782	1.768039
Cu3	-0.000732	-0.038782	-1.768039
Cu4	0.189400	-1.167259	0.000000
Li	-1.809654	2.221892	0.000000

Table. 7: The optimized coordinates for $LiCr_6$ nanocluster.

atom	$X(A^o)$	$y(A^o)$	$z(A^o)$
Cr1	0.000000	0.000000	3.438662
Cr2	0.000000	1.082084	1.206728
Cr3	0.000000	-1.082084	1.206728
Cr4	0.000000	1.354767	-1.159661
Cr5	0.000000	-1.354767	-1.159661
Cr6	0.000000	0.000000	-2.849291
Li	0.000000	0.000000	-5.468043

Table. 8: The optimized coordinates for $LiCu_6$ nanocluster.

atom	$X(A^o)$	$y(A^o)$	$z(A^o)$
Cu1	0.000000	0.000000	-0.536298
Cu2	0.000000	0.000000	1.599635
Cu3	0.000000	1.830474	-1.413589
Cu4	0.000000	- 1.830474	-1.413589
Cu5	0.000000	1.877476	0.685603
Cu6	0.000000	-1.877476	0.685603
Li	0.000000	0.000000	3.795463

V. Optimized parameters

The optimized parameters that were calculated in this study: bond lengths, bond angles and dihedral angles. Bond length represents the average distance between the nuclei of two bonded atoms in a molecule. Molecular geometry depends on the orbitals configuration with respect to other through center of the atom, in other words depends on angles, in which the orbitals make angles in space through center of the atom, this angles called bond angles. Dihedral angle is the angle between two planes, this angle can be watched at edge on levels along intersection line [13].

Table. 9: The optimized parameters for Cr4 nanocluster.

Bond Length(Ao)		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

Table. 10: The optimized parameters for Cu4 nanocluster

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

Table. 11: The optimized parameters for Cr6 nanocluster

Bond Length(A°)		Bond Angle(Degree)		Dihedral Angle(Degree)	
Bond	Value	Bond	Value	Bond	Value
R(1,2)	1.75	A(2,1,4)	97.3437	D(4,1,2,3)	0.0
R(1,4)	1.9258	A(1,2,3)	97.3437	D(2,1,4,3)	0.0
R(2,3)	1.9258	A(2,3,4)	82.6563	D(2,1,4,5)	0.0
R(3,4)	2.2423	A(2,3,6)	165.3126	D(1,2,3,4)	0.0
R(3,6)	1.9258	A(4,3,6)	82.6563	D(1,2,3,6)	0.0
R(4,5)	1.9258	A(1,4,3)	82.6563	D(2,3,4,1)	0.0
R(5,6)	1.75	A(1,4,5)	165.3126	D(2,3,4,5)	180.0
		A(3,4,5)	82.6563	D(6,3,4,1)	180.0
		A(4,5,6)	97.3437	D(6,3,4,5)	0.0
		A(3,6,5)	97.3437	D(2,3,6,5)	0.0
				D(4,3,6,5)	0.0
				D(1,4,5,6)	0.0
				D(3,4,5,6)	0.0
				D(4,5,6,3)	0.0

Table. 12: The optimized parameters for Cu6 nanocluster.

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

Table. 13: The optimized parameters for LiCr4 nanocluster.

Bond Length(A°)		Bond angle(Degree)		Dihedral Angle(Degree)	
Bond	Value	Bond	Value	Bond	Value
R(1,2)	2.4497	A(2,1,3)	67.0176	D(3,1,2,4)	0.0
R(1,3)	2.204	A(1,2,4)	103.8642	D(2,1,3,4)	0.0
R(2,4)	2.4497	A(1,3,4)	122.1006	D(2,1,3,5)	180.0
R(3,4)	2.204	A(1,3,5)	118.9497	D(1,2,4,3)	0.0
R(3,5)	2.6117	A(4,3,5)	118.9497	D(1,3,4,2)	0.0
		A(2,4,3)	67.0176	D(5,3,4,2)	180.0

Table. 14: The optimized parameters for LiCu4 nanocluster.

Bond Length(A°)		Bond angle(Degree)		Dihedral Angle(Degree)	
Bond	Value	Bond	Value	Bond	Value
R(1,2)	2.0582	A(2,1,3)	118.41	D(2,1,5,3)	-127.2574
R(1,3)	2.0582	A(2,1,5)	106.5079		
R(1,4)	2.1905	A(3,1,5)	106.5079		
R(1,5)	2.1746	A(2,4,3)	114.1732		
R(2,4)	2.1061				
R(3,4)	2.1061				

Table. 15: The optimized parameters for LiCr6 nanocluster.

Bond Length(A°)		Bond angle(Degree)		Dihedral Angle(Degree)	
Bond	Value	Bond	Value	Bond	Value
R(1,2)	2.4804	A(1,2,4)	160.7083	D(4,2,3,5)	0.0
R(1,3)	2.4804	A(3,2,4)	96.5733	D(1,2,4,5)	0.0
R(2,3)	2.1642	A(1,3,5)	160.7083	D(1,2,4,6)	0.0
R(2,4)	2.382	A(2,3,5)	96.5733	D(3,2,4,5)	0.0
R(3,5)	2.382	A(2,4,5)	83.4276	D(3,2,4,6)	0.0
R(4,5)	2.7095	A(2,4,6)	134.7063	D(1,3,5,4)	0.0
R(4,6)	2.1657	A(3,5,4)	83.4276	D(1,3,5,6)	0.0
R(5,6)	2.1657	A(3,5,6)	134.7063	D(2,3,5,4)	0.0
R(6,7)	2.6188	A(4,6,7)	141.2769	D(2,3,5,6)	0.0

		A(5,6,7)	141.2769	D(2,4,5,3)	0.0
				D(2,4,6,7)	180.0
				D(3,5,6,7)	180.0

Table. 16: The optimized parameters for $LiCu_6$ nanocluster.

Bond Length(A^o)		Bond angle(Degree)		Dihedral Angle(Degree)	
Bond	Value	Bond	Value	Bond	Value
R(1,2)	2.1359	A(2,1,3)	115.607	D(3,1,2,5)	0.0
R(1,3)	2.0298	A(2,1,4)	115.607	D(3,1,2,6)	180.0
R(1,4)	2.0298	A(3,1,4)	128.786	D(4,1,2,5)	180.0
R(2,5)	2.0882	A(1,2,5)	64.0413	D(4,1,2,6)	0.0
R(2,6)	2.0882	A(1,2,6)	64.0413	D(2,1,3,5)	0.0
R(2,7)	2.1958	A(5,2,6)	128.0826	D(4,1,3,5)	180.0
R(3,5)	2.0997	A(5,2,7)	115.9587	D(2,1,4,6)	0.0
R(4,6)	2.0997	A(6,2,7)	115.9587	D(3,1,4,6)	180.0
		A(1,3,5)	65.6757	D(1,2,5,3)	0.0
		A(1,4,6)	65.6757	D(6,2,5,3)	0.0
		A(2,5,3)	114.676	D(7,2,5,3)	180.0
		A(2,6,4)	114.676	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

VI. INFRARED SPECTRA

The harmonic vibrational frequencies have been investigated for Cr4, Cu4, Cr6, Cu6, LiCr4, LiCu4, LiCr6, LiCu6 nanoclusters at the ground state, B3LYP and 3-21G basis sets. There are two types of stretching variations, symmetric and asymmetric. The symmetric stretching happen when the same atoms vibrate in the same phase, and the asymmetric stretching happen when the bonds vibrate in different phases [14].
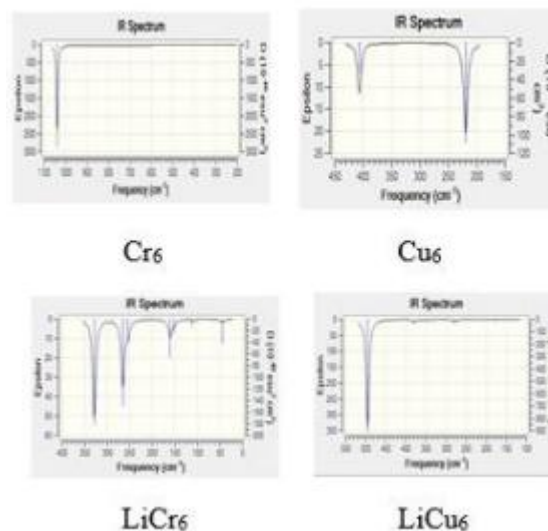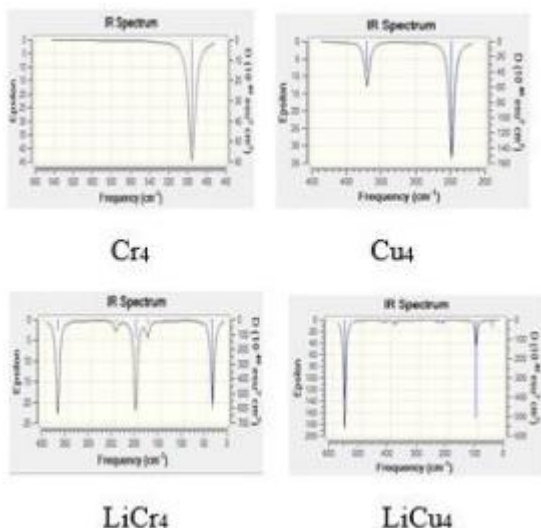

Cr4   Cu4

LiCr4   LiCu4

Cr6   Cu6

LiCr6   LiCu6

Figure. 2: Infrared Spectra for Cr_4, Cu_4, Cr_6, Cu_6, $LiCr_4$, $LiCu_4$, $LiCr_6$, $LiCu_6$ nanoclusters.

VII. ELECTRONIC STATES AND ENERGY GAP (Eg)

The electronic states can be denoted by HOMO and LUMO energies. In which HOMO refers to High Occupied Molecular Orbital, but LUMO stands for Low Unoccupied Molecular Orbital. One can write the difference between HOMO and LUMO as the energy gap (E_g) [15]:

$$E_g = E_{HOMO} - E_{LUMO} \quad \dots (1)$$

Table. 17: Electronic states and Energy gap (Eg) for Cr4, Cu4, Cr6, Cu6, LiCr4, LiCu4, LiCr6, LiCu6 nanoclusters.

system	$E_{HOMO}(eV)$	$E_{LUMO}(eV)$	$E_g(eV)$
Cr_4	-4.4336	-0.07846	2.298701
Cu_4	-4.74352	-0.1139	1.6443
Cr_6	-2.99745	-0.09734	0.348832
Cu_6	-4.78542	-0.11521	1.650559
$LiCr_4$	-3.86355	-0.06676	2.047008
$LiCu_4$	-4.3585	-0.08047	2.168909
$LiCr_6$	-3.95225	-0.10602	1.067448
$LiCu_6$	-3.60043	-0.09302	1.069353

VIII. 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. According to Koopman's theorm someone can write [16]:

$$E_{HOMO} = -I.P \quad \dots (2)$$
$$E_{LUMO} = -E.A \quad \dots (3)$$

$I.P$: Ionization potential
$E.A$: Electron affinity.

Table. 18: $I.P$ and $E.A$ for Cr_4, Cu_4, Cr_6, Cu_6, $LiCr_4$, $LiCu_4$, $LiCr_6$, $LiCu_6$ nanoclusters.

system	$I.P(eV)$	$E.A(eV)$
Cr_4	4.433597	2.134897
Cu_4	4.743519	3.099219
Cr_6	2.997454	2.648621
Cu_6	4.785423	3.134864
$LiCr_4$	3.863548	1.81654
$LiCu_4$	4.358498	2.189589
$LiCr_6$	3.952253	2.884804
$LiCu_6$	3.600427	2.531074

IX. 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 which available to be occupied. A high density of state at a specific energy level means there are many states available to occupied. A density of state zero means no state can be occupied at the energy level. Generally, a density of state is an average over the space and time domains which can occupied by the system. 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 allowed. 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 permits for the waves to propagate in one direction while it suppresses the wave propagation in another direction. Hence, it can happen that many states are available at a specific wavelength at this associated energy, while no states are available at other energy levels. This distribution is characterized by the density of states. Density of states can be investigated for electrons, photons and phonons according to quantum mechanics. In general, density of states influenced by topological properties of the system [17-20].
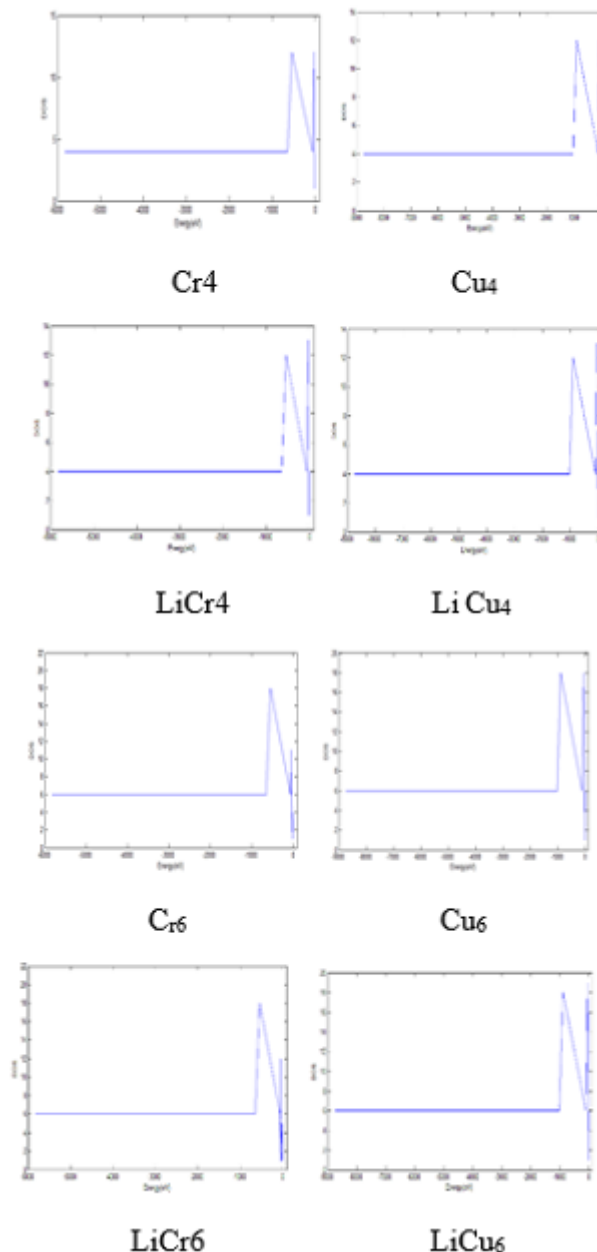

Figure. 3: Density of States for Cr4, Cu4, Cr6, Cu6, LiCr4, LiCu4, LiCr6, LiCu6 nanoclusters.

Discussion

Table. (1)-Table. (8) represents the optimized coordinates for Cr4 , Cu4, Cr6 , Cu6, LiCr4, LiCu4, LiCr6, LiCu6 nanoclusters respectively. The optimized coordinates have been investigated by using sophisticated algorithms in Gaussian 09 program with density functional theory. The optimized coordinates result throughout geometrical optimization procedure. The geometrical optimization continues until Gaussian 09 finds stationary point. When Gaussian program finds static point, the geometrical optimization stops and at this positions the force resultant on the atoms equals to zero. Naturally, Gaussian 09 employs harmonic oscillator model (the second derivative with respect to nuclei motion) to calculates the frequencies. The optimized coordinates which result from the geometry optimization represent the best values to get the nanoclusters. The optimized coordinates denot to configuration of atoms in the nanoclusters. When an atom adds to the nanocluster, it tends to change in configuration of atoms in nanocluster. One can

see effect of adding alkali atom to transition metal from these tables. It is very clear influence cromiume nanoclusters and copper nanoclusters by adding one lithium atom via the difference in optimized coordinates between pure nanoclusters (Crn or Cun) and LiCrn or LiCun nanoclusters. The method which is used to find the optimized coordinates also used in reference [21].

Table. (9)-Table. (16) stand for geometrical parameters for Cr4 , Cu4, Cr6 , Cu6, LiCr4, LiCu4, LiCr6, LiCu6 nanoclusters respectively. The geometrical parameters(bond lengths in Ao, bond angles in Degrees and dihedral angles in Degrees) which result through geometrical optimization represents the best values for getting these nanoclusters because Gaussian 09 searches on the best optimized parameters. When the best value is found, and the stationary point is found the geometry optimization stops. The values of the bond lengths, bond angles and dihedral angles which get during the geometry optimization represent the optimized parameters for getting the optimized nanoclusters. Adding an alkali atom to the nanocluster affects clearly on the values of the optimized parameters. Some can see obviously influence bond lengths, bond angles and dihedral angles when a Lithiume atom is added to the transition metals through these tables. Sometimes it has been observed there is difference between the theoretical and experimental data. This occurs because the theoretical data deals with isolated nanoclusters in gaseous phase, but experimental results study the nanoclusters in solid state. Also orbital hybridization causes difference in the optimized parameters. The mthod that used to investigate the optimized parameters also used in reference [22].

Fig. (2) describe IR spectra Cr4, Cu4, Cr6, Cu6, LiCr4, LiCu4, LiCr6, LiCu6 nanoclusters respectively. IR spectra gives harmonic vibrational frequencies, torsion vibrations appears at low frequencies, and the number of atomic modes depend on the number of the atoms in the nanocluster. Each value or each range stands for vibration mode, the vibration either elastic or inelastic. In the figures, it has been observed peaks, and these peaks refer to the bonds between atoms. When someone compares between Cr4 nanocluster and LiCr4 nanocluster it has been seen new active groups appear in LiCr4 nanocluster because of adding Lithium to pure chromium nanocluster. One can see obviously Cr4 nanocluster has only one clear peak, but LiCr4 nanocluster has five clear peaks.. Everyone can conclude (Li-Cr bonds) generated in LiCr4 nanocluster. Also one can note after adding Li atom to Cr4 nanocluster, the structure LiCr4 nanocluster has three clear peak because the geometrical optimization makes the interaction with the three Cr atoms more than the rest atom. This limit peaks appears because of the shielding procedure. Another comparison Cr6 has only one clear peak, but LiCr6 has four clear peaks, too this means new (Li-Cr bonds) have been generated in LiCr nanocluster. The method used to investigate IR spectra is also used in reference [23].

Table. (17) stand for the electronic states and energy gap in (eV) for Cr4, Cu4, Cr6, Cu6, LiCr4, LiCu4, LiCr6, LiCu6 nanoclusters respectively. The energy gap of some nanoclusters close to the energy gap of semiconductors. For example, Cu4 has energy gap (1.6443 eV) and this value closes to energy gap of CdTe which has energy gap (1.61 eV) at absolute zero. Another example LiCu6 nanocluster has energy gap (1.069353 eV) and this value closes to energy gap of silicon which has energy gap about (1.2 eV) at absolute zero. But Cr6 nonocluster has non zero energy gap (0.348832 eV), i.e. Cr6 nanocluster has non-metallic properties, because the metals have no energy gap in which the valence band is interacting with the conduction band. The values of energy gap that result from this study in good agreement with the experimental data [24 - 26].

Tables. (18) stand for the ionization potential and electron affinity in (eV) for Cr4, Cu4, Cr6, Cu6, LiCr4, LiCu4, LiCr6, LiCu6 nanoclusters respectively. The ionization potential is close to the work function for the solid chromium and copper. The work function for LiCr4, LiCu4 and LiCu6 decrease dramatically when the alkali atom such as Lithium adds to pure Cr4, Cu4 and Cu6. The experimental data of the work function for solid copper approximately (4.59eV) and for solid chromium approximately (4.37 eV). One can see Cr6 nanocluster has work function difference from the work function of solid chromium, that is because the configuration of atoms in the molecular structure of Cr6 nanocluster. The values of work function which result from this study is in good agreement with the experimental data and solid state physics [27 - 31].

Fig. (3) stand for density of states for Cr4, Cu4, Cr6, Cu6, LiCr4, LiCu4, LiCr6, LiCu6 nanoclusters respectively. A high density of state at a certain energy level means that there are many available states being occupied. When the density of state equals to zero, that means there is no available energy level to be occupied. The local vibrations generate local density of state (LDOS). If the density of state for an undistributed system is zero, LDOS will not probably be zero. This is result from existing the local potential. When the electron energy increases, the density of state increases. Many states become available to be occupied. The density of state also influence by the topological properties of the system. Density of states is a very important property in solid state physics. As one can observe from these figures, density of states gradually rises small when Lithium atom is added to Cr4 nanocluster. This means there are many orbitals have been generated under certain value of energy. One can see clearly from this figure, density of state rises in LiCr4 nanocluster. This means there are many orbitals that are available to be occupied. LiCr4 nanocluster has more states than other nanoclusters. The method which is used to investigate DOS also used in references [32-34].

Conclusion:

Throughout the study the molecular structure, the optimtimized coordinates, bond lengths, bond angles and dihedral angles have been achieved. The values of the optimized coordinates stand for the best values to obtain the nanoclusters. IR spectra demonstrates new peaks when an alkali atom like Lithium adds to the transition metal nanocluster, and this peaks denote to new bonds generate in mixed nanoclusters. Energy gap values show that some

nanoclusters have semiconductor properties, but Cr6 nanocluster has semi-metallc properties, Cr6 has value of energy gap equal to (0.348832 eV). The nanocluster LiCr4 has the lowest work function among all nanoclusters, it has value of work function about (1.81654 eV), hence its electrons need less energy to escape from the surface of the nanoclusters, and this can consider clear improvement in the electronical properties. Density of states diagrams appear new states when Lithium atom adds to the transition nanoclusters, this refers to new orbitals will originate, and the electrons can go up to these orbitals.

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