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Density Functional Theory Investigation For Ni6, Co5, Au12, Y5 and Ni6Li, Co5Li, Au12Li, Y5Na Interactions

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Abstract

Geometry optimization for pure transition metals structures Ni6 , Co5 , Au12 , Y5 and alkali-transition metals structures Ni6Li , Co5Li , Au12Li , Y5Na at B3LYP level, 3-21G and LaNL2DZ basis sets has been investigated by using Density Functional Theory (DFT) throughout Gaussian09 package. Electrostatic potential, contours, infrared spectra, symmetry, energy gap has been studied for all structures. Total energy for pure transition metals structures is greater than the total energy for alkali-transition metals structures, One can say that the orbitals that generate between Lithium and atoms of pure Nickel structure will be from anti-bonding type. Dipole moment for some pure Nickel structure has zero value because it is homostructure, the other pure transition structures has nonzero values although they are homostructures this is result because of the geometry structures, but the dipole moment for all alkali-transition structures has nonzero numerical values because it is hetrostructures. Energy gap for Y5Na is the smallest value of energy gaps of the structures under study, it approaches to the energy gap of GaAs, this property is very useful in electronic applications such as manufacturing of processors of laptops, Eg of Y5Na = 0.95 eV, Eg of GaAs = 0.8 eV.

Keywords: **DFT, IR, DOS, Contours, Binding energy, Symmetry.**

I. INTRODUCTION

One can investigate the electronic structure of particular atoms, molecules, nanoclusters and substances by using quantum mechanics methods such as Hartree-Fock approximation, post Hartree-Fock methods and density functional theory (Assadi, 2013). Density functional theory (DFT) treats with the systems that have many particles throughout the electron density (Mark, 1987). Electron density is the likelihood of determining places of the electrons at certain space (Matthews, 1974). Density functional theory suppose that the electron density rather than the wave function, and also it assumes the electron density only depends on three spatial coordinates without regarding how the electrons are found in the systems, while the wave function approximation considers 3N variables,

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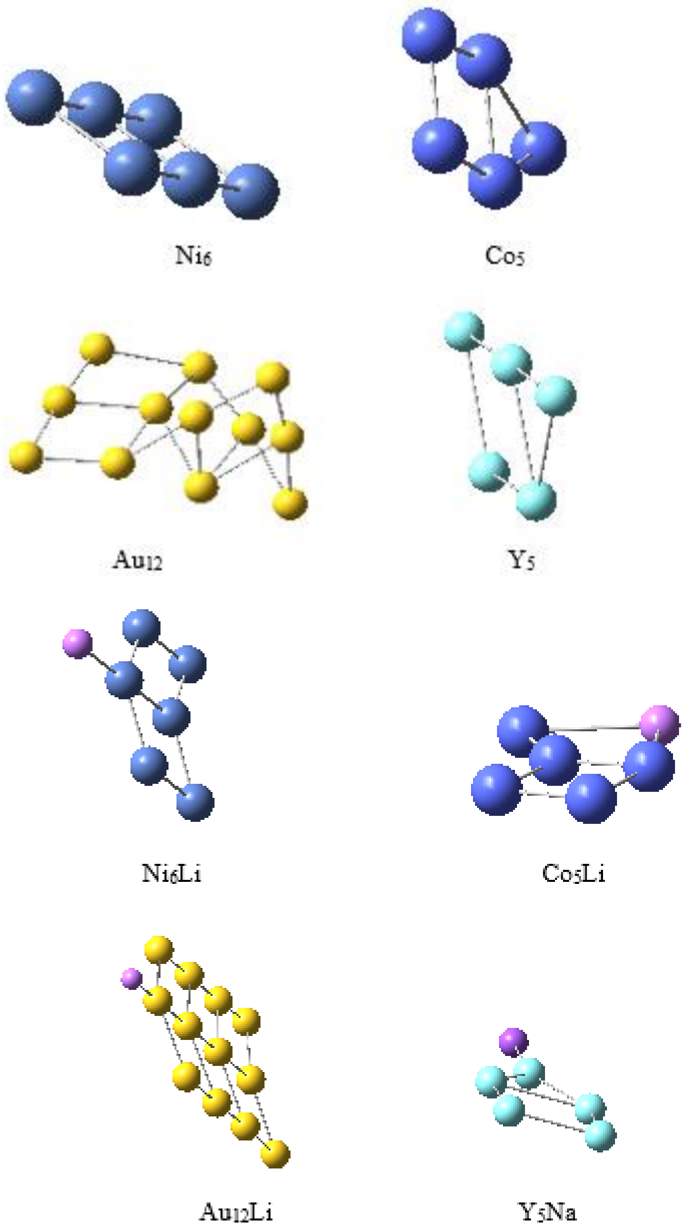
three spatial coordinates, one coordinate for spin by assumption the nuclei location is fixed (Robert and Weitao, 1994). With this theory one can find out the credits of a many electron system throughout the functionals i.e. functions of another function (Holthausen and Koch, 2001). DFT is one of most popular methods that had been used in search of the electronic properties of solid state matters by using the computational physics and chemistry (Ali, 2009). The consequences of DFT calculations for solid state systems jibe extensively with the experimental data (Kittel, 1986). Density functional theory has been submitted in two research papers in the 1960's by Hohenberg-Kohn (Stefan, 2006). However, DFT had not been regarded accurate enough in quantum chemistry calculations until 1990s (Koch and Holthausen, 2000). DFT goals are to evaluate the energy of the ground state of N electron system depending on its density without considering the wave function of the system (Carmer, 2002).Walter Kohn with John Pople win Nopel prize in chemistry in 1998, Pople develops DFT computationally by using quantum chemistry concepts (Ali, 2009).

II. MOLECULAR GEOMETRY

Molecular structure point out the configuration of atoms in the material, it denotes to the positions of atoms in the system (Richtmyer and Cooper, 1976). Geometry optimization with density functional theory thought had been utilize in order to inquire the molecular structure for Ni_6 , Co_5 , Au_{12} , Y_5 and Ni_6Li , Co_5Li , $Au_{12}Li$, Y_5Na by using Gaussian 09 software package. DFT had been used at 3-21G basis set, B3LYP level at the ground state.



Ni_6 Co_5

Au_{12} Y_5

Ni_6Li Co_5Li

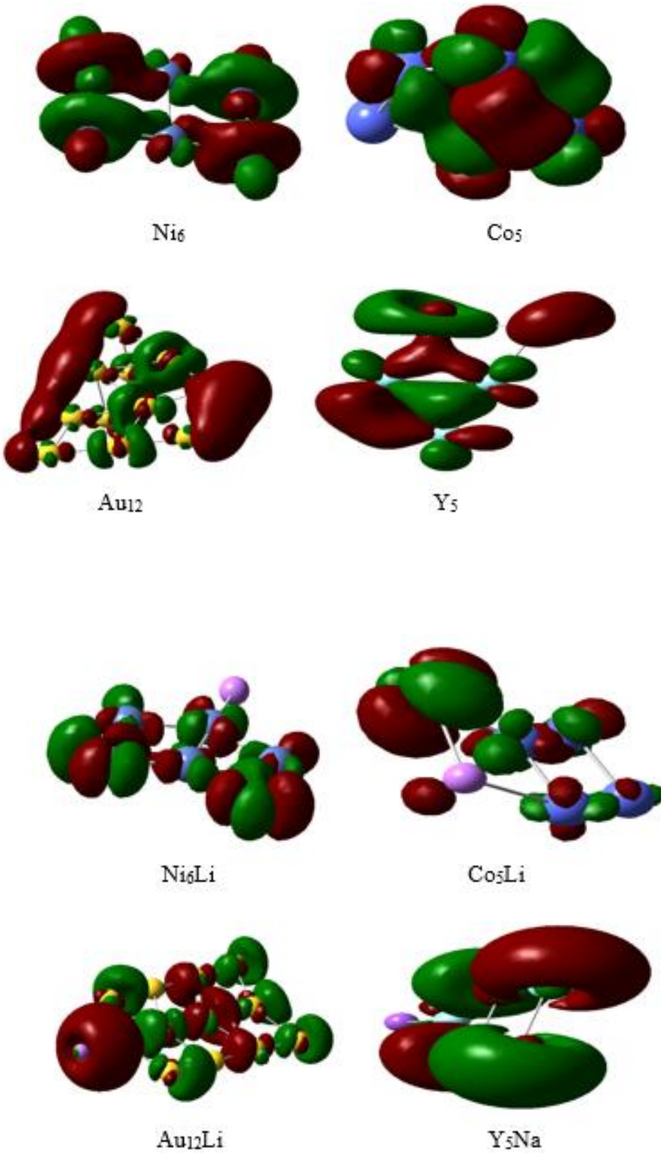
$Au_{12}Li$ Y_5Na

Figure(1)

Molecular structure for pure transition metals and alkali-transition metals

III. SURFACES

Surfaces had been investigated by utilizing molecular orbitals (MOs) at HOMO, LUMO electronic state. Surface shapes was accomplished through the geometrical optimization procedure (Trucks and Schlegel, 2009). The geometry optimization process is stopped when the stationary point is discovered, i.e. force resultant equal to zero. Electrostatic potential for Ni_6 , Co_5 , Au_{12} , Y_5 and Ni_6Li , Co_5Li , $Au_{12}Li$, Y_5Na is accommodated by using Gaussian 09 software package.

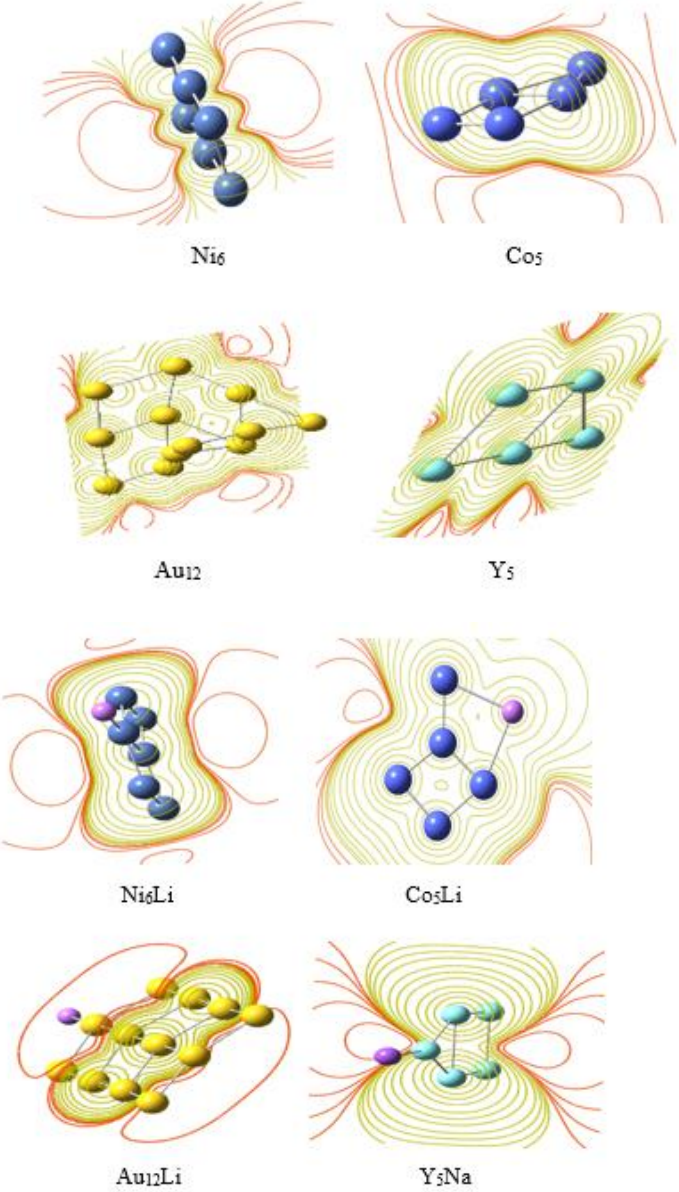


Figure(2)

Electrostatic potential for pure transition metals and alkali-transition metal

IV. CONTOURS

Electronic density contours is an impressive shapes wear to describe the electrostatic potential (Blakemore, 1969). Contour maps submit another method for describing potential surface. Electronic density maps for Ni_6 , Co_5 , Au_{12} , Y_5 and Ni_6Li , Co_5Li , $Au_{12}Li$, Y_5Na is carried out throughout Gaussian 09 software package.

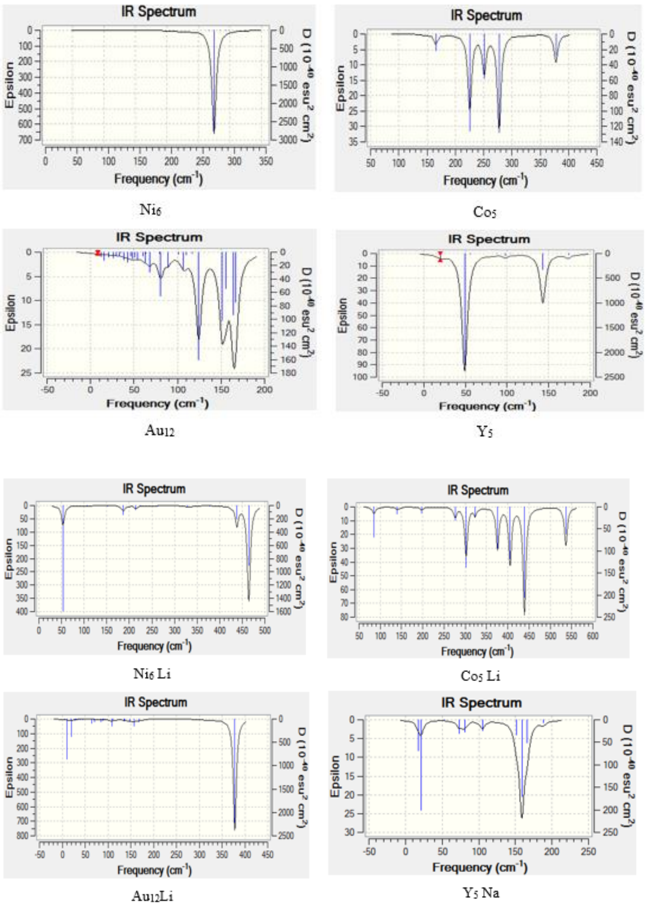


Figure(3)

Contour maps for pure transition metals and alkali-transition metals

V. INFRARED SPECTRA

The harmonic oscillational frequencies can be investigated throughout infrared spectroscopy (IR) (Mohsin and Aboud, 2013). The oscillations was either symmetric or asymmetric, symmetric vibrations result from oscillating atoms with the same type, otherwise the asymmetric vibrations result from oscillating atoms with different type (Hafedh and Aboud, 2013). Infrared spectra diagrams for Ni_6 , Co_5 , Au_{12} , Y_5 and Ni_6Li , Co_5Li , $Au_{12}Li$, Y_5Na is performed throughout DFT idea.



Ni_6 Co_5

Au_{12} Y_5

Ni_6 Li Co_5 Li

$Au_{12}Li$ Y_5 Na

Figure(4)

Infrared spectra for pure transition metals and alkali-transition metals

VI. CALCULATIONS

VI.I. INDIVIDUAL ATOMS CALCULATIONS

Computations of individual atoms possess high-stacks for discussion some properties of materials, some of these properties total energy, electronegativity and electronic states.

Table (1) shows electronic properties for the individual atoms (Sodium and Lithium)

atom	HOMO(eV)	LUMO(eV)	Total energy(eV)
Li	-3.6654591	-0.8835087	-203.8242054
Na	-3.3612513	-0.6097761	-0.504699243

VI.II. ELECTRONIC STATES AND ENERGY GAPS (Eg)

High occupied molecular orbital (HOMO) and low unoccupied molecular orbital (LUMO) stand for the electronic states for existence the electrons in orbital. Energy gap (E_g) emerged of the energy difference between two electronic levels (Aboud, 1987).

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

Table (2) illustrates HOMO, LUMO energies and energy gap (E_g) for Ni_6 , Co_5 , Au_{12} , Y_5 and Ni_6Li, Co_5Li , $Au_{12}Li$, Y_5Na.

System	HOMO(eV)	LUMO(eV)	E_g(eV)
Ni_6	-4.77726	-3.41948	1.35778
Co_5	-4.28748	-2.74141	1.54607
Au_{12}	-6.01259	-3.92069	2.0919
Y_5	-3.27663	-2.18959	1.08704
Ni_6Li	-4.82025	-3.47444	1.34581
Co_5Li	-4.22163	-2.94086	1.28077
$Au_{12}Li$	-5.33534	-3.59145	1.74389
Y_5Na	-2.97487	-2.01653	0.95834

VI.III. DIPOLE MOMENT

Dipole moment is consequence for multiplication between the charge and displacement, it gets between two charges with different signs the distance between them is r. When any direction of the displacement change, the dipole moment change. It can be expressed by the equation (Catherine and Alan, 2008).

$$P = q * r \qquad \dots \quad (2)$$

Where P defined as the displacement, q is the charge and r represents the displacement.

Table (3) appears dipole moment for Ni_6 , Co_5 , Au_{12} , Y_5 and Ni_6Li , Co_5Li , $Au_{12}Li$, Y_5Na.

System	Dipole moment (Debye)
Ni_6	0.000000
Co_5	2.175404
Au_{12}	2.511754

Y_5	1.091537
Ni_6Li	3.722187
Co_5Li	3.545572
$Au_{12}Li$	14.028297
Y_5Na	0.851257

VI.IV. ELECTRONIC ENERGY

According to density functional thought the total energy can be divided in to four parts which is summarized by the equation (Oftadeh and Hamadanian, 2011).

E_T refers to the electronic kinetic energy, E_v denotes to the electronuclear interaction energy, E_J stands for the electron-electron repulsion and E_{XC} represents the exchange correlation term.

Table (4) shwos the total energy for Ni_6 , Co_5 , Au_{12} , Y_5 and Ni_6Li , Co_5Li , $Au_{12}Li$, Y_5Na

System	**Electronic energy(eV)**
Ni_6	-27635.8365
Co_5	-187211.8746
Au_{12}	-44242.9158
Y_5	-5154.88008
Ni_6Li	-245256.7908
Co_5Li	-187409.4192
$Au_{12}Li$	-44448.3513
Y_5Na	-5160.32208

VI.V. BINDING ENERGY

The binding energy of a system predicts how energetically the atoms are entangled in the system during its formation. The binding energy of the X_nY_m is given by the equation (Kumar and Roy, 2015):

$$E_B = nE_X + mE_Y - E(X_nY_m) \quad \ldots \quad (4)$$

Where E_B is the binding energy of the system, E_X defined as the energy of the molecule X , E_Y is the energy of the molecule Y, $E(X_nY_m)$ represents the energy of the molecule X_nY_m, n stands for the number of atoms of the molecule X and m indicate to the number of atoms of the molecule Y.

Table (5) demonstrates the binding energy for Ni_6Li , Co_5Li , $Au_{12}Li$ and Y_5Na

System	**Binding energy(eV)**
Ni_6Li	2912.089217
Co_5Li	-27521.27078
$Au_{12}Li$	-17885.72078
Y_5Na	-757.6105483

VI.VI. SYMMETRY

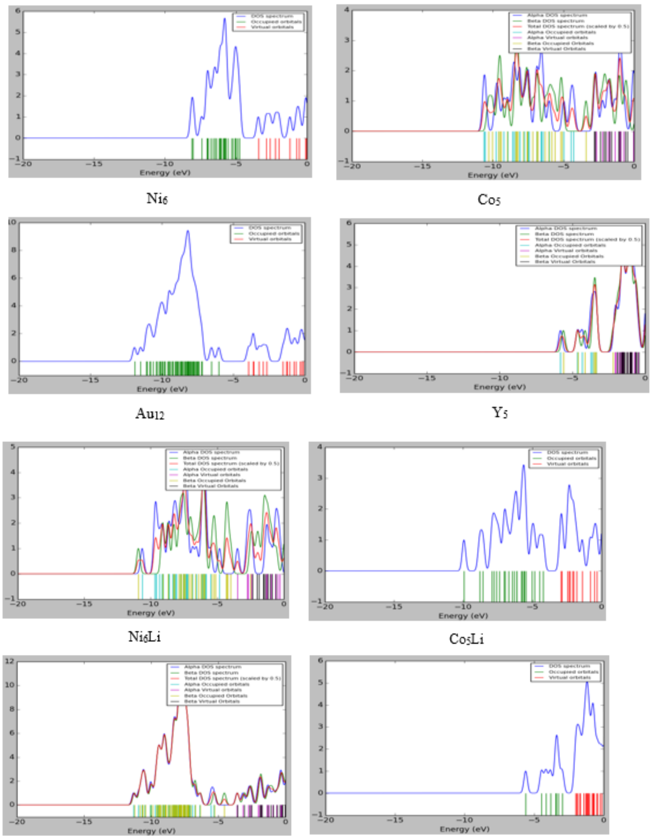
The sphere is regarded more symmetric as compared with the cube, the sphere looks the same when rotates through any angle, while the cube look the same only if the rotation gets at certain angles around certain centerpiece. Symmetry play a vital role in acknowledgement properties of molecules without calculations (Lesk, 2004).

Table (6) appears point group symmetries for Ni_6 , Co_5 , Au_{12} , Y_5 and Ni_6Li , Co_5Li , $Au_{12}Li$, Y_5Na

System	**Point group symmetry**
Ni_6	D_{2h}/C_1
Co_5	C_{2v}/C_1
Au_{12}	C_1
Y_5	C_s/C_1
Ni_6Li	C_{2v}/C_1
Co_5Li	C_s/C_1
$Au_{12}Li$	C_{2v}/C_1
Y_5Na	C_{2v}/C_1

VI.VII. DENSITY OF STATES

In solid state physics density of states describe the number of states for every energetic interval at every energy level in which the energy level can be occupied by electrons (Kittel, 1991). Density of states can be investigated for electrons, photons and phonons according to the physics of quantum mechanics (Ziman, 1972). Density of states of Ni_6 , Co_5 , Au_{12} , Y_5 and Ni_6Li , Co_5Li , $Au_{12}Li$, Y_5Na have been found out by Gaussian sum 03 program package.



Ni_6 Co_5

Au_{12} Y_5

Ni_6Li Co_5Li

$Au_{12}Li$ Y_5Na

Figure(5)

Density of states for pure transition metals and alkali-transition metals

VII. DISCUSSION

From figure (1) one can visualize the molecular geometry which results from the geometry optimization procedure of the ground state. The geometry optimization procedure depends on the calculations of second derivative of the energy with respect to the atomic positions with harmonic oscillator pattern. The geometry optimization procedure goal is to obtain the minimum energy in order to reach the stationary of the system. The atoms with blue color refers to Nickel or Cobalt atoms, the golden atoms indicates to Gold atoms, Violet color represents Lithium or Sodium atom, but the turquoise color stands for Yttrium atoms. Molecular structures demonstrates position of atoms in the Cartesian coordinates.

From figure (2) it is very clear that the HOMO, LUMO surfaces throughout the new colors Green and Red. Electrostatic potential surfaces result in the linear combination of the atomic orbitals, i.e. molecular orbitals will compose because of the electronic transition between orbitals. Molecular bonds with type sigma and or pi will result. Green color point out the positive partition of the wave function that accompany the motion of electron, but the Red color represents the negative partition of the wave function that accompany the electron.

From figure (3) one can observe apparently the contours diagrams of the pure transition metals surfaces change after adding the alkali atom to the pure transition surface. The interaction between the transition surface and the alkali atom make a deformation in contour maps. The shape of Gold surface becomes more decoration when Lithium atom adds to the gold surface, i.e. $Au_{12}Li$ is more regularly than pure gold surface. Therefore one can say addition Lithium atom to the Gold surface enhances the geometry properties.

From figure (4) one can watch new peaks in Ni_6Li system, the new peaks are interpreting by new metallic bonds (Ni-Li) results as a result to the interaction between Nickel and Lithium. Adding Lithium to the gold surface leads to appear only one clear peak in $Au_{12}Li$, that is to say many peaks in Gold disappear because of shielding procedure gets, the geometry optimization makes the interaction with at least one atom of gold surface frequent than the other atoms. New bonds (Co-Li), (Au-Li), (Y-Na) results from the interactions between the transition surfaces Cobalt, Gold and Yttrium with the alkali atoms Lithium and Sodium.

One can make a comparison between Table (1) and Table (2) to conclude that HOMO energy of Nickel is more than HOMO energy of Lithium therefore Nickel surface will donate by electrons to Lithium, one can say Nickel surface will behave as donor, but Lithium becomes an acceptor. The electrons of Nickel will release to the unoccupied orbitals in Lithium. For the same reason Gold surface, Cobalt surface will become a donors, while Lithium atom will be an acceptor. In (Y_5Na) Sodium atom behaves as a donor, but Yttrium surface become an acceptor, hence the electrons of Sodium will release to adhesive on Yttrium surface, one can say physisorption procedure gains throughout the interaction between Yttrium surface and Lithium atom.

Form figure (2) one can find out (Y_5Na) has the minimum value of energy gap among the samples under the study, it has the value (E_g= 0.95834) which approaches the energy gap of Gallium Arsenide (GaAs), E_g = 0.78) for (GaAs), his property is very important in manufacture of electronic devices such as processors of laptops. The energy gap of all systems in this paper in the range of semiconductor energy gaps. Also adding alkali atom to transition surface makes the energy gap less. So one can conclude when manufacture transition nanomaterial or alkali-transition nanomaterial covert to semiconductor, while they are metals when they are bulk.

From table (3) it can be note the dipole moment of Nickel surface (Ni_6) has zero value as it is homonuclear surface. The other homonuclear surfaces has nonzero values although they are homonuclear surfaces, this takes place because the atoms configuration in the system, molecular structure and the symmetry. Adding Lithium to Hold makes the dipole moment to the hybrid surface ($Au_{12}Li$) much more than the dipole moment to the pure surface (Au_{12}). All hybrid systems in this study has nonzero value of the dipole moment, that is because they are hetronuclear surfaces. All systems that have nonzero dipole moment result rotational spectra.

When one compare between table (4) and table (1) can visualize that the total energy of Co_5Li larger than the total energy of Cobalt plus the total energy of Lithium, i.e. the total energy of the resultant system is more than the total energy of the summation of the individual systems (Cobalt system and Lithium atom). The increasing in the total energy because originating non-bonding orbital between Cobalt and Lithium. Non-bonding orbital will generate in all other hybrid systems Ni_6Li, $Au_{12}Li$ and Y_5Na because of the increasing in energy of the resultant systems.

From table (5) one can see values of binding energies of the hybrid systems. Y_5Na system has the lowest binding energy among all hybrid systems, Y_5Na needs less energy to enter binding state. While Co_5Li has the highest binding energy therefore, it needs the highest energy to income binding state. Binding energy is playing vital role in coexist of the system, it is keeps existence of the system. The difference in values of the binding energy because of the entanglement.

From table (6) one can see symbols indicates to different types of the symmetries. The systems which have the symmetry C_1 because rotation the system by 360^o, it is sort of the symmetry C_n, the symmetry of this kind gets through (360^o/n). D_{2h} symmetry means that the systems that have this type of symmetry has two fold axes of symmetry and two fold axes perpendicular to C_n , also this systems has horizontal mirror plane. Co_5 system has the point group symmetry C_{nv} which has vertical mirror plane σ_v . The system which have C_s type of symmetry means that those systems contain two elements horizontal mirror plane and identity.

Figure (5) shows density of states sketches, Addition of Lithium to Nickel surface convert its properties to anti-ferromagnetic properties, new type of orbitals emerges in Ni_6Li alpha and beta orbitals, i.e. this hybrid system is open shell system. Also adding Lithium to Gold surface make it has anti-ferromagnetic properties. Density of states denotes to the states that can be occupied by electrons. Build up on density of states diagrams values of energy gaps can be known easily, it is the difference in energy between conduction band and valence band. Sometimes topological geometry makes electrons occupy certain orbitals, Also hybridization procedure affects on density of states.

VIII. CONCLUSIONS

Geometry optimization procedure is the way for arriving to the best geometrical structure (the ground state geometry), geometry optimization stops when it finds stationary point on the potential surface, this procedure gives the most geometry structure to the surface. Adding one Lithium atom to Gold surface make the geometrical structure more regularly than the pure Gold (Au_{12}), that s very clear in contour maps. Shielding procedure gains after adding Lithium to Au_{12} surface, this is show apparently through infrared spectra graphs. The best values of the energy gap is for the systems Y_5Na and Co_5Li, this credit is very useful in the industry of the electronic devices. Some systems has nonzero dipole moment although they are hetronuclear systems, this is belong to many reasons such as symmetry and molecular geometry. The orbitals between the alkali atoms and transition atoms in the hybrid systems are non-bonding. Y_5Na system has the highest binding energy among all hybrid systems. Throughout density of states diagrams one can conclude change the magnetic properties, demonstration new orbitals of the type beta confirm this property, this kind of systems considers open shell system.

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