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Density functional theory investigation for $\mathrm{Au_n}$, $\mathrm{Au}_n\mathrm{Li}$ (n=8,9) and $\mathrm{Y_n}$, $\mathrm{Y_nCa}$ (n=6,8) interactions

Maha Kassar, Abbas Shwya, Lafy Faraj

Thi-Qar University, College of science
Email: abbasalwan@hotmail.com

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Abstract

Geometry optimization for pure transition metals structures Au_8, Au_9, Y_6, Y_8 and alkali − transition metals structures Au_8Li, Au_9Li, Y_6Ca, Y_8Ca at B3LYP level, LaNL2DZ basis sets has been investigated by using Density Functional Theory (DFT) throughout Gaussian09 package. Electrostatic potential, contours, infrared spectra (IR) , HOMO LUMO energies, band gap, electronic energy, binding energy symmetry and density of states (DOS) have been achieved for all $Au_8, Au_9, Y_6, Y_8, Au_8Li, Au_9Li, Y_6Ca$ and Y_8Ca. The energy gap for Y_8 approximately equal to the energy gap of Gallium arsenide ($GaAs$), this value of energy gap is in the range of values of band gaps of semiconductors, one can say like this sample of nanocluster (Y_8) play a vital rule in manufacturing of pieces of electronic devices such as transistors of processors in computers. The dipole moment of Au_8 and Y_6 are approximately zero values because they are homonuclear geometries, adding Lithium to Gold surfaces make the values of dipole moment increase dramatically, this distinct values results from they are hetronuclear structures, Diagrams of density of states give clear picture about the vacant orbitals that the electrons can occupy, one can visualize the interaction between gold surface and Lithium atom make the new structure (Au_8Li) possess the antiferromagnetic property, otherwise addition of Lithium atom to the Golden surface Au_9 make it loses the antiferromagnetic property.

Keywords: Contours, Binding energy, Symmetry, HOMO, LUMO, IR, DFT.

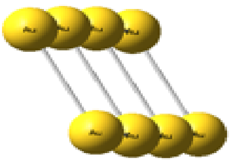
Introduction

The electronic structure and some other properties of atoms, molecules, nanoparticles and materials can be found using several famous methods such Hartree-Fock approximation, post Hartree-Fock methods and density functional theory [1]. Density function theory (DFT) deals with systems with multiple molecules throughout the electron density instead of the wave function [2]. Electron density shows the location of the electron in a given space [3]. DFT is one of the most important and most common methods used to search for the electronic properties of solid-state problems using computer physics and computational chemistry [4]. The objectives of DFT are to assess the ground state energy of the electron system N based on its density without regard to its wave function [5].Walter Kohn with John Pople win Nopel prize in chemistry in 1998, Pople develops DFT computationally by using quantum chemistry concepts [6]. Density functional theory can be implemented in order to investigate the electronic structure (basically energy of the ground state must be the lowest) of many body systematics, especially atoms, molecules and condensed phases [7]. According to DFT the characterstics of a many electron system can be found out by using functionals, it means functions of another function where this state is the spatially dependent the density of electron [8]. In several cases the consequences of density functional theory calculations for solid state molecules agree completely satisfactorily with practical data [9].

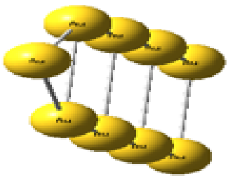
Results and discussions

Molecular Geometry

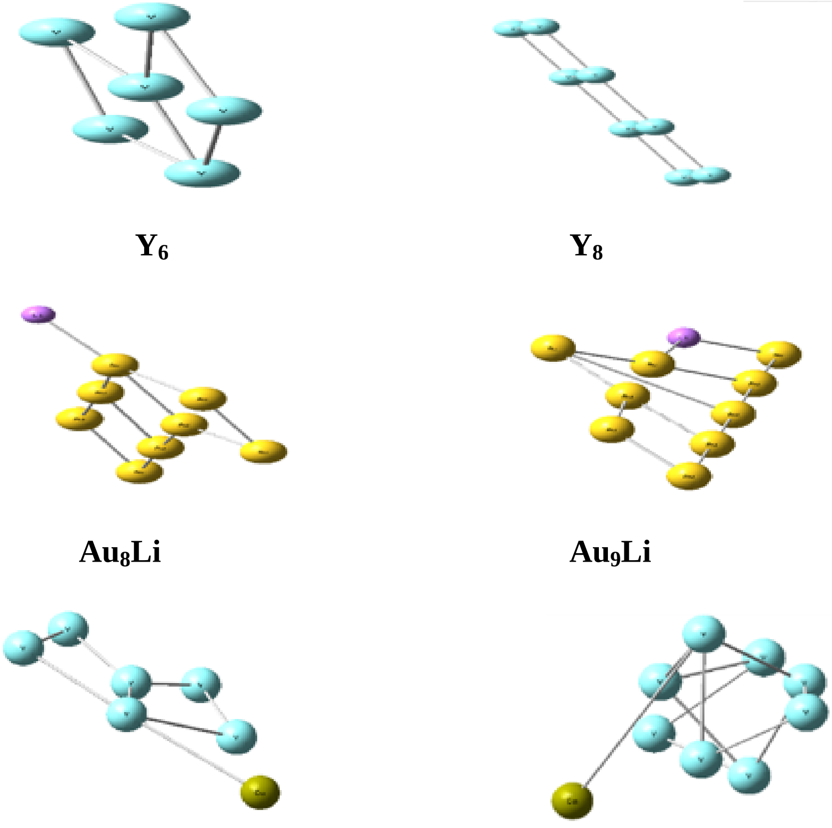
Molecular structure point out the configuration of atoms in the materials, it denotes to the positions of atoms in the systems [10]. Geometry optimization procedure with using density functional theory (DFT) thought had been utilize so as to inquire the molecular structure for $Au_8, Au_9, Y_6, Y_8, Au_8Li, Au_9Li, Y_6Ca$ and Y_8Ca by using Gaussian 09 software package at 3-21G, LANL2DZ basis set, B3LYP level at the ground state.



Au_8



Au_9



Y_6 **Y_8**

Au_8Li **Au_9Li**

Y_6Ca **Y_8Ca**

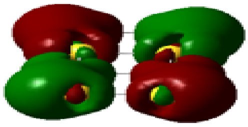
Figure (1)

Molecular structure for pure Au_n , Au_nLi (n=8,9) and Y_n , Y_nCa (n=6,8)

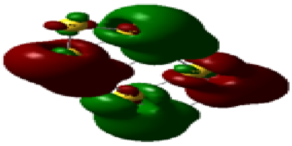
In figure (1) one can visualize the geometrical shapes that produced by the optimal geometry of theunder study systems. The purpose of the geometry optimization of the systems is to obtain the minimum energy to reach a more stable systems. In DFT method the convergence of the geometry of the lowest energy can get by calculating the gradient (first derivative) of the energy with respect to the atomic positions. The geometric structure of the systems is detected in the Cartesian coordinates with X, Y, Z dimensions. The surfaces with the golden color represent Gold surface. The turquoise color refer to Yttrium surfaces. The violet color represents Lithium atom, but the yellowish green color denotes to the calcium atom. One can see apparently how the shape of molecular structure of (Y_8) surface become different completely after adding one Calicum atom to that surface, also throughout figure one can note that the bonds look at interlock state.

Current surfaces

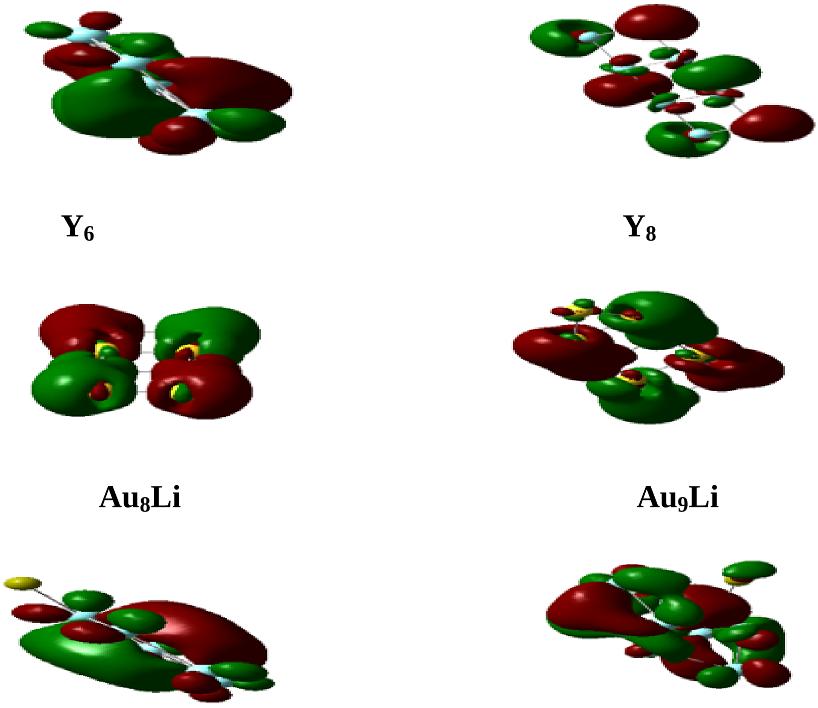
Surfaces had been investigated by utilizing molecular orbitals (MOs) at HOMO, LUMO electronic states. Surface shapes was accomplished through the geometricy optimum process [11]. The geometry optimization process stops when the stationary point is discovered at the potential surface, i.e. force resultant on the atoms equal to zero (stationary state) [12]. Electrostatic potential for $Au_8, Au_9, Y_6, Y_8, Au_8Li, Au_9Li, Y_6Ca$ is accommodated by using Gaussian 09 software package throughout DFT at 3-21G, LANL2DZ basis set, the hybrid functional (B3LYP).



Au_8



Au_9



Y_6 **Y_8**

Au_8Li **Au_9Li**

Y_6Ca **Y_8Ca**

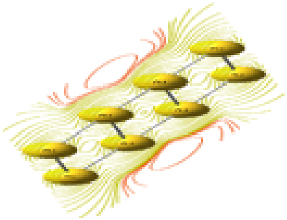
Figure(2)

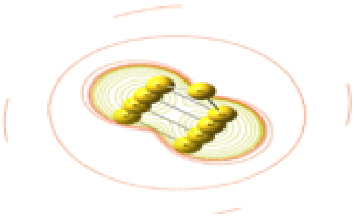
HOMO, LUMO surface for pure Au_n, Au_nLi (n=8,9) and Y_n ,Y_nCa (n=6,8)

Figure (2) show effect the transition surfaces by adding alkali atom to each surface. The interaction between the atomic orbitals gives molecular orbitals may be sigma or pi. Green color point out the positive partition of the wave function that accompany the motion of electron, but the red color represents the negative part of the wave function that accompany the electron motion. Thoughout the interaction among the alkali atoms and the transition surfaces new energy levels originate can be occupied by electrons which transfer from the transition surface to the alkali atom or the opposite gets, this electronic transfer makes one of them behave as donor and the other became as an acceptor.

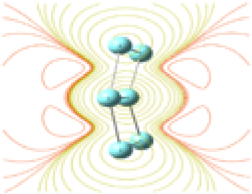
Contours

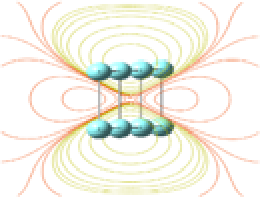
Electronic density contours is an impressive shapes are used to describe the electrostatic potential. Contour maps submit another method for describing potential surface [13]. Electronic density maps $Au_8, Au_9, Y_6, Y_8, Au_8Li, Au_9Li, Y_6Ca$ are investigated throughout DFT at 3-21G, LANL2DZ basis set, the hybrid functional (B3LYP) utilizing, Gauss view 05, Gaussian 09 software program.



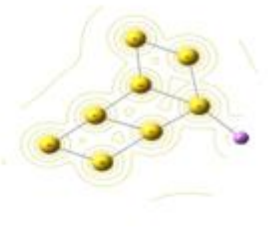


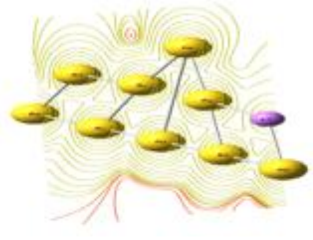
Au_8 **Au_9**



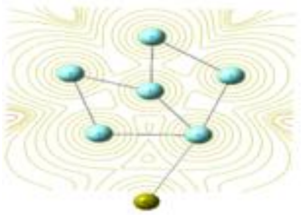


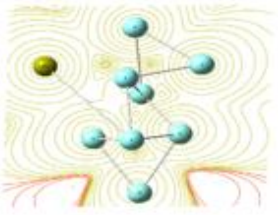
Y_6 **Y_8**





Au_8Li **Au_9Li**





Y_6Ca **Y_8Ca**

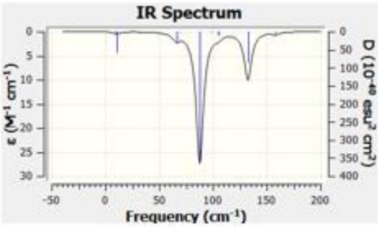
Figure(3)

Contour maps for pure Au_n ,Au_nLi (n=8,9) and Y_n, Y_nCa (n=6,8)

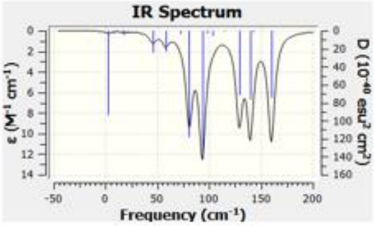
Figure (3) exhibits that the interaction between the single alkali atoms and transition metal surfaces make a distortion in contour maps schematics, this means charge transfer or charge exchange gains between the atoms and the surfaces. Also one can say the electrostatic potentials of transition metals surfaces become with new geometrical properties differ completely after the interaction with the alkaline atoms. The change in the configuration of atoms in the hybrid systems (transition surface-alkali atom) gets through the geometry optimization procedure. Bond lengths, bond angles and dihedral angles influence clearly after the interaction as a result to hybridization procedure.

Infrared spectra (IR)

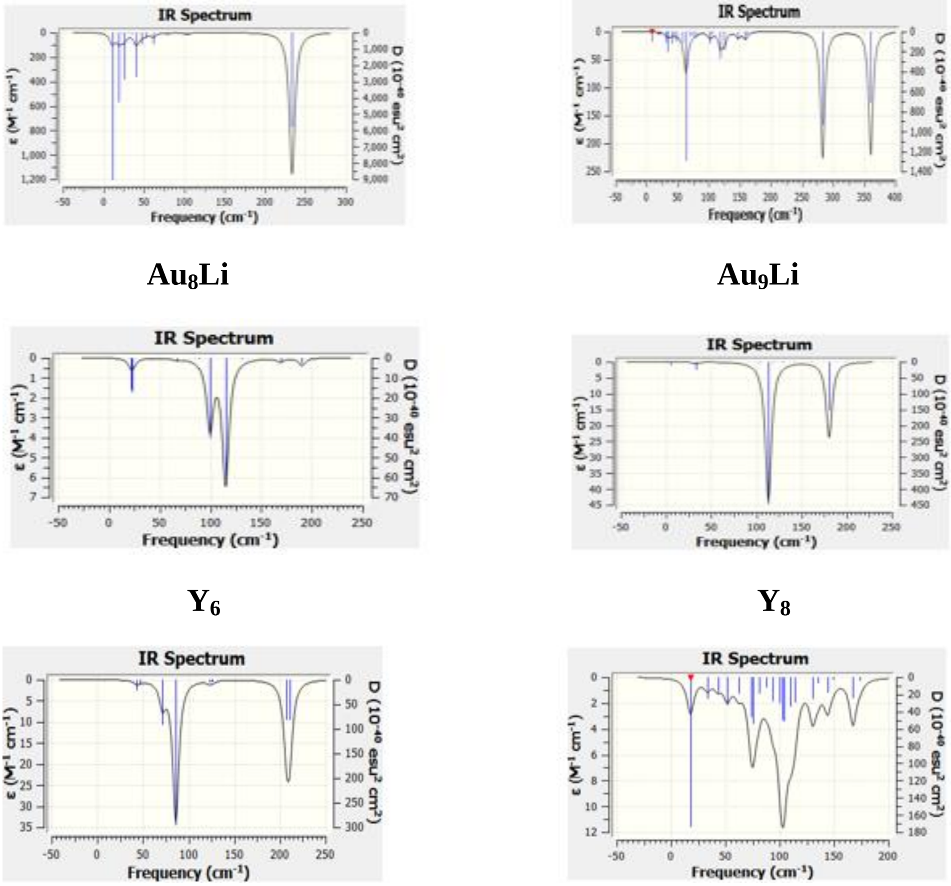
Through the infrared spectroscopy schemes the harmonic oscillational frequencies can be examined [14]. The symmetric or asymmetric vibrationss were caused by oscillation atoms of the same type, while the oscillating atoms of the different kind are as a consequence of asymmetric vibrations [15]. DFT ideas are carried out to gain the infrared spectrum diagrams for $Au_8, Au_9, Y_6, Y_8, Au_8Li, Au_9Li, Y_6Ca$.



Au_8



Au_9



Au_8Li **Au_9Li**

Y_6 **Y_8**

Y_6Ca **Y_8Ca**

Figure (4)

Infrared spectra Au_n ,Au_nLi (n=8,9) and Y_n ,Y_nCa (n=6,8)

In figures (4) one can observe new peaks in the system (Y_8Ca) as compared with (Y_8), The structure (Y_8Ca) has only two clear peaks, but (Y_8Ca) has six clear peaks , the new peaks in the new structure (Y_8Ca) refers to new bonds (Y-Ca) originate because of the interaction between the alkali atom (Ca) and Yuttrium surface (Y_8). One can make a comparison between (Au_9) surface and (Au_9Li) structure to find out that shielding procedure gets, disappearance of some peaks which means some bonds disappear as a result to the shielding procedure, one can see apparently that (Au_9) has five clear peaks as compared with (Au_9Li) which possess only three clear peaks, i.e two clear peaks disappear as a result to the shielding procedure.

Calculations of the individual atoms

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

Table (1) shows electronic properties for the individual atoms (Calcium , Lithium)

atom	HOMO(eV)	LUMO(eV)	Total energy(eV)
Li	-3.6654591	-0.8835087	-203.8242054
Ca	-4.4159109	-1.2094845	-994.5446014

Electronic states and energy gaps (E_g)

High occupied molecular orbital (HOMO) and low unoccupied molecular orbital (LUMO) stand for the electronic states for existence the electrons in orbitals [16]. Energy gap (E_g) originate as a result to the energy difference between two electronic levels and can be yield by the equation [17].

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

Table (2) illustrates HOMO, LUMO energies and energy gaps (E_g) for Au_8, Au_9, Y_6, Y_8 and Au_8Li, Au_9Li, Y_6Ca, Y_8Ca

System	HOMO(eV)	LUMO(eV)	E_g(eV)
Au_8	-5.9483781	-4.8605223	1.0878558
Au_9	-5.8615782	-4.9470501	0.9145281
$Au_8\ Li$	-12.590067	-10.8293079	1.7607591
$Au_9\ Li$	-5.7932811	-4.2651675	1.5281136
Y_6	-3.0145959	-2.4012825	0.6133134
Y_8	-3.1335036	-2.3493114	0.7841922
$Y_6\ Ca$	-2.8771854	-2.0551713	0.8220141
Y_8 Ca	-3.1849305	-2.2478181	0.9371124

The energy gap for $Y_8 \approx$ the energy gap of Gallium arsenide ($GaAs$), this value of band gap is in the range of energy gaps of semiconductors materials, one can say the nanostructure (Y_8) can be used as a semiconductor material in manufacturing of pieces of electronic devices such as transistors of processors in computers. Y_6Ca has value of energy gap approaches to (0.82 eV), one can consider the nanocluster Y_6Ca semiconductor nanocluster, but the energy gap of (Y_6) is near (0.61 eV), this value classify the nanocluster (Y_6) as a semimetal nanocluster. One can make a comparison between HOMO energies in the two tables (1) and (2) to find out that HOMO energy of Au_8 and Au_9 is greater than HOMO energy of Lithium atom, hence the electrons should release to the unoccupied orbitals in Au_8 and Au_9, therefore Lithium atom will behave as a donor in (Au_8Li) and (Au_9Li) while Au_8 surface and Au_9 surface will behave as acceptors. HOMO energy of Y_6 is greater than HOMO energy of Calcium atom, so the electrons must release to the empty orbits in Ca, therefore Calcium atom will behave as an acceptor, but Y_6 surface will behave as a donor. Otherwise, HOMO energy of Y_8 is smaller than HOMO energy of Ca atom, hence, the electrons should release to the unoccupied orbits in Y_8, therefore Calcium atom will behave as a donor, while Y_8 surface will behave as an acceptor.

Dipole moment

Dipole moment is the consequence of the multiplication of the charge and the displacement, the distance between the two charges with different signs is r. Whenever the displacement direction changes as well as the moment of the dipole changes [18]. The equation of the diple moment can be expressed as:

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

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

Table (3) appears dipole moment for Au_8 , Au_9 , Y_6, Y_8 and Au_8Li , Au_9Li, Y_6Ca, Y_8Ca

System	Dipole moment (Debye)
Au_8	0.00001
Au_9	0.473997
$Au_8\,Li$	13.384187
$Au_9\,Li$	3.833793
Y_6	1.049361
Y_8	0.000328
$\mathrm{Y}_6\,\mathrm{C}a$	0.099196
$\mathrm{Y}_8\,\mathrm{C}a$	0.847795

The dipole moment of Au_8 is approximately zero because this surface is homonuclear surface. Although the nanocluster is homonuclear structure, it has dipole moment more than 1 this is results because many factors such as symmetry, hybridization and the geometrical structure throughout the nanocluster information procedure. The optimized parameters and hybridization procedure are an important factors to make the hetronuclear nanocluster (Y_6Ca) has very small value of dipole moment. (Au_8Li) nanocluster is the highest dipole moment nanocluster among the all, it has the value (13.38 Debye), this nanocluster gives rotational spectra changes through the rotation. One can see that the dipole moment of Au_8 surface effects dramatically when one Calcium atom adds to this surface.

Electronic energy

According to density functional thought the total energy can be divided in to four parts which is summarized according to the equation [19]:

$$E = E_T + E_v + E_J + E_{XC} \qquad \dots (3)$$

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 Au_6 , Au_8 , Au_9 , Y_4, Y_6, Y_8 and Au_6Li , Au_8Li , Au_9Li, Y_6Ca,

Y_8Ca

System	Total energy(eV)
Au_8	-29493.08093
Au_9	-33179.49486
$Au_8\,Li$	-29683.15233
$Au_9\,Li$	-33387.67857
Y_6	-6186.534278
Y_8	-8247.656895
$Y_6\,Ca$	-7181.979095
$Y_8\,Ca$	-9248.568772

One can make a comparison between table (1) and table (4) to say the orbital which originate in (Au_8Li) nanocluster are bonding orbitals because value of the total energy of Au_8 plus the value of total energy of Lithium atom is smaller than the total energy of (Au_8Li) nanocluster. But the total energy of Au_9 plus the value of total energy of Li atom is larger than the total energy of (Au_9Li) nanocluster, hence one can find that the orbitals will emerges in (Au_9Li) non-bonding according to molecular physics concepts. For the same reasons the orbitals which originate in (Y_6Ca) and (Y_8Ca) will be non-bonding orbitals, and this subjects to molecular physics ideas.

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 [20]:

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

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 Au_6 , Au_8 , Au_9 , Y_6, Y_8 and Au_6Li , Au_8Li , Au_9Li , Y_6Ca, Y_8Ca

System	Binding energy(eV)

$Au_8 Li$	13.7528054
$Au_9 Li$	-4.3595046
$Y_6 Ca$	-0.9002156
$Y_8 Ca$	-6.3672756

The absorption energy of Lithium on (Au_8) and (Au_9) surfaces depends on the binding energy, so it speculate linking of atoms in the nanocluters through system emergence process. Also binding energy connect apparently with the stability of nanocluster. The distance between transition metal surfaces (Y_8), (Y_9) and Calcium atom effects clearly on the electronic energy of the ground state (the lowest energy). Also the bonding nature another parameter influences activately on binding energy characterstic, one can assert the bond lengths can regard an effective parameter to show if the atom will adsorb on the surface or the atoms will transfer from the transition surface to the alkali atom energy levels, in this situation one can say the orientation of the correct bonding will be chosen.

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 credits of molecules and systems without calculations [21].

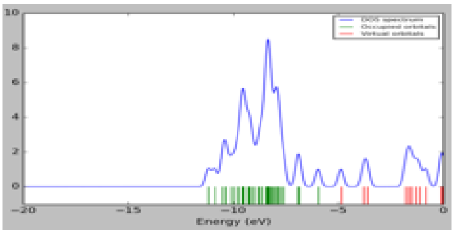
Table (6) appears point group symmetries for Au_8 , Au_9 , Y_6, Y_8 and Au_8Li , Au_9Li , Y_6Ca, Y_8Ca

System	Point group symmetry
Au_8	D_{2h}/C_1
Au_9	$C2v/C_1$
$Au_8\,Li$	Cs/C_1
$Au_9\,Li$	Cs/C_1
Y_6	C_{2v}/C_1
Y_8	D_{2h}/C_1
$Y_6\,Ca$	C_{2v}/C_1
$Y_8\,Ca$	C_1

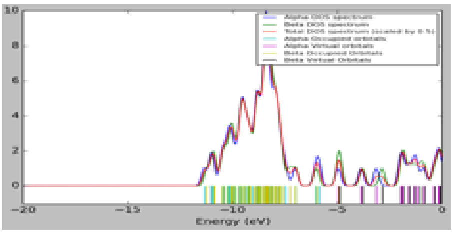
One can visualize that adding Lithium atom to (Au_8) nanocluster makes the symmetry difference, (Au_8) surface has the symmetry (D_{2h}/C_1) but the nanocluster (Au_8) owns the symmetry (D_{2h} /C_1), the surface (Au_8) has two fold symmetry axes (C_n) and two fold symmetry axes perpendicular to (C_n), also the symmetry C_1 makes (Au_8) rotate the nanocluster by (360/n) degrees around the axis, so it has horizontal mirror plane (σ_h). While (Au_8Li) nanocluster contains only two elements identity and mirror plane. (Y_6) and (Y_6Ca) surfaces have the point group symmetry (C_{2v}/C_1), The type of symmetry C_1 make (Y_6) and (Y_6Ca) circulate the nanocluster by (360^o/n) about certain axis, also reflect the nanocluster throughout plane (σ_v) which include the major axis.

Density of states (Dos)

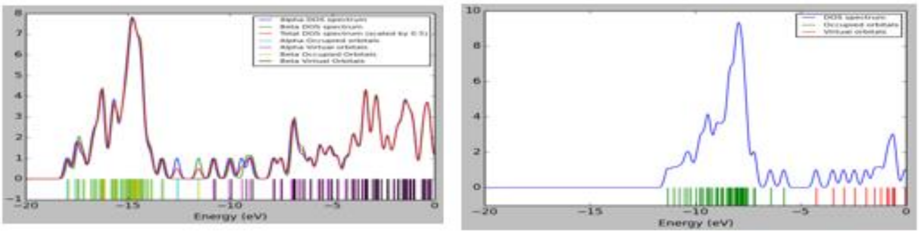
In solid state physics density of states (DOS) describes the number of states for every energetic interval at every energy level in which the energy level can be occupied by the electrons [22]. Density of states can be investigated for electrons, photons and phonons according to the physics of quantum mechanics [23]. Density of states have been found out for $Au_8, Au_9, Y_6, Y_8, Au_8Li, Au_9Li, Y_6Ca$ by Gaussian sum 03 program package.



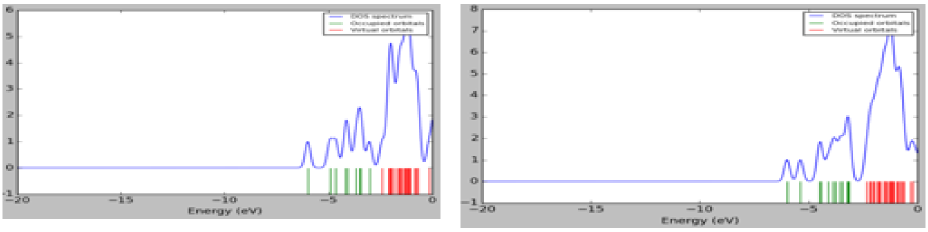
Au_8



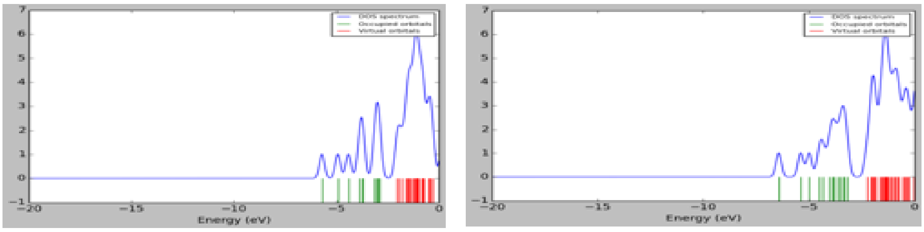
Au_9



Au_8Li **Au_9Li**



Y_6 **Y_8**



Y_6Ca **Y_8Ca**

Figure(5)

Density of states for Au_n , Au_nLi (n=8,9) and Y_n ,Y_nCa (n=6,8)

Figures of density of states (DOS) demonstrate apparently how the magnetic properties dramatically changes when an alkaline atom (Li) adds to (Au_8) and (Au_9) surfaces. Adding Lithium atom to (Au_8) surface makes the new structure (Au_8Li) has anti-ferromagnetic properties because it has two kinds of orbits alpha (α) and beta (β). Reversly, addition of Lithium atom to the nanocluster (Au_9) makes it lose the anti-ferromagnetic credit, it become possess only alpha (α) orbitals. DOS diagrams show the number of states for every energetic interval at each energy level that available to be occupied with electrons. The electrons look for empty places to occupy in order to the nanocluster becomes more stable.

Conclusions

The molecular engineering of (Y_8) nanocluster becomes different apparently after adding Ca atom to the surface, also one can visualize through it's shape bonds seems at entanglement state. The shapes of electrostatic potentials (contours) of transition metals nanoclusters changes completely after the interaction with the alkaline atoms. Geometrical parameters, bond lengths, bond angles and dihedral angles effects dramatically after the interaction because of the hybridization. (Au_9) surface has five clear peaks, but (Au_9Li) owns only three clear peaks, disappearance of two peaks is caused by the shielding procedure. (Y_8) has energy gap approaches to Gallium arsenide ($GaAs$) energy gap, so the nanostructure (Y_8) can be used in electronic applications. Lithium atom in (Au_8Li) and (Au_9Li) will behave as a donor depending on the value of HOMO energy, but Calcium atom will behave as an acceptor according to HOMO energy. (Au_8Li) surface is the highest dipole moment, it's value (13.38 Debye), this nanocluster gives rotational spectrum changes throughout the rotation. (Au_8Li) orbitals are bonding orbitals, while (Au_9Li), (Y_6Ca) and (Y_8Ca) are non-bonding orbitals according to molecular physics thoughts. The distance between (Y_8), (Y_9) and Calcium atom influencess apparently on the electronic energy of the ground state (the minimum energy). (Au_8) posses horizontal mirror plane (σ_h). (Y_6Ca) has vertical plane (σ_v). (Au_8Li) has (α) and (β) orbitals, but (Au_9Li) has only (α) orbitals depending on spin.

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