Density functional theory investigation for Mo_n and Mo_nCa interactions
(n=5, 6, 7, 8)

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Abstract:

   Geometry optimization using density functional theory method was investigated for Mo_6 with LANL2DZ basis set, B3LYP level through Gaussian 09 codes. Molecular geometry for Mo_5, Mo_8, Mo_5Ca , Mo_6Ca , Mo_7Ca and Mo_8Ca had been implemented at LANL2MB. Adding Calcium atom to Molybdenum nanocluster (Mo_6) make it more symmetric and change the geometrical parameters dramastically. Current surfaces, Contours, Infrared spectra, Electronic states HOMO and LUMO, energy gap(E_g), dipole moment, electronic energy, binding energy, point group symmetries and density of states has been achieved for all nanoclusters under study. Physisorption of Calcium atom on (Mo_6) surface makes the charges distribution about the atoms different. Charges densities around some atoms in the hybrid surfaces is more than the others. (Mo_8Ca) has seven clear peaks as compared with (Mo_8) nanocluster, it has only two clear peaks, one can say (Mo-Ca) bond originates in (Mo_8Ca) nanocluster. (Mo_6) posses at least six apparent peaks, (Mo_6Ca) has only four clear peaks, i.e. two clear peaks disappear, this happens because shielding procedure. In (Mo_6Ca) Calcium atom behaves as an acceptor, but (Mo_6) behaves as a donor. (Mo_5) ha energy gap approximately (1.24 eV), it can use in electronic devices. (Mo_6Ca) is the biggest dipole moment nanocluster, it's value (4.84 Debye), one can say the alkaline atom participates effectively to increase the value of dipole moment. Non-bonding orbitals will generate in (Mo_5Ca) and (Mo_8Ca) nanoclusters, while the orbitals that originate in (Mo_6Ca) and (Mo_7Ca) are bonding. (Mo_5Ca) is minimum value of binding energy which equals to (-2.14 eV), but (Mo_7Ca) is the largest binding energy system. (Mo_5) vertical mirror plane (σ_v), (Mo_5) has two elements identity and mirror plane. DOS schematics of (Mo_7) and (Mo_7Ca) show change in peaks positions and values of intensities, one can say new levels will generate can be occupied by electrons.

Keywords: Binding energy, Ionization energy, Energy gap, IR spectra, DOS, DFT.

1. Introduction:

 Density functional theory (DFT) method is one of popular techniques that used for finding out electronical, optical and structural characterstics for naoparticles, nanoclusters, molecules and polymers [1]. Electron density function is employed instead of the wave function in DFT calculations. It was introduced by Kohn-Sham and Hohenberg-Kohn two seminal papers in 1964 and 1965 respectively [2]. The ground state energy

credits of the system are supplied throughout DFT [3]. It depends on functionals which represent a functions of another functions, where in this state is depending spatially on the electron density [4]. DFT acquires this name because it uses electron density function [5]. Many calculations of computational chemistry, condensed matter physics and computational physics are investigated by using density functional theory technique [6]. It had been employed in solid state physics calculations since 1970's [7]. DFT had been developed to be more accurate throughout using exchange and correlation functions [8]. The consequences of DFT for solid state systems agree completely satisfactorily with the experimental results [9]. The simplified definition of DFT is a technique that is used for obtaining an approached solution for Schrodinger equation of many body systems [10]. DFT depends on computational codes is written in gaussian versions packages [11]. DFT had been considered one of the quantum mechanics technique that are used in quantum chemistry and quantum physics [12].

2. Results and Discussions:
2.1. Molecular Geometry:

Molecular structure points out the configuration of atoms in the material, it denotes to the positions of atoms in the system [13]. Geometrical structure had been implemented for Mo_6 with LANL2DZ basis set. Molecular structure for Mo_5, Mo_8, Mo_5Ca, Mo_6Ca, Mo_7Ca and Mo_8Ca had been achieved at LANL2MB basis set. Finally, the molecular structure was investigated for Mo_7 by using the basis set 3-21G B3LYP level through Gaussian 09 codes.
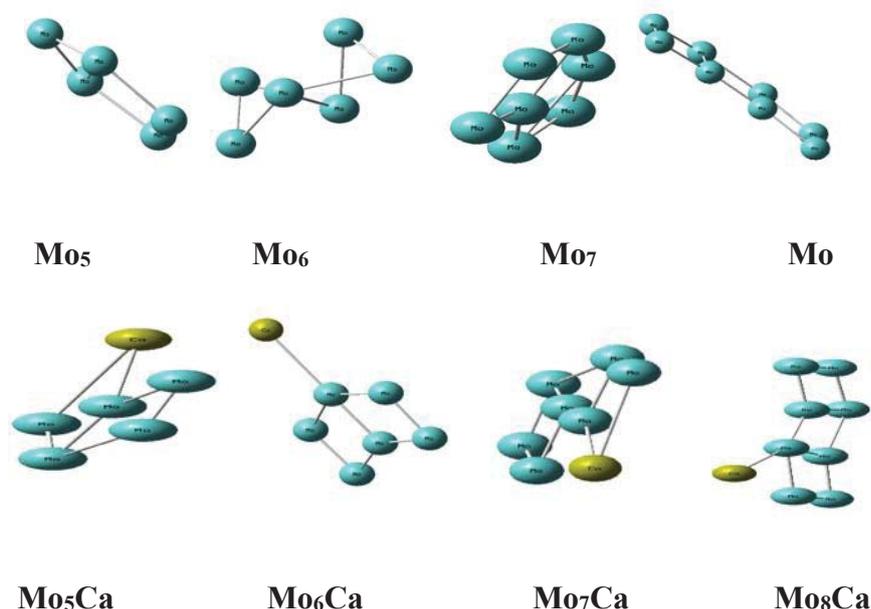

Mo_5 Mo_6 Mo_7 Mo

Mo_5Ca Mo_6Ca Mo_7Ca Mo_8Ca

Figure (1): Molecular geometry for Mo_5, Mo_6, Mo_7, Mo_8, Mo_5Ca, Mo_6Ca, Mo_7Ca and Mo_8Ca.

Figure (1) shows the molecular geometry resulting from the ground state geometry optimization procedure. Geometry optimization procedure depends on the calculations of the second energy derivative with regard to the harmonic oscillator pattern atomic positions. The objective of the geometry optimization procedure is to obtain the minimum energy to make the system stationary. Throughout the engineering optimization process the best coordinates of atoms in Cartesian coordinates (x, y, z) result. The interaction between Calcium atom and Molybdenum surfaces affect apparently on the topological properties. One can see from

the figure add Calcium atom to Molybdenum surface (Mo_6) make it more symmetric and change the dihedral angles dramastically.

2.2. Current Surfaces:

Surfaces were examined using HOMO, LUMO electronic states, in which HOMO represents High Occupied Molecular Orbital, but LUMO represents Low Unoccupied Molecular Orbital. The geometrical optimization procedure has been used to achieve surface shapes. If the stationary point is identified, i.e. the resulting forces equal to zero, the geometry optimization process will stop [14]. Current surfaces had been achieved for Mo_6 with LANL2DZ basis set. Electrostatic potential for Mo_5, Mo_8, Mo_5Ca, Mo_6Ca, Mo_7Ca and Mo_8Ca had been

investigated at LANL2MB basis set. Eventually geometry of the surface was implemented for Mo_7 using 3-21G basis set at B3LYP level through Gaussian 09 package.
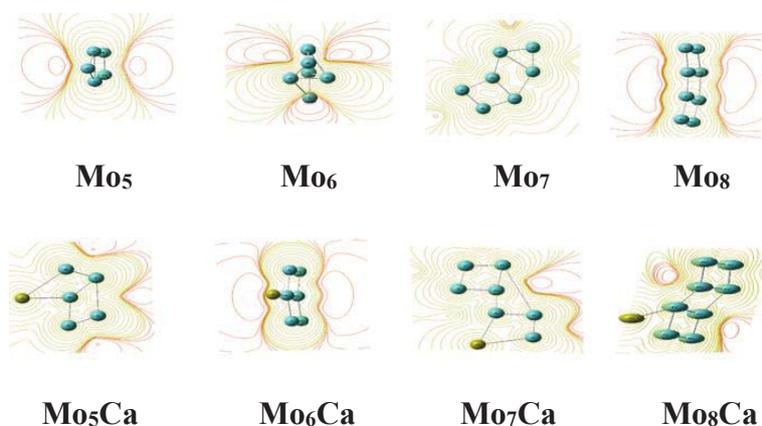

| Mo_5 | Mo_6 | Mo | Mo_8 |

| Mo_5Ca | Mo_6Ca | Mo_7Ca | Mo_8Ca |
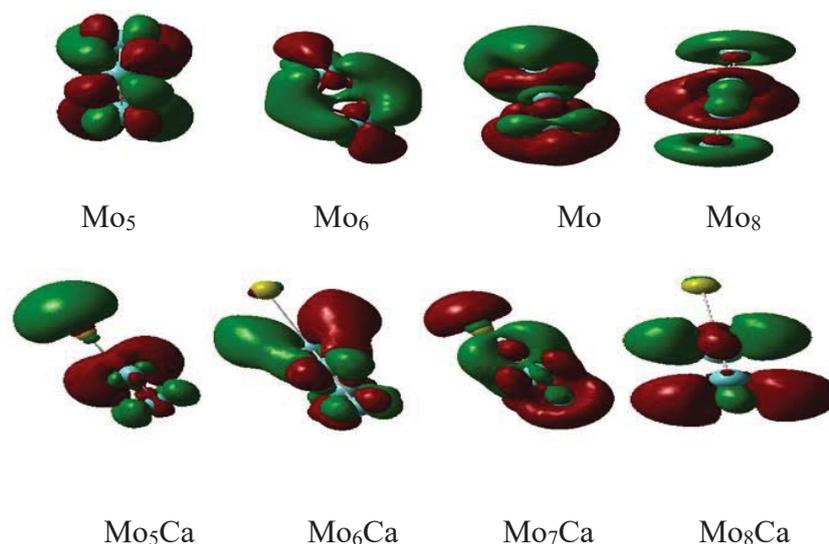
Figure (2): HOMO LUMO surfaces for Mo_5, Mo_6, Mo_7 , Mo_8, Mo_5Ca, Mo_6Ca, Mo_7Ca and Mo_8Ca

It is very clear from figure (2) the electrostatic potential surfaces result from the linear combination of atomic orbitals, i.e. due to the electronic transition between orbitals, molecular orbitals will compose. New bonds with types (σ), (σ^*), (π) and (π^*) will originate as a result to the linear combination of the atomic orbitals s and p. The new colors in HOMO, LUMO surfaces can be interpreted, the green color indicate to the positive electrostatic potential region, but the dark red color denotes to the negative electrostatic potential region. One can visualize shape of the surface Mo_6 change clearly influencing by adding Calcium atom to the surface. Addition Calcium atom to the surface (Mo_8) make charge distribution around atoms variant one can see that is throughout a simplified sight on the shapes of (Mo_8) and (Mo_8Ca). Also physisorption of Calcium atom on (Mo_6) surface changes the charges distribution about the atoms.

2.3. Contours:

Electronic density contours shapes describe how the electrons distribute about the atoms in the geometrical structure. Contours can be regarded another approach to express electrostatic surfaces [15]. Contour density maps had been implemented for Mo_6 at LANL2DZ basis set. Contours were investigated for Mo_5, Mo_8, Mo_5Ca, Mo_6Ca, Mo_7Ca and Mo_8Ca at LANL2MB basis set. Recently contour diagrams were

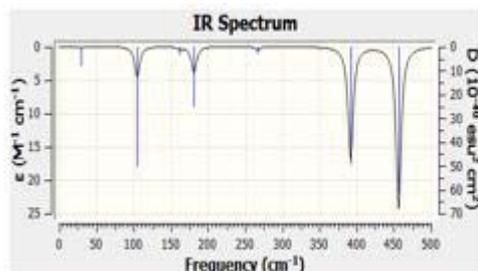investigated for Mo_6 and Mo_7 utilizing 3-21G basis set with B3LYP method throughout Gaussian 09 program.

$$Mo_5 \qquad Mo_6 \qquad Mo_7 \qquad Mo_8$$

$$Mo_5Ca \qquad Mo_6Ca \qquad Mo_7Ca \qquad Mo_8Ca$$

Figure (3): Electrostatic potential for Mo_5, Mo_6, Mo_7 , Mo_8, Mo_5Ca , Mo_6Ca , Mo_7Ca and Mo_8Ca
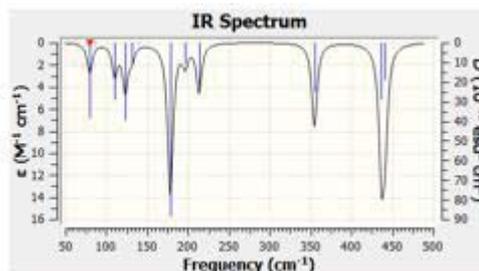
Figure (3) demonstrates the contours diagrams of the pure transition metal surfaces are apparently changing as well as the alkali atom has been added to the surface. The interplay between the surface of transfer and the alkaline atom deforms the contour maps. The shape of (Mo_6) Molybdenum surface becomes more decoration when Calcium atom adding to the surface, i.e. Mo_6Ca is more uniform than pure molybdenum surface (Mo_6). Therefore, one can say adding Calcium atom to the molybdenum surface can enhance the geometrical properties. Geometrical parameters like bond angles and dihedral angles vary when Calcium atom is added to the pure Molybdenum surface (Mo_7) and one can see that apparently when make a comparison between (Mo_7) system and (Mo_7Ca). The charge distribution around the atoms also change after the interaction between Calcium atom and Molybdenum surface, one can say charges densities around some atoms in the hybrid surfaces is more than the others.
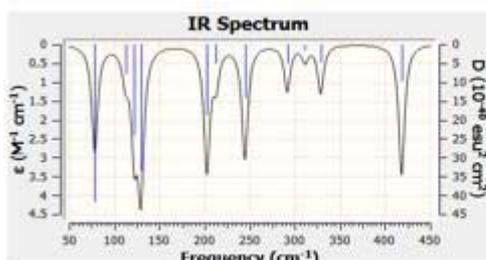
2.4. Infrared spectra:

The harmonic oscillational frequencies could be visualized throughout infrared diagrams (IR). The vibrations may be either symmetric or asymmetric, symmetric vibrations obtain as a result to atoms oscillate with the same species, inversely, the asymmetric vibrations obtain as a consequence to atoms vibrate with different type. Infrared spectra diagrams [16]. Infrared spectra (IR) schematics had been achieved for Mo_6 at LANL2DZ basis set. Infrared spectra (IR) have been implemented for Mo_5, Mo_8, Mo_5Ca , Mo_6Ca , Mo_7Ca and Mo_8Ca with LANL2MB basis set. Eventually IR diagrams have been investigated for Mo_7 employing 3-21G basis set with B3LYP technique throughout Gaussian 09 program.

Journal of Education for Pure Science- University of Thi-Qar
Vol.10, No.2 (June, 2020)
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Mo5

Mo6

Mo7

Mo8
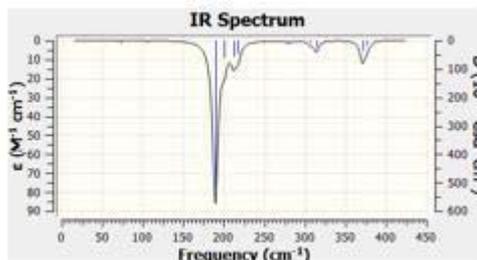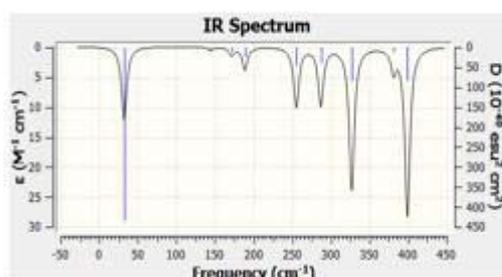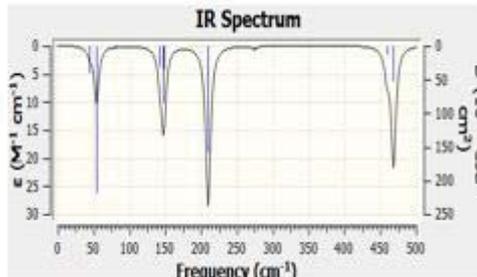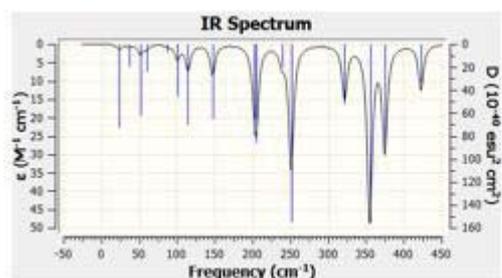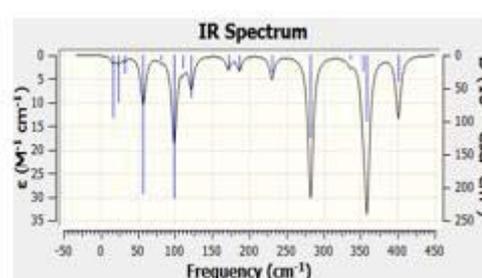
Mo5Ca

Mo6Ca

Mo7Ca

Mo8Ca

Figure (4): Infrared spectra for Mo5, Mo6, Mo7 , Mo8, Mo5Ca , Mo6Ca ,Mo7Ca and Mo8Ca

One can visualize from IR spectra diagrams new bonds appear in hybrid systems as a result to new bonds generate between Molybdenum surfaces and Calcium atom. One can see seven clear peaks in (Mo8Ca) system as compared with (Mo8) surface which has only two clear peaks, the new peaks belong to (Mo-Ca)

bond that originate because of the interaction between Molybdenum surface (Mo_8) and Calcium atom, one can assert new active groups generate. The nanocluster (Mo_6) has at least six clear peaks, while the nanocluster (Mo_6Ca) has only four clear peaks, i.e. two clear peaks disappear as a result to shielding procedure. Shielding procedure shows that Calcium atom trend to interact with some atoms more than the others.

2.5. Individual atoms:

Computations of particular atoms possess high-stacks for discussion some characterstics of materials, some of these credits total energy and electronic states HOMO, LUMO, see table (1).

Table (1) shows electronic properties for the Calcium atom.

atom	HOMO(eV)	LUMO(eV)	Total energy(eV)
Ca	-4.4159109	-1.2094845	-994.5446014

2.6. Electronic states and energy gap(E_g):

High occupied molecular orbital (HOMO) and low unoccupied molecular orbital (LUMO) stand for the electronic states that result from the geometrical optimization procedure. Energy gap (E_g) emerged of the energy difference between two electronic levels, i.e. energy difference between valence band and conduction band. Mathematically one can express the energy gap by the following equation [17]

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

Table (2) illustrates HOMO, LUMO energies and energy gap (E_g) for Mo_5 , Mo_6 , Mo_7 , Mo_8, Mo_5Ca , Mo_6Ca , Mo_7Ca and Mo_8Ca

System	HOMO(eV)	LUMO(eV)	E$_g$(eV)
Mo_5	-4.718214	-3.4698192	1.2483948
Mo_6	-4.1789118	-2.3267271	1.8521847
Mo_7	-3.7979718	-2.6516145	1.1463573
Mo_8	-4.239318	-3.3890055	0.8503125
$Mo_5 Ca$	-4.759029	-2.5672635	2.1917655
$Mo_6 Ca$	-3.7892646	-3.0042561	0.7850085
$Mo_7 Ca$	-4.2080265	-3.2088753	0.9991512
$Mo_8 Ca$	-4.0793232	-3.1800327	0.8992905

When one makes a comparison between table (1) and table (2) shows HOMO energy of Calcium atom is greater than HOMO energy of (Mo_5) surface, that is to say the electrons will release from Calcium orbitals to (Mo_5) surface as a result to charge transfer between the atom and the surface, Calcium will become donor, but Mo_5 surface will behave as an acceptor. Inversely HOMO energy of (Mo_6) is bigger than HOMO energy of Calcium atom, one can say the electrons will release the unoccupied orbitals in Calcium, here Calcium is an acceptor, but (Mo_6) will be donor. The energy gap of (Mo_5) is approximately (1.24 eV), this value is near the energy gap of the semiconductor material Silicon, the energy gap of Si is (1.21 eV), this

value plays a vital rule in the electronic applications such as manufacturing of some of the electronic pieces of computers. So the energy gap of (Mo_6Ca) is equal to the energy gap of Gallium Arsenide ($E_g = 0.78$ eV).

2.7. Dipole moment:

Dipole moment is consequence for multiplication between the charge and displacement, it obtains between two charges with different signal, the distance between them is r. If any direction of the displacement change, the dipole moment will change. Let P defined as the dipole moment, q is the charge and r represents the displacement, hence dipole moment can be described by the equation [18]

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

Table (3) shows dipole moment for Mo_5, Mo_6, Mo_7, Mo_8, Mo_5Ca, Mo_6Ca, Mo_7Ca and Mo_8Ca

System	Dipole moment (Debye)
Mo_5	0.505089
Mo_6	0.346066
Mo_7	0.164776
Mo_8	0.091354
$Mo_5\,Ca$	4.331455
$Mo_6\,Ca$	4.847529
$Mo_7\,Ca$	3.598119
$Mo_8\,Ca$	3.733979

Table (3) illustrates that the dipole moment of the pure transition nanocluster (Mo_8) because it is homonuclear nanocluster, but the other pure transition systems have non-zero values of dipole moment because of the symmetry, molecular structure and hybridization procedure. Non-pure nanoclusters have value of dipole moment more than (3.5 Debye), this occurs because they are hetronuclear nanoclusters. The nanocluster (Mo_6Ca) is the highest dipole moment nanocluster, it has a numerical value approaches to (4.84 Debye), one can say the alkaline atom contributes actively to increase the value of dipole moment in all hybrid systems. The nanoclusters dipole moment stands for a generalized scale of bond characterstics and charge densities in the nnocluster. An important factors affects effectively on the value of dipole moment is the distance between two charges, dipole moment between two charges increase as the distance between them increase.

2.8. Electronic energy:

According to density functional thought the total energy can be divided in to four parts. Let 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, therefore one can write equation [19]

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

Table (4) shwos the total energy for Mo₅ , Mo₆ , Mo₇ , Mo₈, Mo₅Ca , Mo₆Ca , Mo₇Ca and Mo₈Ca

System	Total energy(eV)
Mo_5	-9175.970832
Mo_6	-11018.02057
Mo_8	-14684.28522
$Mo_5\,Ca$	-10172.6613
$Mo_6\,Ca$	-12008.19247
$Mo_7\,Ca$	-13843.56338
$Mo_8\,Ca$	-15680.48898

When one make a comparison between table (1) and table (4) can find out that non-bonding orbital will originate in (Mo₅Ca) and (Mo₈Ca) nanoclusters, the total energy of (Mo₅) approximately equal to (-9175.970832 eV) and for (Mo₈) is close to (-14684 eV) and for Ca atom is about (-994.54 eV), the total energy of (Mo₅) plus the total energy of Ca atom is smaller than the total energy of (Mo₅Ca), therefore the non-bonding orbitals of the types(σ^*) and (π^*) generate. Also for the same reason one can consider the orbitals which result in Mo₈Ca with type of non-bonding. But the total energy of (Mo₆) is equal to approximately (-11018 eV), and approximately (-754072 eV)) for (Mo₇), therefore bonding orbitals of the type (σ) and (π) will generate in the nanoclusters (Mo₆Ca) and (Mo₇Ca), because the total energy of (Mo₆) plus the total energy of Ca atom is bigger than the total energy of (Mo₆Ca), for the same reason the orbitals that generate in (Mo₇Ca) is bonding.

2.9. Binding energy:

The binding energy of a system predicts how energetically the atoms are entangled in the system during formation that system. Let 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, hence, the binding energy (E$_B$) of the X_nY_m is expressed by the equation [20]:

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

Table (5) demonstrates the binding energy for Mo₅ , Mo₆ , Mo₇ , Mo₈ , Mo₅Ca , Mo₆Ca , Mo₇Ca and Mo₈Ca

System	Binding energy(eV)
$Mo_5\,Ca$	-2.1458666
$Mo_6\,Ca$	4.3727014
$Mo_7\,Ca$	741223.0713
$Mo_8\,Ca$	-1.6591586

Table (5) shows the high variance in the values of binding energy, this is because of the nature of bonding that happens in the nanoclusters. The binding energy yields the adsorption of Calcium atom on Molybdenum surfaces or the charge transfer between Calcium atom and Molybdenum surfaces, generally

binding energy describes the entanglement or linking between the atom and the surface, one can say it describe binding strength through information of the nanocluster. one can say the binding energy connects dramastically with the stability of the nanocluster. The ground state electronic energy linked largely with the distance between atoms and Molybdenum surfaces. Another parameter effect clearly on the value of binding energy, is the nature of bonding, it shows the chemical bonding that results from the adsorption procedure of the atom on the surface or the inverse, through choice the orientation the correct bonding. The nanocluster (Mo_5Ca) is lowest value among the four systems under study binding energy of (Mo_5Ca) equal to (-2.14 eV), this nanocluster needs less energy to enter binding state, but the nanocluster (Mo_7Ca) is the highest binding energy nanoclster, it has the value (741223.07 eV), one can say (Mo_7Ca) need more energy to enter binding state.

2.10. Symmetry:

Generally, symmetry can be defined as repetition or corresponding parts certain shape about point, axis or surface. The sphere is regarded more symmetric as compared with the cube, the sphere looks the same when rotates through any angle, while the cube looks the same only if the rotation gets at certain angles around certain centerpiece. Symmetry play a vital role in acknowledgement properties of molecules, nanoclusters, systems and nanoparticles without calculations [21]. Symmetry operations imply the following, rotations, reflections and inversions [22].

Table (6) appears point group symmetries for Mo_5 , Mo_6 , Mo_7 , Mo_8 and Mo_5Ca , Mo_6Ca , Mo_7Ca , Mo_8Ca

System	Point group symmetry
Mo_5	C_{2v}/C_1
Mo_6	C_{2v}/C_1
Mo_7	C_s/C_1
Mo_8	C_{2v}/C_1
$Mo_5\,Ca$	C_{2v}/C_1
$Mo_6\,Ca$	C_{2v}/C_1
$Mo_7\,Ca$	C_s/C_1
$Mo_8\,Ca$	C_s/C_1

Table (6) shows that in (Mo_5) molecule the symmetry reflect the nanocluster throughout plane imply principal axis, this nanocluster has vertical mirror plane (σ_v) , also it is from the kind C_n symmetry, the symmetry takes place through ($360°/n$), and the symmetry repeat the molecule throughout ($360°$) because it is with type C_1 symmetry. The nanocluster (Mo_7) has the symmetry (Cs), that is to say it contains two elements identity and mirror plane. It is very apparent addition of an alkaline atom like Calcium atom contribute effectively to possess new symmetry differs from the symmetry before the interaction, one can discover this when make a simplified counter-posing between the symmetry in (Mo_8) and (Mo_8Ca). The symmetry imposes restrictions to the electrons movement.

2.11. Density of states (Dos):

In solid state physics, density of states (DOS) describe the number of states for every energetic interval at every energy level in which the energy level can be occupied by electrons. Density of states can be investigated for electrons, photons and phonons according to the physics of quantum mechanics [23]. If the density of state equal to zero, no state can be occupied by electrons at the energy levels. In general, density of states influenced by topological properties of the system [24]. Density of states(DOS) for Mo_5, Mo_8, Mo_5Ca, Mo_6Ca, Mo_7Ca and Mo_8Ca with LANL2MB basis set. Density of states had been achieved for Mo_6 at LANL2DZ basis set.

Eventually Density of states have been implemented for Mo_7 employing 3-21G basis set with B3LYP technique throughout Gaussian 09 program.
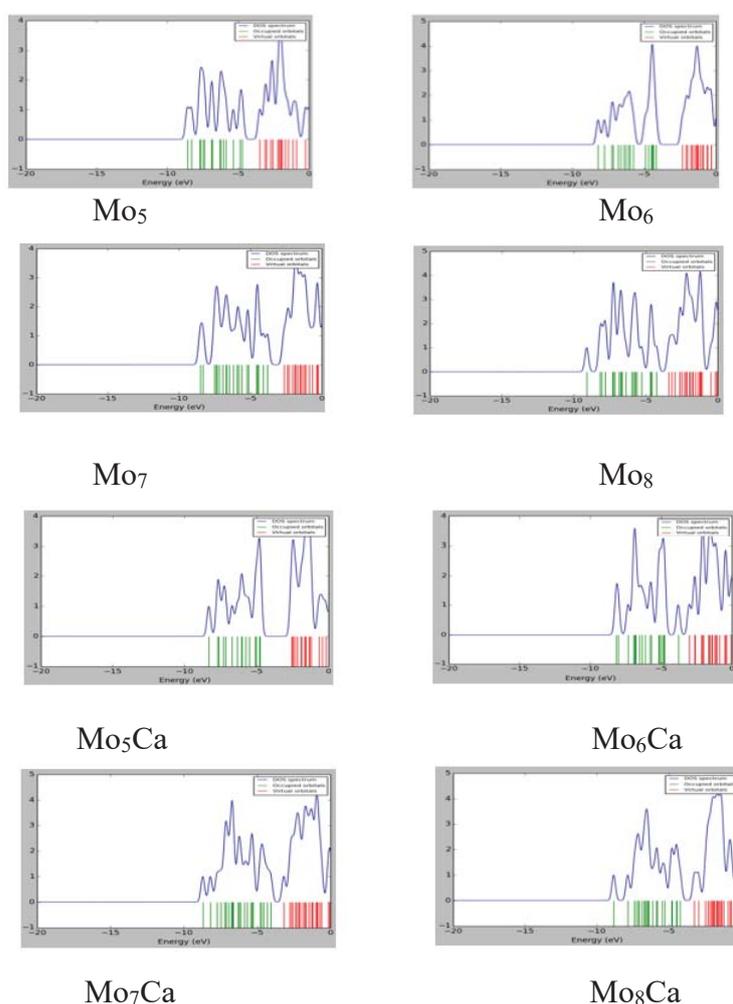
Figue (5): Density of states (DOS) for Mo_5, Mo_6, Mo_7 , Mo_8, Mo_5Ca , Mo_6Ca , Mo_7Ca and Mo_8Ca

Figure (5) shows that density of states (DOS) schematics has only alpha orbitals, throughout the diagrams one can visualize the band gap originates between valence band and conduction band. The graphs demonstrate the levels that can occupied by electrons, density of states at an energy level means existence number of places may be occupied by electrons in order to get stable nanocluster. Several parameters affect on density of states diagrams such symmetry, molecular engineering and topological credits, that is factors may impose restrictions to some electrons to be found in some places or prohibit some electrons to be found in other places. Density of states diagrams affect clearly tremendously when an alkaline atom adds to the

transition metal surface, and this is very clear when one compare between DOS for (Mo_7) and (Mo_7Ca), changing of peaks positions and values of intensity sign that influence, the new peaks and new values of intensities means new energy levels will originate and can be occupied by thee electrons.

3. Conclusions:

Through the geometry optimization procedure, the best coordinates of atoms in Cartesian coordinates (x, y, z) have been resulted. New bonds of the types (σ), (σ^*), (π) and (π^*) will generate as a result to addition of Calcium to Molybdenum surfaces. The decoration of Mo_6Ca is more regularly than (Mo_6) and this explain how the alkaline atom enhances the geometrical characterstics when adds to the transition surface. New bonds of the type (Mo-Ca) will generate in (Mo_8Ca) nanocluster because of the interaction between the atom and the surface, while shielding procedure gets in (Mo_6Ca), the shielding procedure appears that Calcium atom own tendency to interact with some atoms more than the others. In (Mo_5Ca) Calcium will be a donor, while Mo_5 surface will be an acceptor. The energy gap of (Mo_6Ca) is equal to the energy gap of Gallium Arsenide ($E_g = 0.78$ eV), this property is very important in manufacturing of some pieces of computers like ram and processor. Some pure transition systems have non-zero dipole moment because of the molecular engineering, symmetry and hybridization procedure. Non-pure nanoclusters have dipole moments more than (3.5 Debye), this happens because they are hetronuclear. Non-bonding orbitals of the types (σ^*) and (π^*) generate in (Mo_5Ca), but bonding orbitals of the kind (σ) and (π) originate in (Mo_6Ca). Binding energy influences clearly by the nature of bonding, it appearss the chemical bonding that obtain from the adsorption process of the atom on the surface or the reverse, throughout choice the orientation the proper bonding. Binding energy of (Mo_5Ca) is (-2.14 eV), one can say the nanocluster needs less energy to enter binding state, but the nanocluster (Mo_7Ca) is the largest binding energy nanoclster, it has the value (741223.07 eV), one can say (Mo_7Ca) need more energy to enter binding state. . Many types of point group symmetries result throughout the geometry optimization procedure, this types are C_{2v}/C_1 and C_s/C_1. Density of states shapes show the band gap that generates between HOMO and LUMO, Molecular structure nature, symmetry and topological properties affect satisfactorily on the density of states.

References:
[1] Robert, J. (2002). Acritical note on density functional theory studies on rare-gas dimmers. Journal of Chemical Physics., 116 (22): 9620-9623.
[2] Grimme and Stefan. (2006). Semiemperical hyprid density functional with perturbative second order correlation. Journal of Chemical Physics., 124 (3): 034108.
[3] Carmer. (2002). Essential of Computational Chemistry, Chichester, John Wiley and Sons, Ltd, 154-168.
[4] Koch and Holthausen. (2000). A chemist's guide to density functional theory., Wiley-VCH.
[5] Vignale, G. and Mark R. (1987). Density functional theory in strong magnetic fields. Physical Review Letters, American Physical Society., 59 (20): 2360- 2363.
[6] Grimme and Stefan (2006). Semiemperical hyprid density functional with perturbative second order correlation. Journal of Chemical Physics., 124 (3): 034108.
[7] Orio and Pantazis. (2009). Density functional theory, Photosynthesis research., 102: 433-453.
[8] Carmer and Christopher. (2002). Essential of Computational Chemistry. Chichester, John Wiley and Sons, Ltd. Pp. 154-168.
[9] Dreizler and Engel. (2011) Density functional theory, springer.
[10] Koch and Holthausen. (2000). A Chemist's Guide to Density Functional Theory, Wiley-VCH.
[11] Burke. (1983). Perspective on density functional theory, The Journal of Chemical Physics., 136:150901.

[12] Parr. (1989). Density functional theory, Annual Review of physical chemistry, Oxford university press.

[13] Schlegel, J. (1982). Comput. Chem.

[14] Frisch and Trucks. (2009). Gaussian 09, Revision A.02, Gaussian, Inc., PA, Wallingford CT.

[15] Anna Tomberg. (2015). Gaussian09 Tutorial, an introduction to computational chemistry using G09 and Avogadro software.

[16] Mohsin K. and Hamid H. (2013). Int. J. Pure Appl. Sci. Technol.,15(1): 1-13.

[17] Hamid H. (2012). British Journal of Science., 6 (2):1987.

[18] Mc Grow-Hill. (1972). Fundamentals of molecular spectroscopy.

[19] Oftadeh and Naseh. (2011). Computational and Theoretical Chemistry., 966: 20- 25.

[20] Vipin K. and Esha V. (2015). Physica E, Low-dimensional Systems and Nanostructures.

[21] Hamid H. (2013). The first scientific conference, Babylon University. College of science.

[22] Karsten Horn. (2013). Introduction to group theory with applications in molecular and solid state physics.

[23] Charles Kittel. (1991). Introduction to Solid State Physics.

[24] Brown. (1967). The Physics of Solids. New York, W. A. Benjamin.